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Faculty of Chemistry

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ON METHODS AND MATERIALS
FOR SEPARATION PROCESSES

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– THEORY AND PRACTICE 2013

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ŚWIERADÓW ZDRÓJ
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I. LECTURES

HIGHLY SELECTIVE CHEMICAL SEPARATIONS USING MOLECULARLY IMPRINTED POLYMERS

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Molecular imprinting is a highly-attractive method of template-directed synthesis which is used to prepare polymers that are synthetic mimics of antibodies and enzymes (1,2). The molecularly imprinted polymers (MIPs) which are accessed through molecular imprinting methods demonstrate exquisite molecular recognition capabilities (antibody-like behaviour) and, in some cases, catalytic activity (enzyme-like behaviour). Typically, MIPs are porous, infinite polymer networks, so are very distinct to their biological counterparts, not least of all in terms of their chemical make-up and remarkable chemical and thermal stability.

The impressive molecular recognition properties (antibody binding mimicry) and catalytic properties (enzyme mimicry) of MIPs have captured the imaginations of many and encouraged their use in numerous application areas, including analytical chemistry, forensic toxicology, chemical sensing and catalysis. At Strathclyde, we have used MIPs within the context of separation science for environmental, food and bioanalyses, forensic toxicology and protein separations, *inter alia* (3-7). This lecture will focus attention upon specific examples of research programmes in which we have optimised the syntheses of MIPs in appropriate physical forms to enable highly selective chemical separations.

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NEW COMPOSITE MATERIALS FOR AFFINITY SEPARATION BASED ON MODULAR ASSEMBLY OF NANOPARTICLE BUILDING BLOCKS

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Molecular imprinting is a powerful synthetic strategy that can offer tailor-designed affinity materials for many practical applications. Recent developments in this area have brought in many interesting formats of molecularly imprinted polymers (MIPs) that enable fast and efficient separation, simple analytical sample preparation and new chemical sensing systems. Recently, molecularly imprinted nanoparticles have become accessible due to a number of synthetic methods that have been developed. The high molecular binding selectivity, fast binding kinetics and colloidal stability make MIP nanoparticles ideal building blocks for construction of new multifunctional materials and devices for analytical purposes.

In this talk, I will present our recent results on preparing molecularly imprinted nanoparticles and the use of the imprinted nanoparticles as basic building blocks to realize functioning materials and devices. Both fundamental studies and applications of the new materials will be covered. The main focus will be put on several simple yet generic approaches that have been used to assemble different molecular and nanoparticle building blocks. Examples of affinity separation based on the nanoparticle assemblies will be given.

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SPECIATION ANALISIS OF SELECTED IONS BY USING ION CHROMATOGRAPHY WITH ICP-MS OR MS DETECTION

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Speciation analytics as determination of various forms of elements is becoming more and more popular and valuable in areas such as environmental protection, biochemistry, geology, medicine, pharmacy and food products quality control. Its growing importance is related to the fact that what often decides on the toxicological properties of a given element or compound is not its total content but the presence of its various forms, especially ionic. Determination of low concentrations of analytes requires complex and sophisticated analytical methods and techniques. The latest trends in this area concern the so-called 'hyphenated techniques', in which the separation and various detection methods are combined.

At the beginning of the twenty-first century the analytical chemistry (including the environmental analytics) has to face new challenges. First and foremost, this situation is linked to the fact that new data concerning the toxicological properties and forms of elements have been appearing and that there exists the necessity for the detection and determination of gradually lowering analytes concentrations, often in complex matrix samples.

The concept of speciation in chemistry is employed to determine the occurrence of a particular element in its diverse forms (at different oxidation states, in combination with various ligands, etc.) in the examined material such as food, animal tissues or environmental samples. These forms may vary in terms of their physical and chemical characteristics or pathophysiological effects. Speciation analytics (identification and quantity analysis of individual forms of a given element) is becoming more and more important in the environmental protection and medicine despite its considerable cost.

The definitions of chemical speciation found in the literature are equivocal. The terms in use are individual, group, physical or chemical speciation (1). Since all these designations defined the concept of speciation differently, it was necessary to disambiguate it. The International Union of Pure and Applied Chemistry (IUPAC) identifies speciation as a process that is to prove the existence of the atomic and molecular forms of the determined analytes.

The biological activity and toxicity concerning living organisms is demonstrated primarily by the elements existing in ionic forms. All ions of a specific element present in the environment may occur as free anions, cations or ions bound with organic or inorganic ligands in complexes. The simplest and most popular method of the sample separation into the dissolved phase (consisting of different metal ions complexes and metals adsorbed on colloidal particles) and insoluble particulates together with ions absorbed on them is called the physical speciation.

The redox speciation involves the elements that may occur at different oxidation states and consists in the determination of the concentration of the element at each oxidation state. It is especially important in the case of the elements that, depending on their oxidation state, demonstrate highly diversified toxicological characteristics in relation to living organisms.

Reducing the detection limits to the extremely low levels causes that it is not always possible to determine gradually decreasing amounts of the analytes in the examined samples with the analytical methods used so far. Because of that, there is a tendency to combine diverse methods and techniques together, to which the name ‘hyphenated techniques’ is given. It most often engages combining separation methods (e.g. chromatographic ones) with different modes of detection (e.g. spectroscopic techniques).

A specific hyphenated technique should be selective towards the determined analytes; sensitive in a wide range of concentrations, and should enable the best possible identification of the determined analytes. The ones employed the most quickly were the hyphenated techniques using the coupling of gas chromatography with different detectors and creating combinations such as GC-MS (*Gas Chromatography – Mass Spectrometry*), GC-AAS (*Gas Chromatography – Atomic Absorption Spectrometry*), GC-AES (*Gas Chromatography – Emission Atomic Spectrometry*) or GC-ICP-MS-TOF (*Gas Chromatography – Inductively Coupled Plasma – Time of Flight Mass Spectrometry*).

While coupling the gas chromatograph with the mass spectrometry detector was relatively simple, the large eluate volume in the case of the liquid chromatograph was a serious obstacle to the introduction of the HPLC-MS (*High Performance Liquid Chromatography – Mass Spectrometry*) system into the laboratory practice. For technical reasons, systems applying the liquid chromatography methods to the separation of the analyzed elements such as HPLC-MS and HPLC-ICP-MS (*High Performance Liquid Chromatography – Inductively Coupled Plasma – Mass Spectrometry*) appeared at the market some time afterwards.

Ion chromatography as a kind of liquid chromatography is primarily applicable to (in terms of the hyphenated techniques) the inorganic ions determination (2). Determination and separation of ions (which until recently has been thought to be difficult or even impossible to separate especially in the case of complex matrix samples) has become more effective with the implementation of the new high selective stationary phases in the ion-exchange columns and new modes of detection. It concerns the majority of the environmental samples in which the excess of some ions (most frequently - Cl^-, SO_4^{2-}, Na^+) hampers the determination of the remaining analytes on low concentrations levels (6).

The most popular hyphenated techniques employing ion chromatography are IC-ICP-MS (*Ion Chromatography – Inductively Coupled Plasma – Mass Spectrometry*) and IC-MS (*Ion Chromatography – Mass Spectrometry*).

The main applications of ion chromatography in speciation analytics can be divided into three areas:

1. Determination of nitrogen (e.g. NO_2^-, NO_3^-, NH_4^+) and sulfur (e.g. S^{2-}, SO_3^{2-}, SO_4^{2-} $S_2O_3^{2-}$, SCN^-) (3) ions,
2. Determination of inorganic water disinfection by-products (e.g. BrO_3^-, ClO_2^-, ClO_3^-) and other halide ions (e.g. ClO_4^-, IO_3^-) (4),
3. Determination of metals (e.g. Cr(III)/Cr(VI), Fe(II)/Fe(III)) and metalloids (e.g. As(III)/As(V), Se(IV)/Se(VI)) (5) ions.

Determination of nitrogen and sulfur ion forms has been known since the beginnings of ion chromatography and is usually carried out with the classic ion chromatograph equipped with an appropriate anion or cation exchange column and suppressed conductivity detection. From environmental and toxicological point of view, the most important are halides and metals/metalloids ions determinations.

Ion chromatography has the most significant practical meaning when taking into account the necessity of the water disinfection by-products determination at the level of $\mu g/dm^3$. The methods of bromate, chlorite and chlorate determination in water with ion chromatography can be categorized into three groups depending on the detection mode (6):

1. Direct methods (conductivity detection),
2. Indirect methods (UV/Vis detection),
3. Hyphenated techniques (MS and ICP-MS detection).

The direct methods rely on the selective BrO_3^- ions separation in the presence of other anions in the sample and their detection with suppressed conductivity detection. They are relatively simple and inexpensive but their main flaw is the difficulty with the appropriate separation of BrO_3^- and Cl^- ions, whose concentrations in real samples differ significantly. Regardless of the separation conditions, chlorides are leached next to bromate ions. The precondition for obtaining the quantification limits at the level of a few $\mu g/dm^3$ is the appropriate separation of BrO_3^-/Cl^- ion pair. In real samples in which the ratio of BrO_3^- ions concentration to Cl^- ions concentration exceeds 1:10.000, the chloride ions “overlapped” the bromate ions peak, which in turn hampers or even disables their separation and determination. The derivatization methods belong to the indirect methods category. They consist in converting the determined substance (after its separation in the analytical column) into its derivatives that can be then detected with the UV/Vis detector. The third category encompasses the hyphenated techniques such as IC-ICP-MS and IC-MS. These systems are characterized by very high detection and precision of the determinations but due to their high price they have not been routinely used in laboratories hitherto.

The simultaneous separation and determination of metals ions and metalloids at different oxidation states belongs to another important area of ion chromatography applications in speciation analytics (7).

Resuming - due to a strong environmental impact, metals/metalloids and selected halides ions determination and speciation have received significant attention in the last years. Ion chromatography has become one of the main powerful analytical tools for the analysis of complex matrices and speciation studies in that field of analysis. The hyphenated techniques such as IC-ICP-MS and IC-MS create completely new and immense possibilities in speciation analysis. The main advantages of those techniques comprise extremely low detection and quantification limits, insignificant interference influence and high precision and repeatability of the determinations. Like all other methods, the hyphenated techniques have their shortcomings. The limitations include issues such as the high price of the apparatus and their complexity, which causes their practical limited availability and usage in laboratories.

Employing hyphenated techniques requires in-depth understanding of the analytical methodologies and knowing the apparatus in minute details. The discussed systems are expensive and for this reason, so far they are used in the scientific research rather than in the routine analyses. Nevertheless, the development of the hyphenated techniques is becoming more and more important and the growing number of works concerning this subject seems to corroborate it.

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THE ROLE OF PILOT TESTING IN THE DESIGN OF SOLVENT EXTRACTION CIRCUITS

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Bench-scale solvent extraction testwork often leads to verification of the findings by the erection and operation of a continuous pilot plant circuit. The author will draw on 30 years of experience designing, building and operating solvent extraction pilot plant circuits in government and commercial process development laboratories. The role of piloting in the route from bench testwork to a full-scale plant and the reasons that commercial enterprises carry out pilot plants are enumerated. Aspects of the design of pilot plant circuits such as the scale and limitations to it are discussed. There are aspects of a commercial operation that can be successfully modeled and tested in a pilot circuit such as staging requirements while there are other types of data that design engineers, particularly those coming from commercial operations, attempt to obtain in piloting, usually with limited success. The talk will conclude with some comments on the collection and analysis of data generated by pilot plant circuits and dealing with issues such as mass balances.

SEPARATION IN MINERAL PROCESSING – DELINEATION, ANALYSIS AND EVALUATION

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INTRODUCTION

Separations are commonly performed in industry, science and nature. The occurrence of separation in different fields of life since remote past has resulted in the use of various terms, phrases, symbols and ways of description, analysis, and assessment of separation. It frequently causes misunderstanding among specialists of different fields of science and technology dealing with separations. There is a need to develop a self-consistent philosophy of separation with carefully defined terms and relations. Such an attempt is offered in this presentation for separation systems in which solid particulate material is divided into two or more products containing solid particles which differ quantitatively or qualitatively, or both, in at least one property.

SEPARATION DELINEATION

Separation converts the processed material (feed) into separation products called concentrate and tailing, and in some cases middlings (Fig. 1). It occurs under the influence of ordering and splitting forces. The elements of the whole process include delineation, analysis and evaluation (Fig. 2). Separation is possible due to a complex sequence of events (Fig. 3).

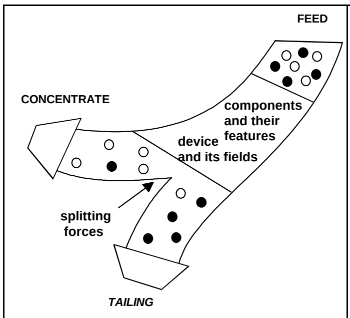

Fig. 1. Principle of separation

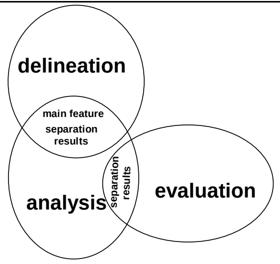

Fig. 2. Elements characterizing separation processes

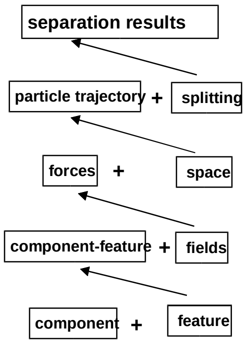

Fig. 3. The structure of separation

The results of separation depend on material, separation device and it surroundings (Fig. 4). The material parameters form a pyramid-like structure (Fig. 5). The top parameter is the main feature utilized in separation. The main feature of separation, combined with field provided by the separating device (electrical E, gravity g, electromagnetic γ etc.) creates a force, which causes stratification of particles and finally, due to the splitting force, products of separation (Fig. 6). The expressions for the forces, for instance, are $F = qE$, $F = mg$, where m is the mass and q charge of the particle. The main parameter can any property including particle size, density, shape, hydrophobicity, capability of adhesion, magnetic properties, electric properties, ability of adsorbing chemical substances, etc.

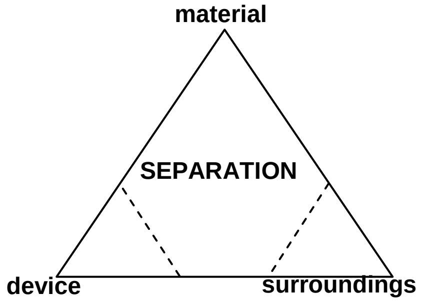

Fig. 4. Parameters of separation are determined by material, device, surroundings and their interactions

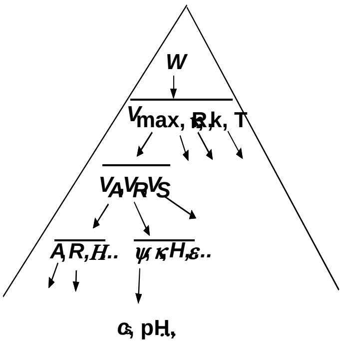

Fig. 5. The parameters form a pyramid-like structure

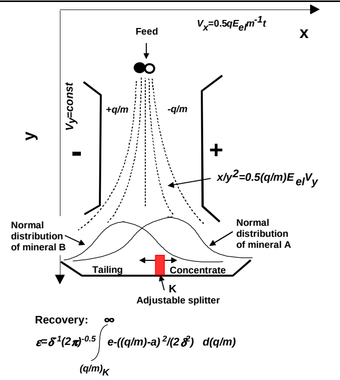

Fig. 6. Separation forces cause stratification and products formation

There are different possible components of separation systems. Their selection is arbitrary and their number is great. Typical components are: deposit, ore, feed, product, subcomponent, fraction, class, group, analytical fraction, mineral, group of minerals, elements, quarks, etc. (Fig. 7). The components and their features form a fractal-like structure (Fig. 8). Four most useful parameters are given in Fig. 9.

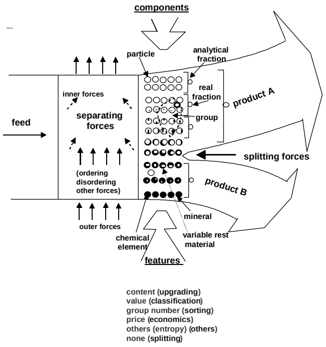

Fig. 7. Component of separation systems

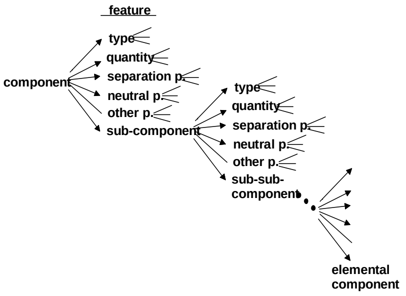

Fig. 8. Fractal-like structure of components and their features

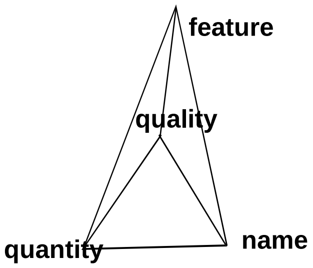

Fig. 9. Four most useful parameters of separation systems

SEPARATION ANALYSIS

Since a meaningful analysis and evaluation of separation results require at least two parameters, four basic parameters shown in Fig. 9 provide 6 ways of their presentation (Fig. 10 and 11).

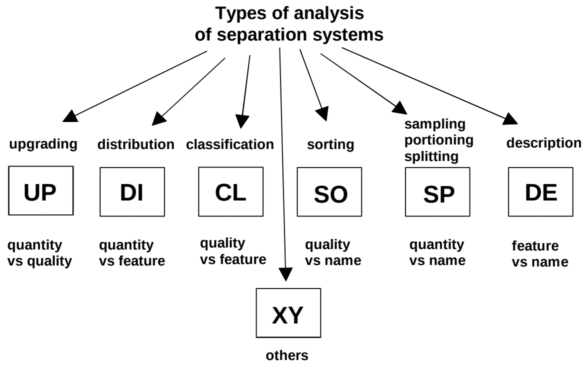

Fig. 10. Six principal ways of analysis of separation results and their proposed symbols

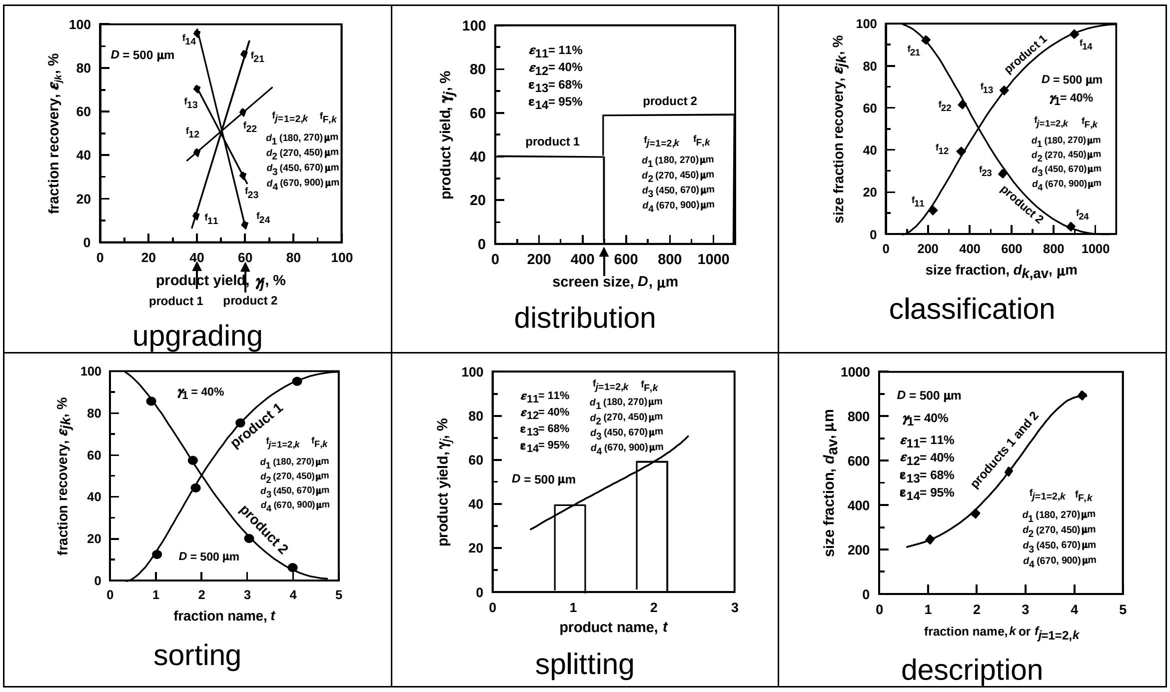

Fig. 11. The same separation results presented by six different approaches

The quality and quantity parameters can be mathematically combined into unlimited number of new parameters characterizing separation results such as recovery (ε), enrichment ratio, Hancock index etc. These parameters provide infinite number of upgrading curves and six of them are shown in Fig. 12.

In the case of variation of the feed grade, either a 3D plot (Fig. 13) or special 2D upgrading curves which somehow compensate the feed grade fluctuations (Fuerstenau (Fig. 14) and other curves) should be used. Grade variation makes the evaluation of separation results possible but somehow complex. When the separation data points are numerous and scattered, statistics has to be used (Fig. 15).

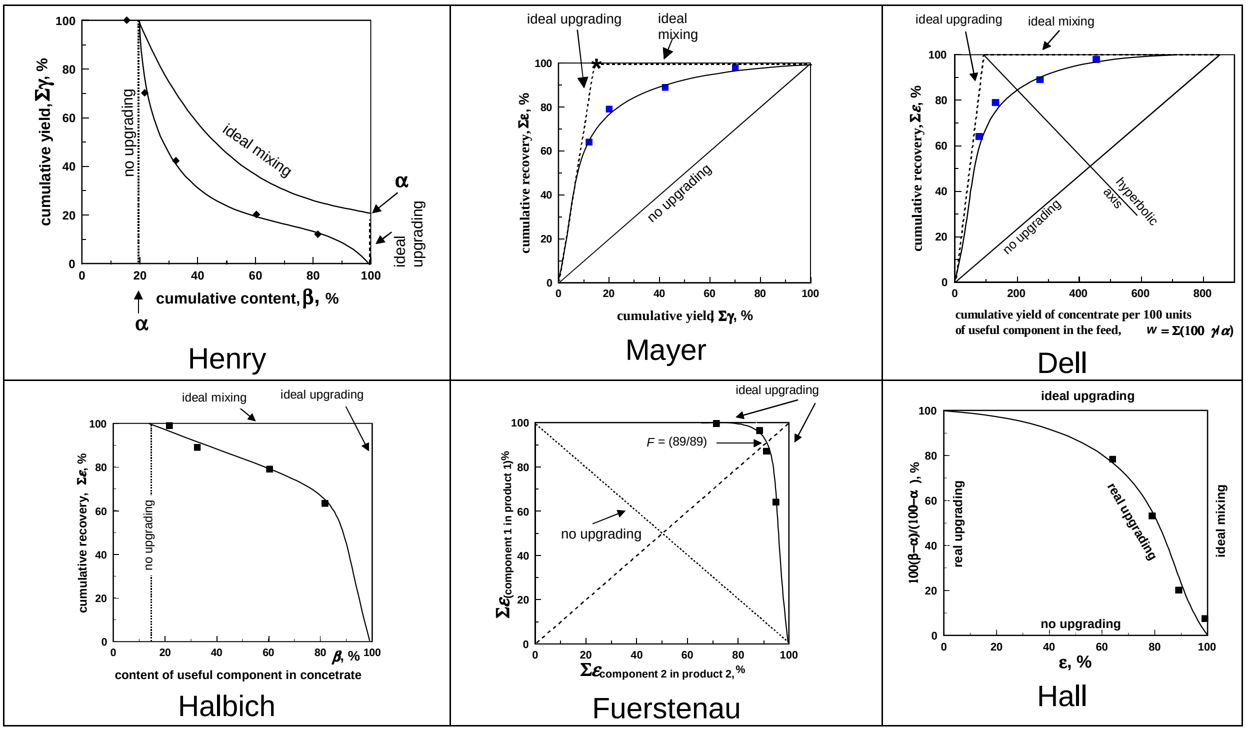

Fig. 12. Examples of infinite number of upgrading curves

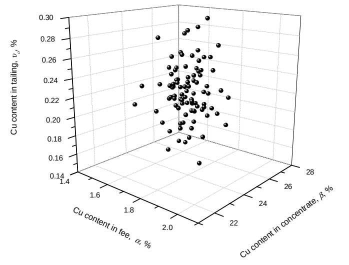

Fig.13. 3D relation between grade of concentrate β, tail ϑ and feed α

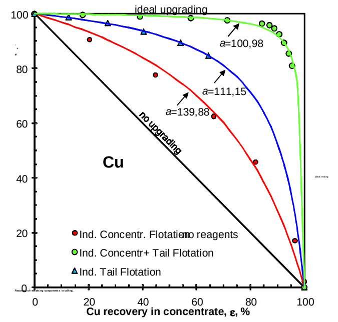

Fig. 14. Fuerstenau's plot $\left(\varepsilon = a\frac{(100-\varepsilon_o)}{(a-\varepsilon_o)}\right)$

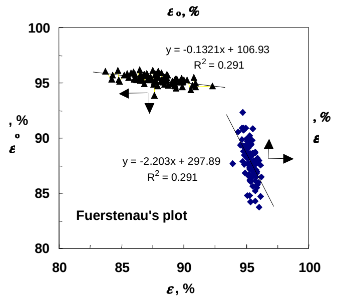

Fig. 15. Industrial data on Fuerstenau's plot (x = f(y) or y = f(x))

SEPARATION EVALUATION

The final stage of technological analysis of separation process is evaluation of separation results. An assessment of a separation process can be accomplished using upgrading curves and either one-adjustable parameter (Fig. 14) or other equations (polynomial, Fig. 15). The obtained equations and their parameters can be used for evaluation and comparing separation results. In all cases attention should be paid to the way of plotting (x = f(y) or y = f(x)) because different results are obtained (Fig. 15). Additional statistical criteria should be imposed to get the best and proper data fit.

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POLYMER-BASED MEMBRANES FOR THE SEPARATION OF CARBON DIOXIDE FROM NATURAL GAS

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Carbon dioxide is an undesirable component of natural gas that decreases its energy content, reduces transporting capacity of pipelines, and in presence of water forms acid that corrodes the pipelines. Membrane-based technologies enabling removal of carbon dioxide from natural gas are simple to operate and promise high separation efficiency while being less capital and energy intensive compared to other common methods such as scrubbing, pressure swing adsorption, and cryogenic separation. In order to make membranes a cost-effective substitute, their preparation has to be simple and scalable. We have developed straightforward single step process affording 100-150 nm thin polyaniline films deposited onto porous polypropylene support. Our efforts focused on the preparation of defect-free membranes with controlled thickness produced by oxidation polymerization of aniline in situ. The preparation methods included precipitation, dispersions, and emulsion polymerization techniques. Subsequent modification of the polyaniline layer using photografting and functionalization afforded membranes exhibiting a CO_2/CH_4 selectivity of up to 600 and a permeability of 3,500 barrer, i.e. values that are significantly better than those found for other known membranes.

II. SHORT LECTURES

PREPARATION OF POLY(N-VINYLIMIDAZOLE) CONTAINING CORE-SHELL TYPE SORBENT FOR REMOVAL OF ACIDIC DYES

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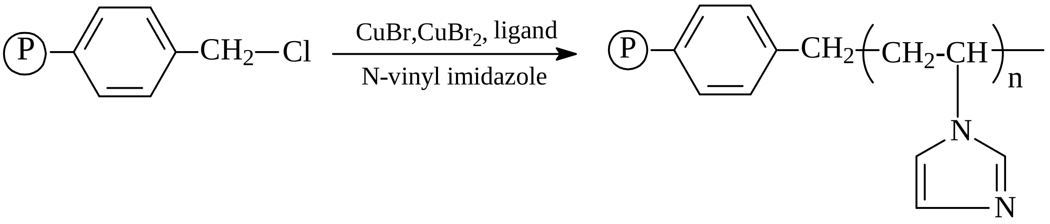
Dyes are used in many industries, such as food, paper, rubber, plastics, cosmetics, and textile to color their products. They usually have synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to biodegrade (1). Reactive dyes are hardly eliminated under aerobic conditions and are probably decomposed into carcinogenic aromatic amines under anaerobic conditions (2). So, the removal of color waste from waste effluents has become environmentally important.

Several types of synthetic adsorbent materials have been prepared and used in the environmental technology applications (3). Controlled living radical polymerization techniques that have emerged in recent years, offer potential use in surface grafting (4). This technique, for instance, provides chain growth mostly on the solid surface, provided that the initiator function is covalently bound to the surface.

In this study, this analogy has been extended to chloromethyl group to prepare poly(N-vinylimidazole) graft chains on crosslinked poly(vinyl benzyl chloride) polymer.



Scheme 1. Preparation of the sorbent

The obtained sorbent has been used to remove acidic dye removal from water. The sorption capacity of the calcon was found as 0.793 g dye / g sorbent.

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3,3'-DIINDOLYLMETHANE IMPRINTED POLYMERS: SYNTHESIS, CHARACTERIZATION AND ANALYTICAL PROCEDURE FOR TEMPLATE ISOLATION FROM BIOLOGICAL MATRIX

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Molecularly imprinted polymers (MIPs) are specially designed, cross-linked polymers, showing high affinity and selectivity towards selected target molecule or group of molecules. These synthetic polymers are widely used sorbents that allow for selective extraction of the analyte in solid phase extraction.

The current research goal was to produce MIP for separation of 3,3'-diindolylmethane (DIM). Furthermore, the molecular imprinting of DIM provides a chance to investigate the formation of specific binding sites using an aromatic heterocyclic template.

DIM is a major condensation product of indole-3-carbinol – a dietary compound that could be found in most cruciferous vegetables of the genus *Brassica* such as broccoli and Brussels sprouts. DIM is also available as a dietary supplement used in the cancer prophylaxis.

The novel sorbent has been developed using DIM as a template molecule in imprinting process during optimized radical, thermal polymerization. Twelve imprinted polymers from seven different functional monomers (e.g. methacrylic acid, 2-hydroxyethyl methacrylate, 2-phenylpropene, allylamine) in six various porogens (e.g. 1,2-dichloroethane, carbon tetrachloride, chloroform) were produced in presence of ethylene glycol dimethacrylate as the cross-linker. The binding capacities were determined and imprinting factors (IF) were calculated. The highest binding specificity was achieved when allylamine as the monomer and carbon tetrachloride as the porogen were used to form bulk polymer (130.4 ± 2.8 $\mu g \cdot g^{-1}$ and 49.03 ± 0.44 $\mu g \cdot g^{-1}$ for imprinted and non-imprinted polymer, IF = 3.12). The morphology of MIP was investigated and micrographs from scanning electron microscopy revealed porous nature of irregular particles. The specific surface area was estimated using methylene blue adsorption methodology (2.529 ± 0.071 $m^2 \cdot g^{-1}$ and 2.059 ± 0.058 $m^2 \cdot g^{-1}$ for imprinted and non-imprinted polymer). Scatchard analysis revealed heterogeneous population of binding sites in MIP but only one class of binding sites in non-imprinted counterpart.

A solid phase extraction protocol was fully optimized. Two methanol – water systems were selected as the most effective for loading and washing steps, while acetonitrile was chosen as the most efficient eluent suitable for recovery of 91.7 ± 3.8% of DIM from MIP. Optimal concentration of DIM and volume of loaded sample were also examined. Loaded volume of 2.5 mL was the most proper for 0.625 and 1.25 $mg \cdot L^{-1}$. The use of MIP for the separations of DIM from spiked bovine serum albumin was evaluated showing total recovery of 87.7 ± 3.5%. The commercial sorbent C18 was not suitable for such application.

SYNTHESIS AND CHARACTERIZATION OF POLYMERIC ADSORBENT FOR THE REMOVAL OF HERBICIDES FROM WATER

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Common use, toxicity and mobility in the environment make herbicides removal from water a significant issue. In past decades problem of contamination with herbicides, including atrazine has been investigated in research groups (1,2). One of the most efficient method of water purification is adsorption using polymer materials, which can be easily modified, regenerated and are characterized by great surface area. Numerous possibilities of modification and implementing of various functional groups into polymer structure was used in synthesis of selective adsorbents, which interact with specific substances.

In order to obtain specific polymer adsorbent for atrazine removal, the poly(divinylbenzene) beads were synthesized in radical polymerization using bead polymerization, and modified with maleic acid anhydrate in Diels-Alder reaction (3,4), as shown in Figure 1.

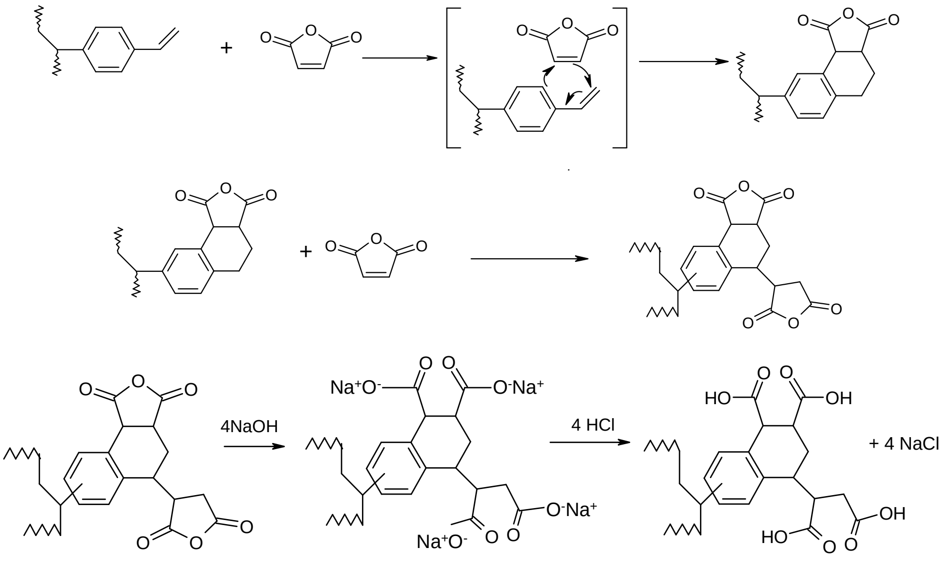


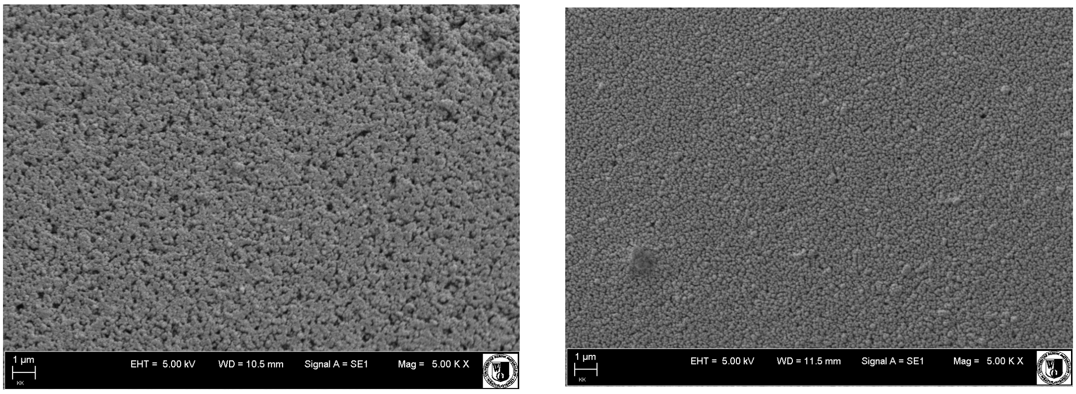
Fig. 1. Modification of poly(divinylbenzene) with maleic anhydride

By performing synthesis under varied conditions the porous structure was designed. Depending on used solvents mixture both porous and gel polymers were synthesized. In absence of solvents gel polymer was prepared, presence of toluene provided an expanded gel, whereas porous materials were received by using mixture of toluene and heptane. Pore size and surface area (BET) were obtained by examining nitrogen adsorption at the liquid nitrogen temperature. Content of carboxylic groups was measured by reversed hydrogen chloride titration. Characteristics of adsorbents is presented in Table 1.

Table 1. Characteristics of adsorbents

Symbol	Morphology	Solvent mixture heptane:toluene (w/w)	Carboxylic group content [mmol/g]	Surface area [m^2/g]	Pore size [nm]	Atrazine sorption capacity [mg/g]
G1	Gel (expanded)	Only toluene	2.6	479	2.80	28.02
G2	Gel	Without solvents	2.3	-	-	5.48
P1	Porous	1:1	2.8	517	8.98	22.05
P2	Porous	1:7	1.8	737	6.96	32.63

Using *non-* solvent (*n*-heptane) resulted in worse solvatation of divinylbenzene, pore size became higher, what caused the decrease of the surface area. Using toluene as a porogen gave smaller pores and higher surface area. Described differences in pore structure of adsorbents P1 and P2 are noticeable on scanning electron microscopy images which are presented in Figure 2.



a b

Fig. 2. SEM images of porous adsorbents a - P1, b - P2

Carboxylic group content in the case of G1, G2 and P1 adsorbents is similar. However, polymer P2 is characterized by lower carboxylic groups content, which is ascribed to higher degree of crosslinking and lower amount of pedant vinyl groups that could be modified.

To examine relationship between adsorbent structure and atrazine removal the sorption studies were performed. In order to obtain sorption isotherms series of adsorbents and various volume of 10 ppm atrazine solution were mixed for 24 hours. Equilibrium concentration of atrazine in solution was measured using UV-Vis spectroscopy. Results are presented in Figure 3. According to IUPAC terminology the analyzed systems atrazine-adsorbent can be assigned to IV type isotherms, characteristic for mesoporous materials. Maximum sorption capacity (32.6 mg/g) was achieved for adsorbent P2, what can be ascribed to the greatest surface area. For the same reason minimum sorption capacity (5.5 mg/g) was observed for polymer G2, which removes atrazine due to specific interactions between herbicide and carboxylic groups on the adsorbent surface, excluding trapping in pores. Increase of sorption capacity on G1 adsorbent in relation to P1, despite low surface area can be explained with average pore size. More efficient atrazine uptake is observed when pore size value is 2.8 nm (G1), in the contrary to twice greater pores in P1.

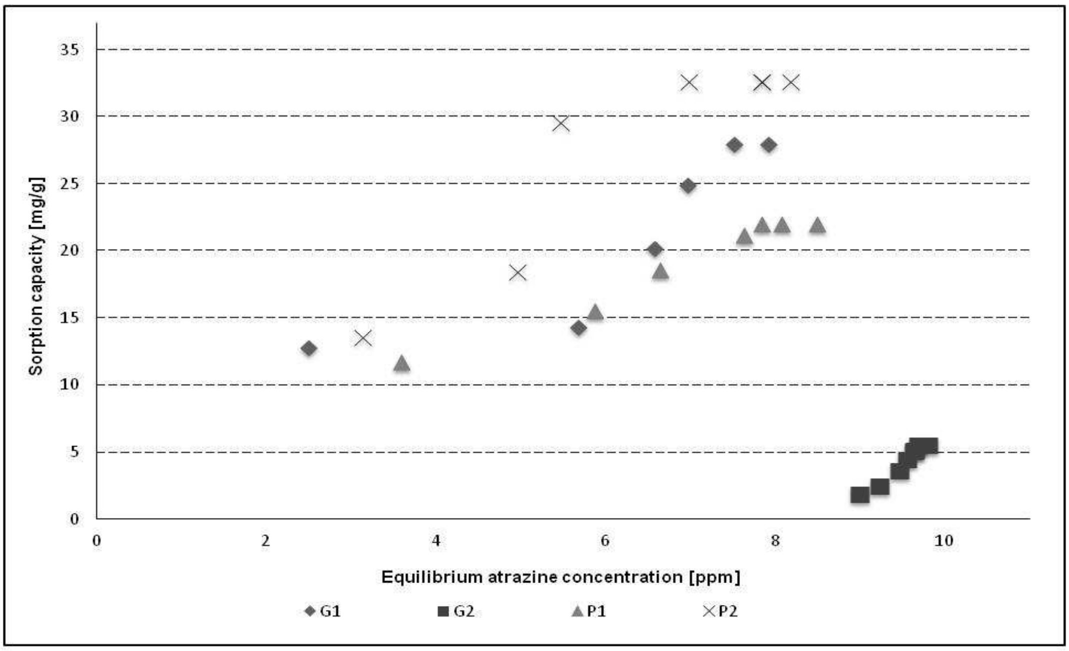


Fig. 3. Sorption isotherms for atrazine and analyzed adsorbents

Sorption kinetics was examined by mixing adsorbent with 10 ppm atrazine solution, collecting samples at fixed times and analyzing the residual herbicide concentration. Reaching the equilibrium depends on adsorbent structure. Due to carboxylic groups situated on the polymer G2 surface and their availability equilibrium was reached after 120 minutes. Adsorption is based entirely on chemical interactions between adsorbent and adsorbate. In the case of porous adsorbent P1 equilibrium time is 120 minutes as well, however it is ascribed to greater average pore size and, so that, quick atrazine diffusion. Adsorbents P2 and G1 are characterized by smaller average pore size, therefore process is slower – equilibrium was reached after 210 minutes.

Intensification of sorption due to specific interactions between adsorbent and atrazine was confirmed by comparison of sorption on polymers before and after maleic acid anhydrate modification. Increase of maximum sorption capacity (approximately 5 mg of atrazine per 1 g of adsorbent) after modification of poly(divinylbenzene) was observed.

In order to characterize adsorbent-adsorbate interactions quantum mechanics studies were performed using Density Functional Theory (DFT) calculations at B3LYP/6-31+G level by Gaussian09. To simplify calculations instead of polymer, the molecule of modified divinylbenzene (monomer) was taken into consideration. Analysis were performed in water, using Polarizable Continuum Model (PCM). Parameters of hydrogen bonding were obtained for the most stable conformer, energy calculations were performed in compliance with Basis Set Superposition Error (BSSE). Structure of the complex characterized by the lowest energy is presented in Figure 4.

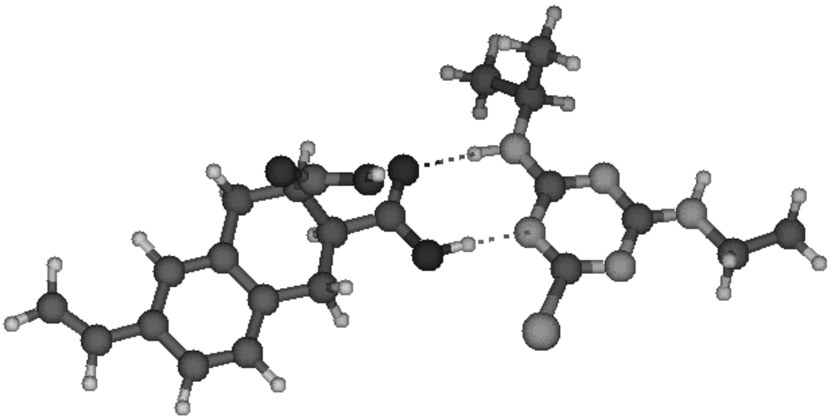


Fig. 4. Complex of atrazine and modified divinylbenzene

As a result of the theoretical calculations, strong interaction between atrazine and modified divinylbenzene can be found (20 kcal/mol). It is consisted of two hydrogen bonds: between hydroxyl hydrogen atom of carboxylic group from modified divinylbenzene and nitrogen atom containing free electron pair from atrazine (O-H---N) and between hydrogen atom of atrazine amine group and carbonyl oxygen atom form modified divinylbenzene (O---H-N). Bond length of O-H---N is in the range of 1.5-1.6 Å, whereas O---H-N is approximately 1.8-1.9 Å. Therefore, it is possible to assume that greater influence on atrazine sorption using modified divinylbenzene has hydroxyl hydrogen atom than carbonyl oxygen atom.

Results based on quantum mechanics confirmed experimental data. Intensification of atrazine sorption using synthesized sorbent is caused by specific interactions between herbicide and poly(divinylbenzene) containing carboxylic groups. Diels-Alder modification with maleic acid anhydrate leads to obtain selective adsorbent for atrazine removal from water, which can potentially find application for instance in solid phase extraction .

Acknowledgements: This work was financially supported by Wrocław University of Technology grant No. S20096/Z0309. Calculations have been carried out in Wrocław Centre for Networking and Supercomputing (http://www.wcss.wroc.pl), grant No 227.

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PLASTIC ANTIBODIES

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Molecularly Imprinted Polymers (MIPs) are generic alternatives to antibodies and natural receptors in diagnostics and in separation. Here, we report an efficient and flexible method for automatic synthesis of MIP nanoparticles using solid-phase automated photo/chemical reactor. Our approach requires a cartridge with an immobilised template docked into a thermostatic computer-controllable reactor, thereby allowing controlled manufacturing of affinity nanoparticles with narrow size distributions in the range 20-400 nm. We demonstrate the synthesis of water-soluble affinity nanoparticles for various targets such as melamine, vancomycin, peptides, proteins and virus particles with minimal manual intervention and short reaction-cycle times. The developed reactor allows easy functionalisation of nanoparticles with fluorescent, electrochemical or magnetic labels. The affinity of all synthesised nanoparticles is at the picomolar-nanomolar level, which makes them suitable for practical applications in assays, sensors and in affinity chromatography. The synthesised nanoparticles also possess bioactive properties. Thus, specific MIP nanoparticles made for enzymes are capable of activating or inhibiting enzyme activity, depending on binding mechanism. With this new development in MIP synthesis we foresee a time when the application of natural antibodies in diagnostics would be challenged by appearance of new sensor devices and assays that utilize stable and inexpensive "plastic antibodies" with integrated recognition and signalling functionalities. Equally exciting could be *in vivo* applications for such materials which would be discussed in the present paper.

POROUS POLYMERIC MATERIALS PREPARED BY MOLECULAR IMPRINTED TECHNIQUE IN PRESENCE OF SILICA OR SILSESQUIOXANES AS A POROGENS

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Molecular imprinted technique is expanding method of preparation of polymers for variety of applications (1-3). One of the promising methods to obtain porous materials consists of usage of nanosilica and silsesquioxanes (POSS) as a porogens. This approach allow to obtain narrow diameter and pore size distribution due to the uniform size of silica and POSS particles (4). Additionally, polyhedral oligomeric silsesquioxanes possess rigid and well defined shape with high functionalities allowing the introduction of molecular imprinting into polymer matrix (5) (Fig. 1).

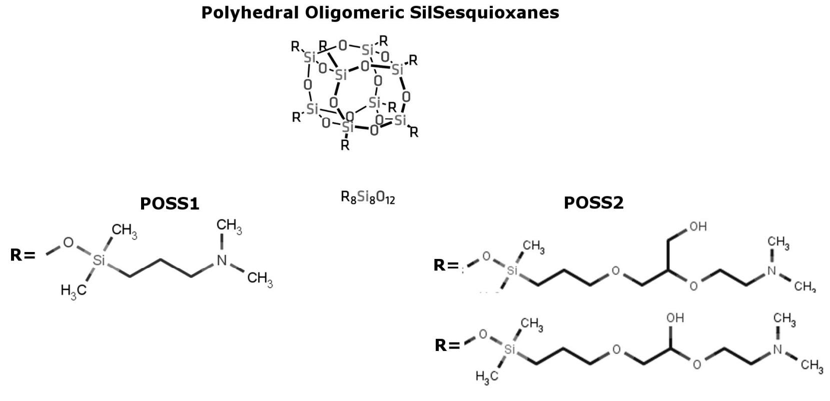

Fig. 1. Schematic representation of polyhedral oligomeric silsesquioxanes structures with functional groups

This work presents the preparation of molecularly imprinted polymers in bulk polymerization of methacrylic acid with ethylene glycol dimethacrylate as a crosslinker (65 wt.%) in the presence of silica nanoparticles (15-20 nm diameter)/POSS. In order to obtain the appropriate porosity the preliminary polymerizations were performed at several percentage contents (w/w [%]) of silica nanoparticles to monomers ca. 6%, 12% and 18%). Subsequently, two polymers were prepared with silsesquioxanes (POSS1,2) as a functional porogens. Both silsesquioxanes and nanosilica were removed from the polymer matrix by using 3M ammonium hydrogen difluoride, leaving a porous structure, and in the case of POSS molecular imprinting on the surface of the pores.

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ELECTROPHORESIS AND LIQUIOD CHROMATOGRAPHY TECHNIQUES ORTHOGONALLY COMBINED INTO CONTINUOUS TWO-DIMENSIONAL SEPARATION PROCESS

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Combination of liquid chromatography and electrophoresis into two-dimensional (2D) separation mode has been often reported in scientific literature. Such separations are characterized by high efficiency due to different selectivity of the techniques involved. 2D separation process is usually realised consecutively - separation with the first technique is followed by separation with the second one or this order can be reversed. There are also reports on 2D separations in which both techniques are combined into single separation process, i.e. processes of liquid chromatography and electrophoresis proceed simultaneously and orthogonally (e.g. paper (1) on continuous annular electrochromatography). Such separations are rather rare due to technical problems, which researchers face out when they try to apply the method. However, the method seems very attractive in respect of possible high separation efficiency especially for preparative separations.

In our department we have been involving in development of relatively new separation technique named pressurized planar electrochromatography (PPEC), which was introduced by Nurok et al. in 2004 (2). In this technique mobile phase is driven into movement against adsorbent layer by electric field. So in PPEC electrophoresis and partition processes are involved in separation of components of any sample mixture. PPEC shows quite different separation selectivity relative to liquid chromatography and electrophoresis. With regard to this feature this technique seems to be very attractive to 2D separations (3). Furthermore, it is also very attractive to 2D separation, in which both electrophoresis and liquid chromatography are performed orthogonally and simultaneously as a single process.

In the presentation we will show prototype device for such 2D separation technique. The device can operate in analytical and preparative modes. We will demonstrate some examples of both analytical and preparative separations. In addition we will discuss variables, which can influence efficiency of separation with this new technique. We have named this technique as orthogonal pressurized planar electrochromatography (OPPEC).

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APPLICATION OF THE ION-IMPRINTING TECHNOLOGY TO THE DESIGN AND SYNTHESIS OF NICKEL(II) IMPRINTED POLYMERS

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Metal ion extraction and quantification in the aqueous environment is a major issue because of their high toxicity. Among the various methods that can be used for metal ion separation, solid-phase extraction using ion-exchange or chelating materials offers many advantages such as easy separation process, reducing of the disposal costs as well as solvent uses and exposure. Anyway, this method usually suffers from a lack of selectivity. Ion-imprinting technology is a perfectly suited method to prepare selective sorbents (1). Imprinted polymers can be prepared by copolymerization of a functional monomer and a crosslinker in the presence of a template ion (or molecule). The removal of this template generates inside the polymer network binding sites with high affinity and selectivity towards the template. The selectivity of such imprinted materials has been compared to that of the antibody-antigen system. Still the main advantages of imprinted polymers toward biological systems are their robustness, easy preparation and low cost.

Our objective was the elaboration of ion-imprinted polymers (IIPs) for selective extraction of nickel(II) from an aqueous matrix. Although bulk polymerization is currently used for the preparation of IIPs, it leads to particles without well-defined forms after tedious steps of crushing, grinding and sieving. As we wanted to prepare particles in a bead format, we choose to use suspension polymerization. To avoid the transfer of the metal ion in the aqueous phase, inverse suspension polymerization was performed using mineral oil as the continuous phase. We thus reported the first attempt to prepare IIPs by a nonaqueous suspension polymerization (2). We now compare two different ways of introducing the metal template during the IIP synthesis.

Vinylbenzyliminodiacetic acid (VbIDA) was polymerized with EDMA in the presence of nickel(II). IIP1 was prepared without prior complexation of Ni by VbIDA, whereas for IIP2 the $(VbIDA)_2Ni$ complex was previously isolated. The efficiency of the IIPs for nickel retention in presence of interfering species (Co, Pb and Zn) was measured by batch experiments with metal quantification by ICP-AES, and compared with non-imprinted polymers and Amberlite IRC-748 (a commercial resin with IDA moiety). Both resins IIP1 and IIP2 present high sorption capacities for nickel (10.8 and 10.7 mg/g). As shown in Fig. 1, in presence of interfering ions, the sorption capacities remain very high with a significantly improved selectivity for IIP2. The comparison with Amberlite IRC-748 emphasizes the selectivity of both IIPs towards nickel.

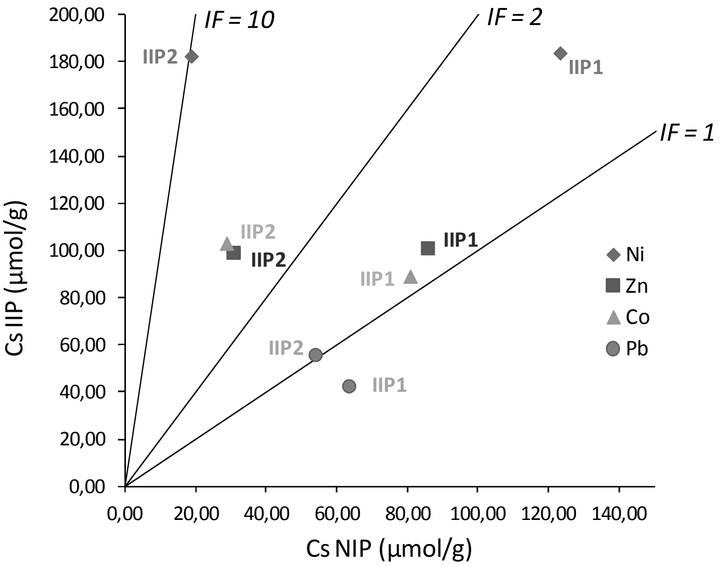
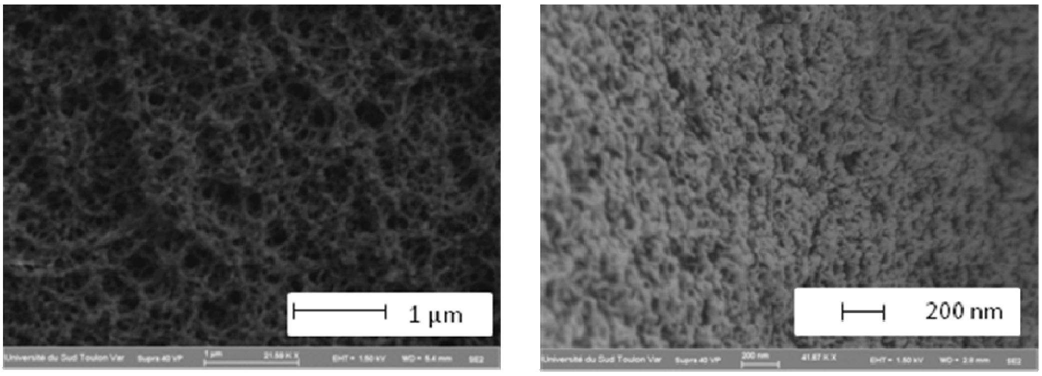


Fig. 1. Sorption capacities of imprinted polymers vs non-imprinted polymers (IF = imprinting factor)



(a) (b)

Fig. 2. SEM pictures of IIP1 (a) and IIP2 (b)

The characterization of the polymers porous structure by SEM (Fig. 2) and nitrogen adsorption/desorption revealed that IIP1 present a micro-, meso- and macroporosity whereas IIP2 was only macroporous. The BET surface area calculations lead to 275 and 27 m^2g^{-1} for IIP1 and IIP2 respectively. These results prove the importance of preforming the complex between the functional monomer and the metal template since IIP2 has a comparable sorption capacity with IIP1 and is much more selective with a less porous structure.

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EFFECT OF COORDINATIVELY-INERT ALKYL GROUPS ON SIZE-DISCRIMINATING EXTRACTION OF ALKALI METAL IONS WITH PROPYL-ACETIC ACID CROSSED TYPE CALIX[4]ARENE

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Calixarenes have been prepared by condensation reaction of the corresponding phenol with formaldehyde and extensively employed as host compounds in host-guest chemistry. A number of review articles have been published on their use for ion discrimination (1-6). Calixarene derivatives exhibited size-discriminating property due to their specifically preorganized cyclic frameworks. In the previous work, calix[4]arene tetraacetic acid was prepared to investigate alkali metal extraction. It exhibited high sodium selectivity and forms 1:2 complex with sodium ion in chloroform. It took place by “self-coextraction” mechanism of two sodium ions based on allosteric effect (7,8). In our recent work, alkali metal extraction with crossed carboxylic acid type of calix[4]arene derivatives containing two longer carboxylic acid and two acetic acid at distal position has been reported (9). All of them selectively form complexes with sodium ions among three alkali ions, although their extraction abilities are lower compered with calix[4]arene tetraacetic acid derivative. The rest two different groups from two acetic acid groups is important for extraction ability and metal separation efficiency.

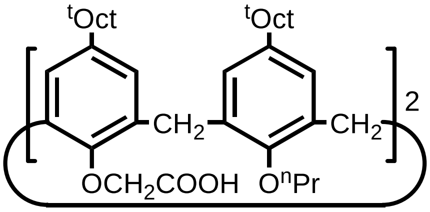


Fig. 1. Structure of acetic acid-propyl crossed type of *p*-t-octylcalix[4]arene

In the present study, calix[4]arene derivative containing two coordinating-inert propyl groups and two acetic acids at distal position has been prepared to investigate extraction behavior of alkali metals. Chemical structure of acetic acid-propyl crossed type of *p*-t-octylcalix[4]arene is shown in Fig. 1. The extractant was prepared by 4 steps from *p*-t-octylphenol and was identified by IR and ^{1}H-NMR spectra. Synthetic scheme of acetic acid-propyl crossed type of *p*-t-octylcalix[4]arene is shown in Fig. 2.

The individual and competitive extractions of lithium, sodium, and potassium, rubidium, and cesium ions, were carried out by a batchwise method. Organic phase was prepared by dissolving the extractant into chloroform to be 5 mM. Aqueous phase was prepared by dissolving each alkali chloride into 0.1 M HCl or 0.1 M HEPES buffer to be 0.1 M. Equal volumes of both phases were shaken at 30℃ for the desired time. The concentration of alkali ion stripped from organic phase after the extraction was measured by atomic absorption spectrophotometer (abbreviated as AAS, Shimazu AA-6800). In ^{1}H-NMR study, $CDCl_3$ was used instead of $CHCl_3$. After equilibrium, the spectra of the extractant molecule in the organic phase were recorded by ^{1}H-NMR spectrophotometry.

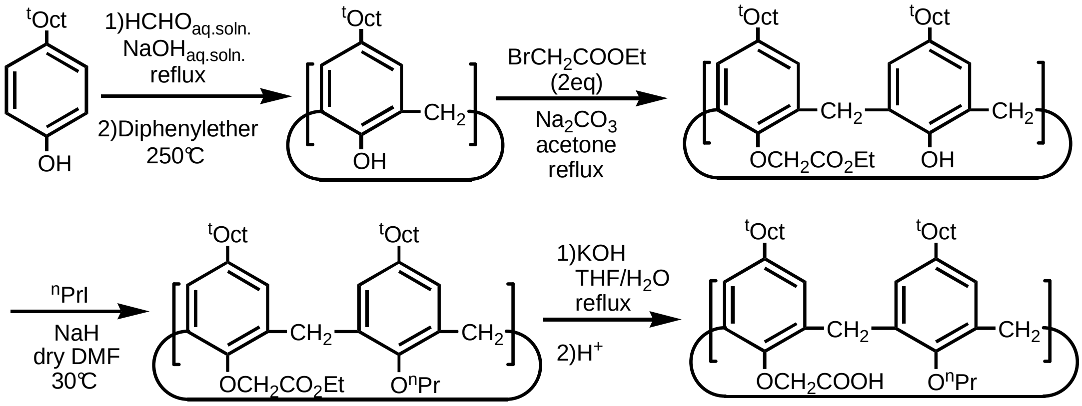


Fig. 2. Synthetic scheme of acetic acid-propyl crossed type of *p*-t-octylcalix[4]arene

Effects of alkali metal loading with acetic acid-propyl crossed type of *p*-t-octylcalix[4]arene in individual and competitive systems are shown in Figs. 3(a) and (b).

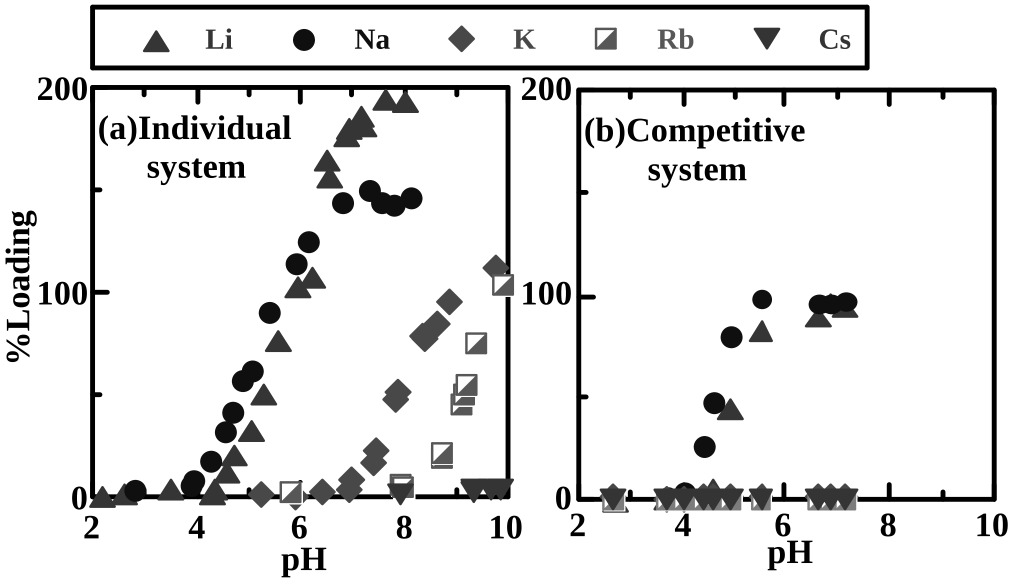
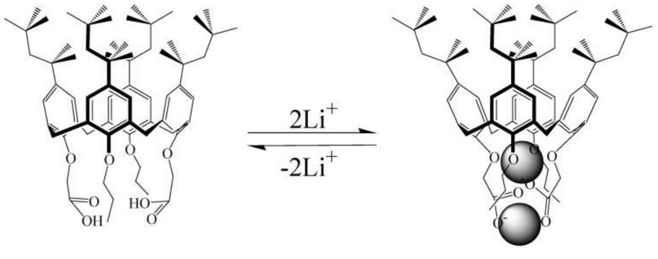
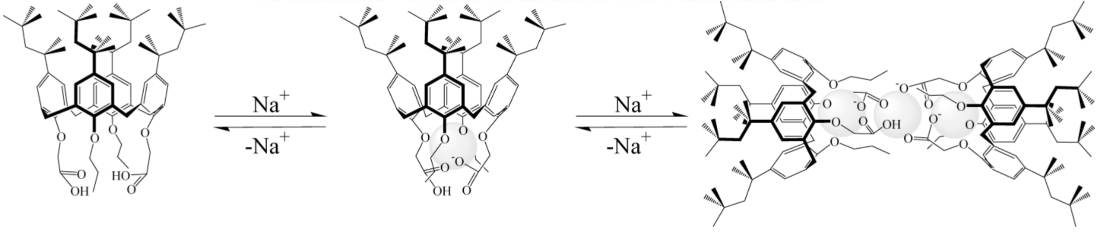


Fig. 3. Effect of alkali metal loading with acetic acid-propyl crossed type of *p*-t-octylcalix[4]arene in individual and competitive systems

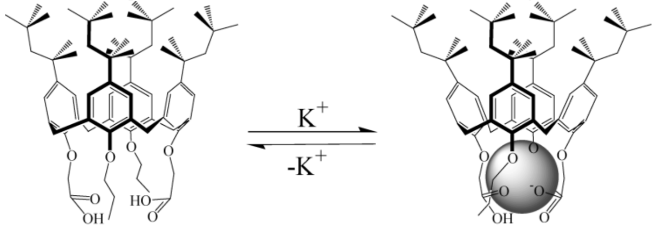
In the individual system, lithium ion was loaded on a single molecule of the extraction reagent up to 200% under the present condition, while sodium and potassium ions were loaded up to 150% and 100%, respectively. The present extraction reagent forms 1:2, 2:3, 1:1 complexes with lithium, sodium, potassium ion, respectively in the individual system. In the competitive system, lithium and sodium ions were loaded up to 100% respectively, whereas potassium ion was hardly extracted. After the first sodium ion was extracted, lithium ion as the second metal ion was extracted and the extraction reagent froms 1:1:1 complex with lithium and sodium. Extraction equations of alkali metal ions with the present extractant in individual and competitive systems are proposed and shown in Fig. 4. The different stoichiometry and selectivity is attributed to the size discriminating property. This proposal was supported by relationship between the chemical shift percentage of the extraction reagent based on ^{1}H-NMR spectroscopy and the metal loading percentage based on AAS measurement.



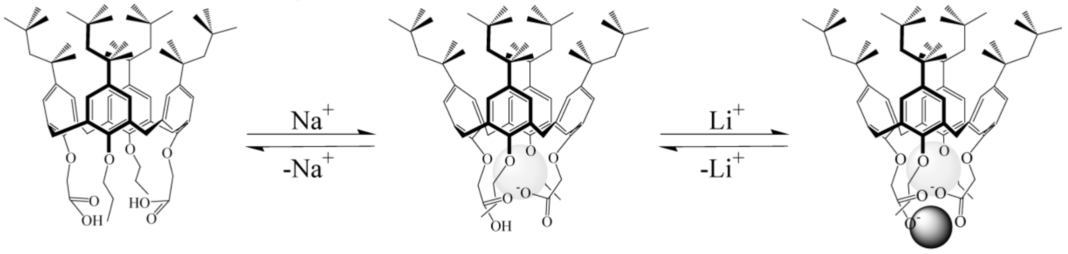
(a) Simultaneous extraction mechanism of Li in individual system.



(b) Stepwise extraction mechanism of Na in individual system.



(c) Extraction mechanism of K in individual ststem.



(d) Stepwise extraction mechanism of Li and Na in competitive system.

Fig. 4. Extraction models of alkali metals in individual and competitive systems: (a) lithium, (b) sodium, (c) potassium ion loadings in individual system, (d) lithium and sodium loading in competitive system

Role of disubstituted coordinatevely-inert propyl groups on not only decreased coordination number as a negative effect but also steric and lipophilic-hydrophilic suppression for allosteric coextractive separation as a positive contribution was also discussed.

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APPLICATION OF SOLVENT EXTRACTION FOR RECOVERY OF MAJOR COMPONENTS FROM ZINC ELECTROLYTE

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Material for investigation

Zinc electrolyte, circulating within electrolytic zinc production circuit, contains mainly zinc sulphate, free sulphuric acid, and, in smaller amounts, magnesium and manganese sulphates. Such elements as Na, K, Cl, F are usually present within their permissible limits. The crude pregnant leach zinc-bearing solution is being purified by chemical methods: Fe, As, Al, Si, Sb, Ge are rejected by oxyhydrolysis, while Cd, Cu, Co, Ni, Pb - by cementation. Irremovable by these methods are Mg, Ca, Na, K, chlorides, fluorides. In general, zinc electrolyte, used in electrolytic zinc metal production, because of necessity to maintain high parameters of current efficiency and product purity, except of established range of their typical components (e.g. 100-135 kg/m^3 Zn, 0-30 kg/m^3 H_2SO_4, 15-30 kg/m^3 Mg, 10-12 kg/m^3 Mn, 4-8 kg/m^3 Na) constitutes a product of very high purity (Ni, Co, Cu, Cd < 0.001 g/dm^3). In particular it does not contain iron, aluminium or silica. This favours possibility to apply solvent extraction technique to zinc recovery from this part of the solution, which from technological reasons has to be removed from the circuit.

The composition of the treated electrolyte was as follows:

H_2SO_4	Zn	Mg	Mn	Na	K	g/dm^3
155.3	59.3	14.3	2.84	5.23	1.43	
Ca	Al	Si	Pb	Cl	F	
0.55	0.011	0.058	< 0.001	0.36	0.0055	

For effective zinc extraction the treated solution must be nearly neutral. One of the early ideas of this work was applying ammonia solution for sulphuric acid neutralization, both present originally in electrolyte and evolving during extraction. Using 25 % ammonia for neutralization of free sulphuric acid leads to precipitation over 70 % of zinc and in the less extent the rest of cations in a form of hydrated crystalline sulphate phases. There is no possibility for distinct separation of components of ammonia neutralized zinc electrolyte by simple crystalline and mother liquor phases separation. On the other hand, to maintain all electrolyte components in solution one should dilute it with water taken in amounts of ≥ 1.6 litres per litre of electrolyte. Therefore the trials to utilize ammonia in order to prepare the solution for zinc extraction with conversion of all excessive sulphuric acid into ingredient of ammonia-magnesium type fertilizer do not justify themselves. Detailed discussion of this problem, especially on influence of preliminary dilution on composition of crystalline phases and further treatment of ammonium-magnesium raffinates, authors will provide at Mineral Engineering Conference MEC2013.

The solution for investigation of zinc extraction has been prepared by the method utilizing fine grained mineral calcium carbonate for acid neutralization.

Crystalline gypsum $CaSO_4{\cdot}2H_2O$ was produced as a by-product. The composition of resulting solution further subjected to zinc extraction was as follows:

Zn	Mg	Mn	Na	K	Ca	Cl	F		pH
51.70	12.6	2.65	4.99	1.38	0.56	0.305	0.007	g/dm^3	5.6

Zinc extraction

First trials were done with 36 % (vol.) di(ethylhexyl)phosphoric acid (DEHPA) dissolved in hydrocarbon diluent Exxsol D80, but, because of too high viscosity, its concentration during further experiments has been limited to 18 % (vol.) /about 0.50 M/. Fig. 1 and 2 contain graphs showing concentrations of Zn and contaminants in organics versus equilibrium pH. The 36 % organic phase, as more viscous, bears increased amounts of impurities. The relationships were investigated using 25 % ammonia as increasing pH neutralizing agent.

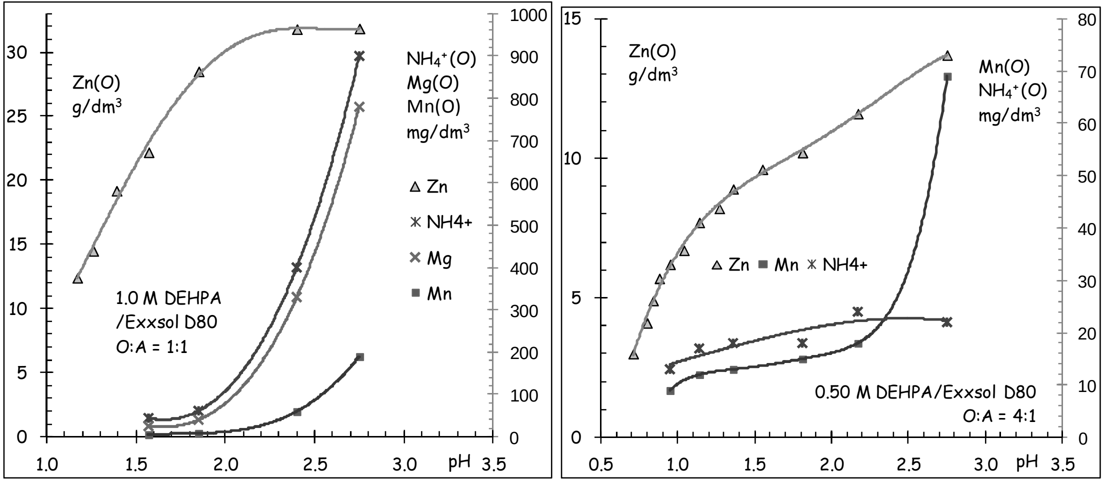

Fig. 1 & 2. Concentrations of Zn and contaminants in organics v. equilibrium pH

Next stage comprised zinc extraction isotherm examination at equilibrium pH of 2.5 ± 0.1. The isotherms have been obtained with 25 % NH_3 at ambient and elevated (40ºC) temperature and 5.0 M NaOH (at ambient temp.) used as neutralizing agents. The results are shown in figures 3 and 4.

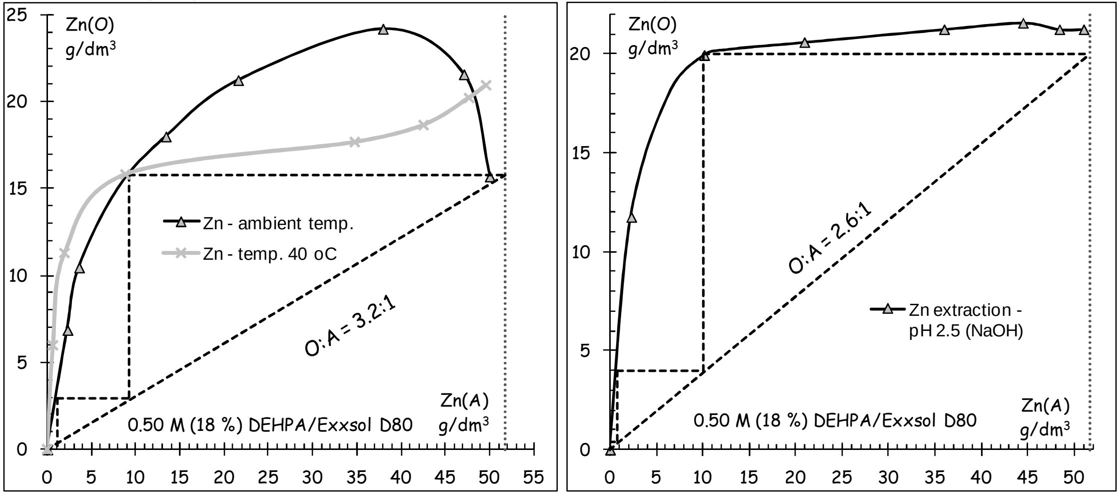

Fig. 3. & 4. Zn extration isotherms with ammonia and NaOH used as neutralizing agents

The results obtained with NaOH involved are advantageous - extractions can be conducted at lower phases ratio (O:A) because of practical possibility to utilize higher level of organic phase saturation with Zn(II) /≥ 20 g/dm^3/. More on that theme one can find in earlier works of the authors (1,2). About so called preneutralization of the extractant with soda lye - within other references, e.g. (3).

Stripping isotherm (Fig. 5), prepared with organic phase saturated to the level of 13.7 g/dm^3 Zn(II) (at pH = 2.5 ± 0.1, stabilized by ammonia) and 2.4 M sulphuric acid, indicate, that concentrations of about 155 g/dm^3 Zn(II) can be obtained in stripped solution already applying only two steps of counter-current stripping.

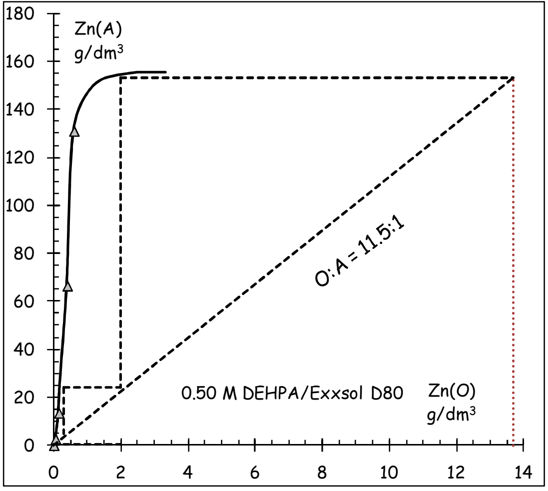

Fig. 5. Zn stripping isotherm with 2.4 M sulphuric acid

Exploiting directives, obtained by investigations in a form of the isotherms and their's McCabe-Thiele interpretations, multistage laboratory trial has been carried out. The way it was done is shown as the scheme on Fig. 6.

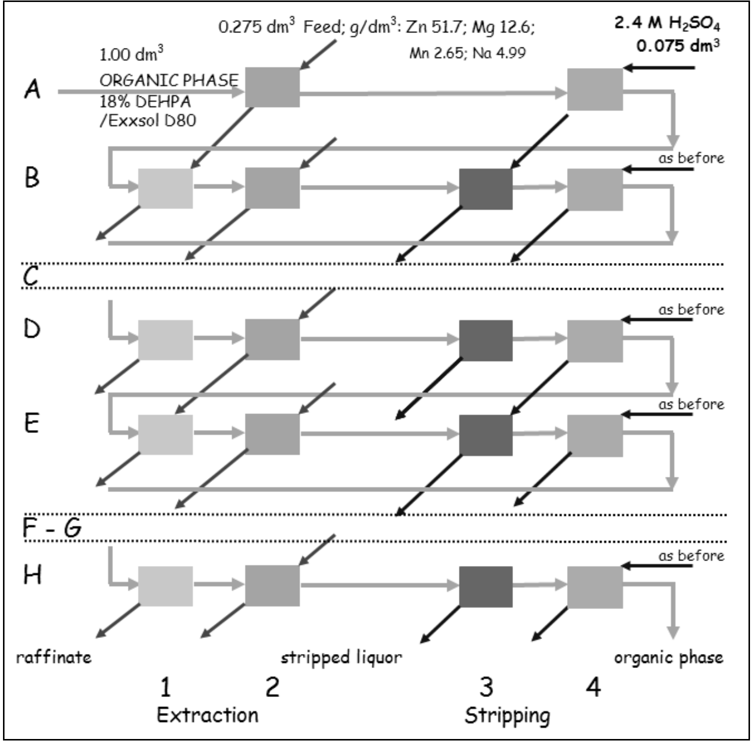

Fig. 6. Scheme of extractive system realizing course of counter-current extraction and stripping of zinc(II)

Starting from the cycle E amount of organic phase was increased to 1.20 litre.

Results obtained are presented in the table below. It contains ammonia consumption, obtained equilibrium pH and concentrations of components in raffinates and stripped solutions.

	Raffinates								Strip liquors	
	1 (final)					2 (immediate)			3*)	4
Cycle	NH_3	pH	Zn	Mg	Mn	NH_3	pH	(Zn)	(Zn)	(Zn)
	ml	-	g/dm^3	g/dm^3	g/dm^3		-	g/dm^3	g/dm^3	g/dm^3
A	-	-	-	-	-	32.0	2.52	6.86	-	-
B	7.0	2.50	0.099	-	1.1	23.0	2.58	16.34	157.2	134.7
C	11.0	2.60	0.22	-	-	20.0	2.70	22.88	156.9	143.9
D	14.5	2.70	0.39	12.6	2.7	15.0	2.61	30.07	150.7	141.5
E	17.5	2.55	1.40	-	-	12.0	2.53	36.28	157.6	144.8
F	23.0	2.65	0.82	-	2.2	13.5	2.50	33.34	164.1	150.7
G	21.0	2.50	0.17	-	2.6	15.5	2.50	38.90	161.5	152.0
H	24.0	2.60	3.40	12.4	2.5	8.0	2.65	43.15	147.1	150.0
Cumulative stripped liquors*)										
Sample Nos (cumulative)			Zn	Mg	Mn	NH_4^+	Cl	F		
			g/dm^3	g/dm^3	g/dm^3	g/dm^3	mg/dm^3	mg/dm^3		
B3 + C3 + D3			154.0	1.46	0.54	0.095	42	< 1.0		
E3+F3+G3+H3			163.0	1.38	0.29	0.13	52	< 1.0		

Summary

Generally it can be stated, that:

1) zinc recovery from preneutralized acidic zinc electrolyte, using solvent extraction technique with 18 vol.% DEHPA as extractant and 25 % ammonia as neutralizing agent, with the aim of parallel utilization of raffinate as a mineral fertilizer solution, can be realized on two ways:

i) after electrolyte substantial dilution with water to the level of some 3.0 litres from one litre of electrolyte, neutralization with ammonia and zinc(II) extraction at O:A ratio of about 1.5-2:1; or

ii) after acid removal by crystalline gypsum precipitation and zinc(II) extraction at O:A ratio of some 3.6-4:1,

2) to stop an excessive transport of contaminants by organic phase to strip solution it is recommended:
- performing the extraction at the temperature of about 40-45ºC,
- maintain comparatively low pH of extraction of about 2.0-2.5,
- utilize extractive washing system of loaded organic phase,

3) such method of treatment (with ammonia used) slightly spoils conditions of zinc(II) extraction (higher viscosity of loaded organic) in comparison with extraction with the use of soda lye, but it is compensated by obtaining potentially useful solutions of ammonia-magnesium sulphates, suitable for fertilising purposes.

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SOLVENT EXTRACTION OF NICKEL FROM LEACH SOLUTION BY VERSATIC 10 EXTRACTANT

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Introduction

Natural nickel-bearing resources usually are very poor with respect to nickel mineralization. They contain about 1-3 % Ni, and their typical impurities are iron, cobalt, copper and magnesium. Magnesium (15-30 %) is the main cationic component of the ore and the other is iron, which is present in large amounts (5.5-8.5 %). Other important components are silica (35-45 %) and alumina (aluminosilicate). There are also Mo, Cr, Co present in the ore. As the result of ore leaching with sulphuric acid solutions and preliminary treatment of the solution after leaching with magnesium oxide /iron removal/, solutions are produced which contain up to 0.6-1.7 g Ni/dm^3, 25-60 g Mg/dm^3, ~ 0.005 g Fe/dm^3 and other minor impurities (including Al, Mo, Co, silica; concentration level of Na, K and chlorides is very low).

The paper presents results of hydrometallurgical tests of nickel recovery from sulphate leach solutions. Commercially available extractant for nickel(II) extraction was tested: Versatic 10 (neodecanoic acid) at two concentration – 5 and 15%v/v (solvent: EXSSOL D80). Basic extraction properties of extractant at two concentration were examined and compared. The better one was selected for further studies into extraction of nickel(II) from sulphate leach solutions. Process conditions of a system operating continuously in a counter-current way were determined.

Results

The studies presented in the paper were performed in order to examine possibilities for application of cationic ion-exchange extraction method for selective nickel(II) recovery from leach solutions containing magnesium.

The scope of the studies covered:
- examination of basic extraction characteristics of selected extractant with reference to leach solutions,
- identification of optimal concentration of extractant for separation of nickel(II) from magnesium in sulphate solutions,
- determination of process conditions for continuous extraction system with application of selected concentration of extractant.

Trials to determine influence of pH on nickel(II) and magnesium extraction degree for each of the examined organic solutions were made and organic phase behavior during stripping was observed. Degree of extraction versus equilibrium pH can be observed on the Figures 1 and 2.

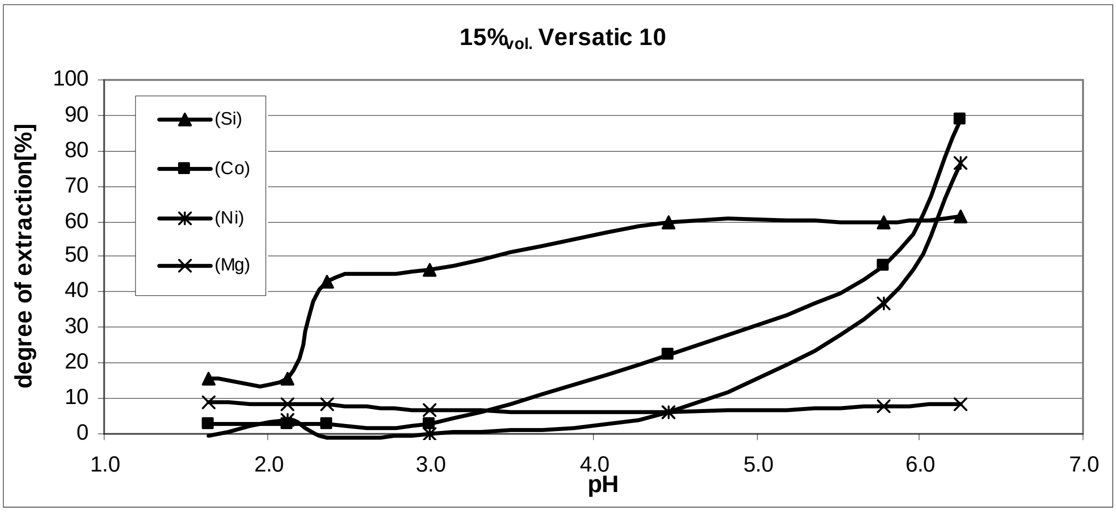

Fig. 1. Degree of extraction [%] v. equilibrium pH (15%$_{v/v}$ Versatic 10)

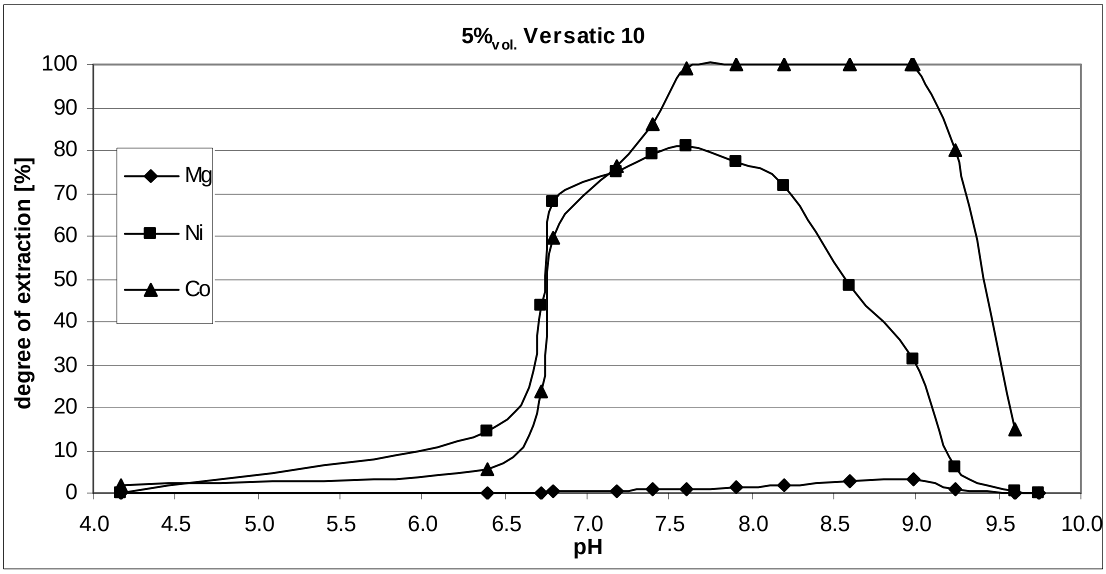

Fig. 2. Degree of extraction [%] v. equilibrium pH (5%$_{v/v}$ Versatic 10)

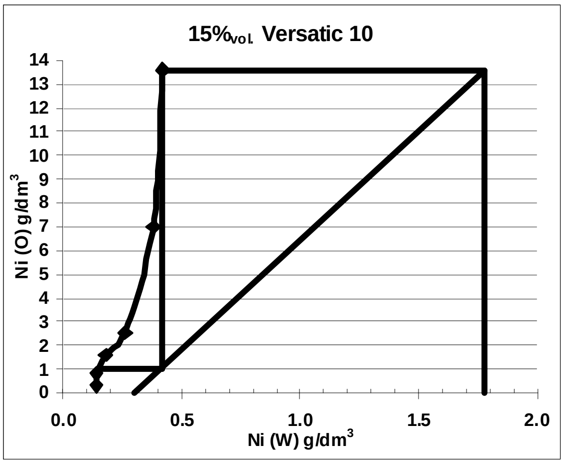

Fig. 3. Isotherm of Ni extraction from leach solution with McCabe-Thiele diagram (15% Versatic 10)

The next step was to determine the extraction isotherm for Versatic 10 and leach solution. Determined curve (Figure 3) shows that the extractant used was of too high concentration (maximum Ni saturation level still not seen). Despite this, McCabe-Thiele diagram has been plotted and a simulated (counter-current) test was performed to saturate the organic phase. Unfortunately, the results obtained clearly showed that the used extractant (15% Versatic 10) needs to be diluted (transmission of the feed solution through the emulsion formed has been observed).

Further extraction tests were performed with Versatic 10 of 5% volume concentration. Figure 4 shows the isotherms of extraction (set at two levels of temperature) for a 5% vol. solution of Versatic 10.

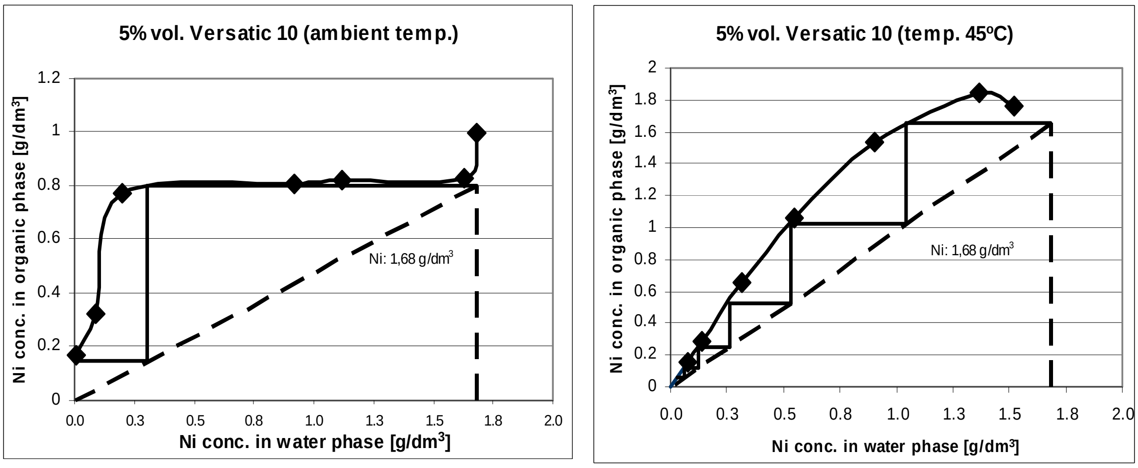

Fig. 4. Isotherms of Ni extraction from leach solution with McCabe-Thiele diagrams ($5\%_{obj.}$ Versatic 10, ambient temp. and 45ºC)

The next step was to perform test of continuous and counter-current solvent extraction using the pilot plant (Figure 5) for that. The continuous test was performed with the 5% vol. Versatic 10 at ambient temperature.

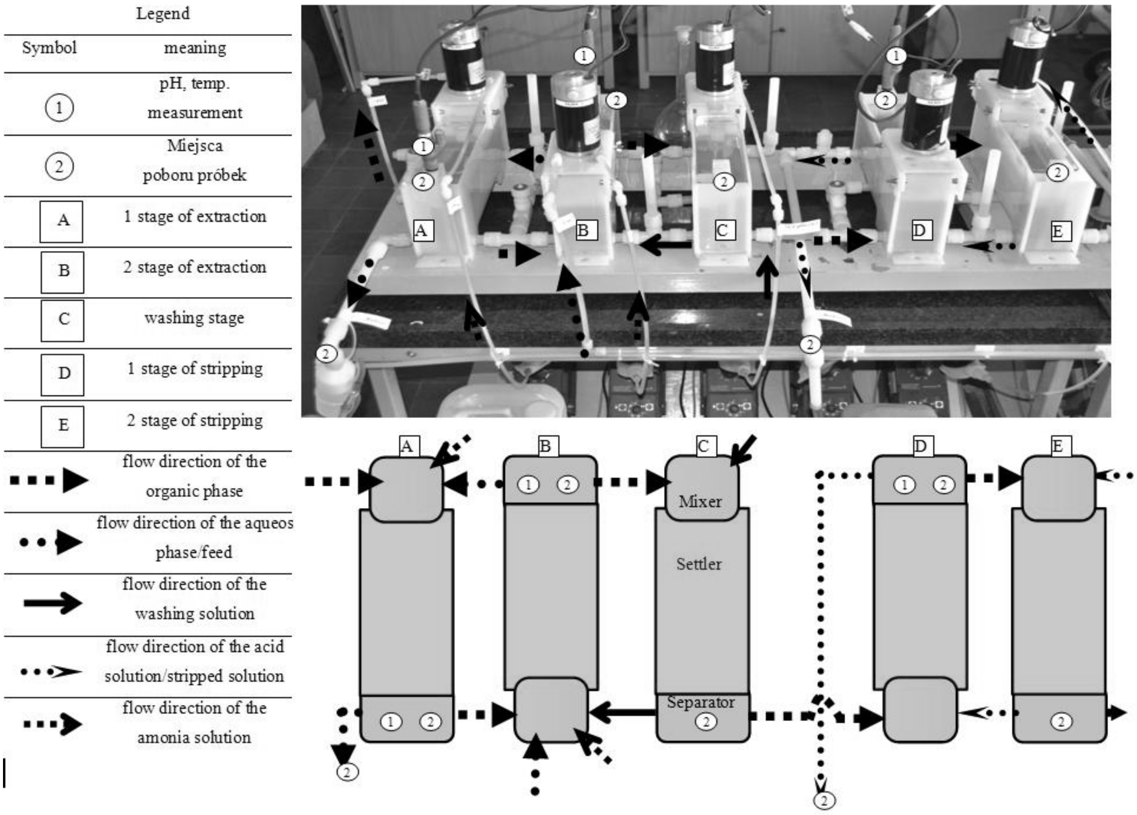

Fig. 5. Diagram and illustrative photograph of used apparatus with marked places for measuring of pH and temperature and directions of flow of solutions

Results of the continuous, counter-current test are presented in the Table 1. Samples of raffinates and stripped solutions were taken in two ways, directly from the separator and by collecting of one-hour portions of flowing down solutions (1 h sample A and D).

Table 1. Compositions of solutions of nickel extraction process (SX of Ni from leach solution) (5%$_{\text{vol.}}$ Versatic 10)

sampling place	analyzed ions [g/dm^3]				
	NH_4^+	Co	Mg	Ni	Fe
A	5.76	-	32.7	0.24	-
B	5.1	-	33.90	0.61	-
A (1 h)	5.45	-	32.93	0.24	-
C („washings”)	0.2	-	0.62	-	-
D	0.032	0.14	1.3	6.70	<0.0005
E	-	-	0.098	8.00	-
D (1 h)	0.029	0.15	1.3	7.10	<0.0005

Summary

- the development of a technology for production of nickel sulphate solution of parameters which provide possibilities to crystallize the hydrated nickel(II) sulphate(VI) is possible.

- extraction process of Ni, run under conditions of counter-current extraction, should consist of two stages of countercurrent extraction, two stages washing the organic phase and two degrees of stripping.

- performed studies suggest next steps of researching condition for separation nickel from magnesium in aqueous leaching solution.

- there is a need for further studies into optimization of the counter-current process (flow of the reactants and their concentrations, phase proportions, temperature of the process)

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ARSENIC REMOVAL FROM GROUNDWATER BY SEVERAL ADSORBENTS

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1. INTRODUCTION

Arsenic (As) contamination of groundwater spreads in all over the world. In these water, As exists in As(III) (1) and As(V), and toxicity of As(III) is 25 – 60 times higher than As(V) (2). Since World Health Organization (WHO) indicates the maximum contaminated level (MCL) As as 10 µg/L and As concentration is greater than MCL in groundwater of many places. Because drinking of As-contaminated water causes skin cancer and other cancer diseases, the removal of As from groundwater is desired. In the present work, the adsorption of As was investigated by three kinds of inorganic ion exchange adsorbents, TiO_2, Fe_3O_4 and Al_2O_3, to compare As removal from the groundwater from the view points of batchwise and chromatographic operations.

2. EXPERIMENTAL

The powdery adsorbents were synthesized as follows. In the case of TiO_2, ammonia solution is added to $TiCl_4$ solution until pH 7 to produce $Ti(OH)_4$, and H_2O_2 is then added to the suspended solution of $Ti(OH)_4$. The mixture was hydrothermally synthesized at 120ºC for 5 h to produce anatase-type TiO_2. In the case of Fe_3O_4, the aqueous solution $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were mixed with molar ratio of 1 : 2, and then NaOH solution was added to the mixture solution until pH 12. The precipitates were washed with deionized water and then were dried in vacuum at 50ºC. In the case of Al_2O_3, commercial alumina-based binder, Cataloid AP-1, was just used. Granulation of powdery adsorbents was conducted with Cataloid AP-1 as a binder. Prepared adsorbents of Fe_3O_4, TiO_2, and Al_2O_3 were characterized by an X-ray diffractometer, an automatic surface area and pore size distribution analyzer, and a zeta potential analyzer. Mean particle sizes of the adsorbents, measured by a flow type particle image analyzer, was 1.60 µm, 1.73 µm and 1.30 µm, respectively.

Batchwise adsorption was conducted with the powdery adsorbents. The adsorbents (20 mg) were contacted with aqueous solution (10 cm^3) of As(III) or As(V) to be shaken for 24 h at 25ºC. Ionic strength of the aqueous solution was not adjusted in the present work. The As concentration was fixed to 10 $mmol/dm^3$ in the case of pH influence experiments, while it was varied in the range of 0.5 - 25 $mmol/dm^3$ in the case of adsorption isotherm experiments (As(III); $pH_{eq} = 8.13 \pm 0.05$ (Fe_3O_4), 8.37 ± 0.05 (TiO_2) and 8.53 ± 0.05 (Al_2O_3), or As(V); $pH_{eq} = 8.25 \pm 0.05$ (Fe_3O_4), 8.65 ± 0.05 (TiO_2) and 5.59 ± 0.05 (Al_2O_3)). After filtration and pH measurement, As concentrations were analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES). The adsorption amount of As on adsorbent, q_{As} (mmol/g), was determined by:

$$q_{As} = \frac{(C_{As,0} - C_{As}) \cdot L}{W} \tag{1}$$

where $C_{As,0}$ and C_{As} are initial and equilibrium concentrations of As in the aqueous phase (mmol/dm^3), respectively, L is volume of aqueous solution (dm^3), and w is weight of adsorbent (g).

Granulation of the adsorbents was also conducted for applying to the chromatographic operation. In the cases of Fe_3O_4 and TiO_2, the powdery adsorbents and Cataloid AP-1, as alumina-based binder, were mixed at weight ratio of 1 : 1, together with a small amount of deionized water. In the case of Al_2O_3, Cataloid AP-1 was mixed with small amount of deionized water. The kneaded mixture were extruded through 1 mm diameter hole and dried at room temperature for overnight. The mixture was then calcined at 550ºC for 3 h in an electrical oven and cut for 0.5 - 1 mm lengths. The granulated adsorbent (wet volume = 2 cm^3) was packed into glass column and conditioned with deionized water. The aqueous solution of As(III) was fed upward through the column at a flow rate of 0.2 cm^3/min (S.V. = 6.0 h^{-1}; ratio of flow rate to wet volume of adsorbent). The effluent was collected with a fraction collector, and As concentration in the effluent was measured by ICP-AES. The bed volume (B.V.) was calculated by:

$$\text{B.V.} = vt / V \qquad (2)$$

where v is the flow rate of the feed solution (cm^3/min), t is the supply time of the feed solution (min), and V is wet volume of the adsorbent (cm^3).

3. RESULTS AND DISCUSSION

3.1 Batchwise adsorption

The reflection of the XRD pattern of Fe_3O_4 adsorbent prepared is indexed to a pure cubic phase magnetite (Fe_3O_4). In the case of TiO_2, the reflection of the XRD pattern is indexed to anatase-type TiO_2. The commercial alumina based binder was indicated of η-Al_2O_3. BET surface areas of the adsorbents determined by nitrogen gas adsorption were summarized in Table 1. The order of the BET surface area is $Al_2O_3 > TiO_2 > Fe_3O_4$.

Figure 2 shows the zeta potentials of the adsorbents in aqueous solution at various pH. For all adsorbents, zeta potentials in low pH region are positive and then change to negative in high pH region. The isoelectric point (IP) determined by zeta potential data were 6.6, 5.7, and 9.5 for Fe_3O_4, TiO_2 and Al_2O_3, respectively. These values are almost identical to those in the literatures (3, 4)

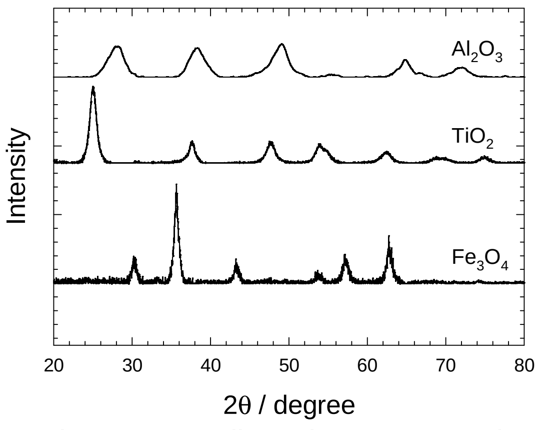

Fig. 1. X-Ray diffraction pattern of the powdered Fe_3O_4, TiO_2 and Al_2O_3 adsorbents

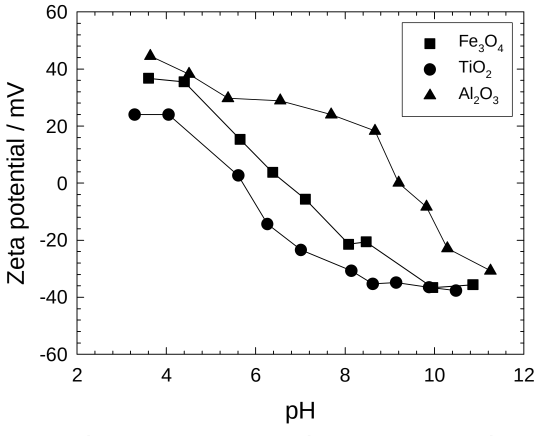

Fig. 2. Zeta potential of Fe_3O_4, TiO_2 and Al_2O_3 adsorbents in aqueous solution at various pH

Table 1. The q_{As0} and K of As(III) and As(V) with powdery adsorbents of Fe_3O_4, TiO_2 and Al_2O_3

		Fe_3O_4	TiO_2	Al_2O_3
BET surface area / $m^2\ g^{-1}$		94.3	167	271
Isoelectric point		6.6	5.7	9.5
As(III)	q_{As0} / mmol g^{-1}	1.135	1.296	1.292
	K / $dm^3\ mmol^{-1}$	0.336	0.516	0.179
As(V)	q_{As0} / mmol g^{-1}	0.368	0.414	0.640
	K / $dm^3\ mmol^{-1}$	0.245	0.444	0.189

Figure 3 shows the effect of pH in the aqueous solution on the adsorption amount of As(III) and As(V). The adsorption of As(III) on TiO_2 and Al_2O_3 shows the maximum value around pH 8 – 9, while that on Fe_3O_4 keeps high value in wide pH range. The difference in the pH value for obtaining the maximum adsorption of As is caused by the difference in the isoelectric point (I.P.) which are 6.1, 6.5 and 9.1 for TiO_2, Fe_3O_4, and Al_2O_3, respectively. The adsorption amount of As(V) on all adsorbents decreases with increasing pH in the solution. Table 1 shows the maximum adsorption amount of As on the adsorbents, determined by Langmuir adsorption isotherms. The maximum adsorption amount of As is in order, $TiO_2 > Fe_3O_4 > Al_2O_3$ in the case of As(III), $Al_2O_3 > TiO_2 > Fe_3O_4$ in the case of As(V). All adsorbents possess higher adsorption ability for As(III) than As(V), these inorganic compounds is suitable for the removal of toxic As from the groundwater in all cases.

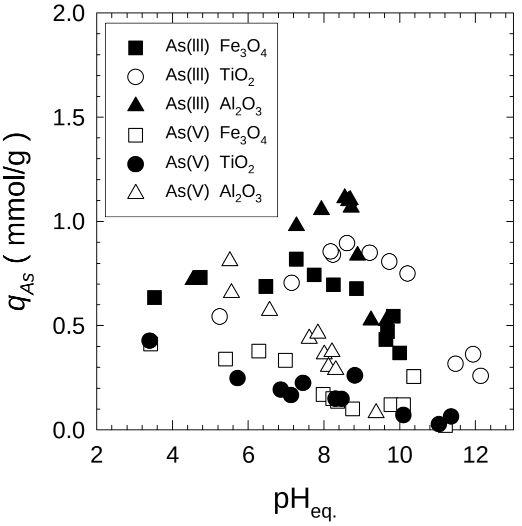

Fig. 3. The effect of pH value on the adsorption amount of As(III) and As(V)

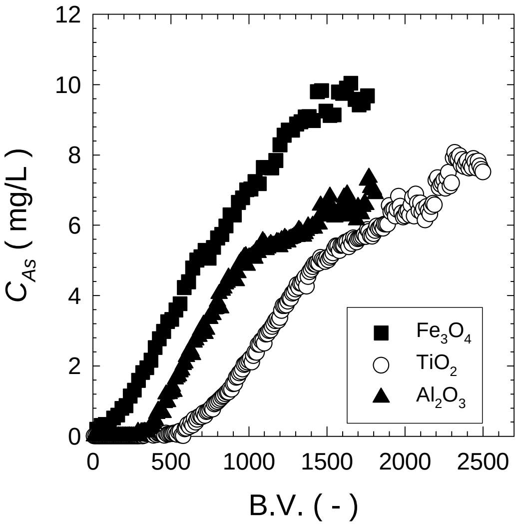

Fig. 4. The breakthrough curves of As(III) with granulated adsorbents

3.2 Column adsorption

Based on the batchwise adsorption, the chromatographic removal of As(III) from the aqueous solution was conducted. Figure 4 shows the breakthrough curves of As(III) with the granulated adsorbents of Fe_3O_4, TiO_2, and Al_2O_3. In all systems, As(III) is quantitatively adsorbed until B.V. = 100 (Fe_3O_4), 500 (TiO_2) and 280 (Al_2O_3), respectively. The value obtained by granulated Al_2O_3 is especially lower than that by granulated TiO_2, although the maximum adsorption amounts of As(III) with powdery Al_2O_3 and powdery TiO_2 are almost the same as shown in Table 1. This may be due to lower adsorption kinetics of As on granulated Al_2O_3. The granulated TiO_2 is therefore the excellent adsorbent for chromatographic removal of As(III) from water.

4. CONCLUSION

Adsorptive separation of As with the inorganic adsorbent of Fe_3O_4, TiO_2, and Al_2O_3 have been investigated. The Chromatographic removal of As(III) from the aqueous solution can be effectively achieved with granulated TiO_2 adsorbent, due to its high adsorption kinetics.

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SELECTIVE EXTRACTION OF Cu(II), Co(II), Ni(II) AND Zn(II) FROM SULPHATE AND SULPHATE/CHLORIDE SOLUTIONS

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Solvent extraction is now a very well-established process in hydrometallurgy. It is used in the hydrometallurgical processing of copper, nickel, cobalt, zinc, the platinum group metals, reprocessing of nuclear fuels, purification of wet process phosphoric acid, nitric acid recovery, etc. Nowadays, a variety of extractant have been proposed for selective extraction of metals from sulphate solution, however, the selective extraction of Cu(II), Co(II), Ni(II) and Zn(II) from chloride/sulphate solution has not been studied so far.

The extraction ability of hydrophobic 2-, 3- and 4-pyridylketoximes towards copper(II), zinc(II), cadmium(II) and iron(III) chlorides from weakly acidic aqueous solutions has been broadly investigated (1-5). Hydrophobic 2-pyridyl ketoximes are strong extractants, which can extract metal ions efficiently even at low chloride ions concentrations. The complexation is due to the fact that they coordinate metal ions by nitrogen and/or oxygen in their oxime group and by nitrogen in their pyridine ring. However, the oximes have not been proposed so far as a selective extractant of Cu(II), Co(II), Ni(II) and Zn(II) ions from multi-elemental solution.

The aim of the work is a study of copper(II), cobalt(II), nickel(II) and zinc(II) ions extraction from multi-elemental sulphate solutions by the 1-(2-pyridyl)tridecane-1-one oxime. The influence of the pH of the aqueous phase and chloride, copper(II) or cobalt(II) ions concentration on the selectivity of the extraction were studied.

1. Experimental

Aqueous feed solutions were prepared by dissolving appropriate amounts of sulphate salts of copper(II), cobalt(II), nickel(II) and zinc(II) in ultrapure water at constant concentration of sulphate (0.5 M) and chloride ions (2 M) but at varying values of pH (from 1 to 5), or at constant pH of 4 and a different concentration of chloride ions (from 0.5 to 4 M).The concentration of each ion in the solutions was 0.01 M.

The organic phase consisted of the oxime of 1-(2-pyridyl)tridecane-1-one (0.1 M) dissolved in toluene with the addition of 10% (v/v) decan-1-ol. The hydrophobic pyridylketoxime was synthesized in the two-stage reaction, as described earlier (4). The yield of synthesized ligand was 50%. FT-IR and NMR (^{1}H, ^{13}C) spectra proved the structure of the compound.

Extraction and stripping were carried out in a test tube using equal volumes (5 ml) of both phases (O/W; 1:1). Both phases were shaken for 30 minutes at room temperature (23-25ºC) using Bio-mix BWR 04. Before and after the extraction and stripping processes the metals concentration in the aqueous phase were analysed with atomic absorption spectrometry (HITACHI Z-8200 Polarised Zeeman). The metals content in the organic phase was determined by a mass balance between the concentration of a metal in the aqueous phases before and after extraction.

2. Results and discussion

The influence of pH on the co-extraction of copper(II), cobalt(II), nickel(II) and zinc(II) ions was studied over the pH range of 1 to 5 at a constant concentration of sulphate ions equal to 0.5 M. It was found that at pH = 4 copper(II) and cobalt(II) ions were extracted into the organic phase to the extent of about 90 and 72%, respectively, whereas co-extraction of nickel(II) and zinc(II) ions was negligible. Better separation of cobalt and copper from nickel and zinc ions was obtained where the aqueous feed also contained small amounts of chloride ions (0.01-0.1 M Cl^-). Then, co-extraction of nickel(II) and zinc(II) ions was negligible over the entire pH range studied (Figure 1).

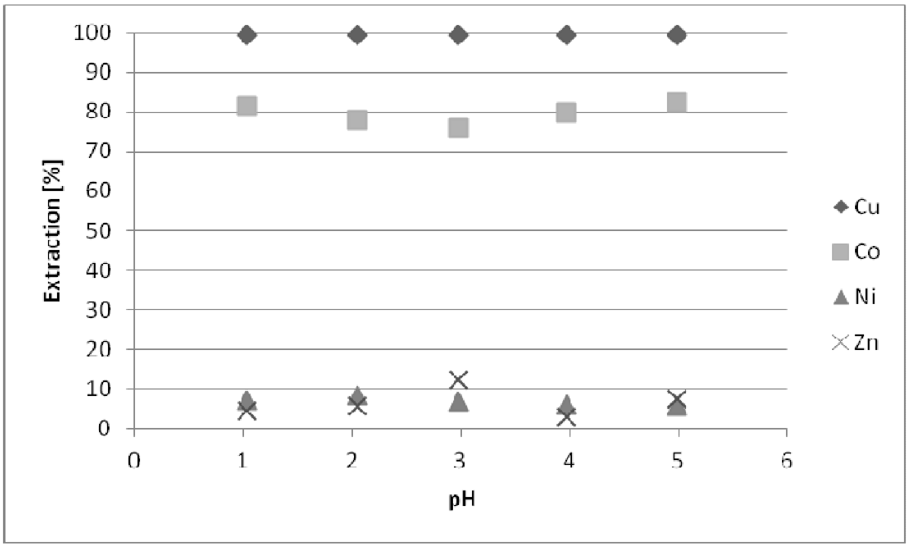


Fig. 1. Influence of pH on extraction process, ($[Me^{2+}]$ = 0.01 M, $[SO_4^{2-}]$ = 0.5 M, [oxime] = 0.1 M)

The influence of addition of chloride ions on the metals separation was also investigated. The obtained results showed that the extraction of copper(II), cobalt(II), nickel(II) and zinc(II) ions increased with increasing chloride ions concentration (Figure 2). Copper(II) extraction from the aqueous solution containing 4 M Cl^- increased from 90% to 100%, cobalt from 83% to 95% and that of nickel and zinc from 5% to 92% and from 7 to 46%, respectively.

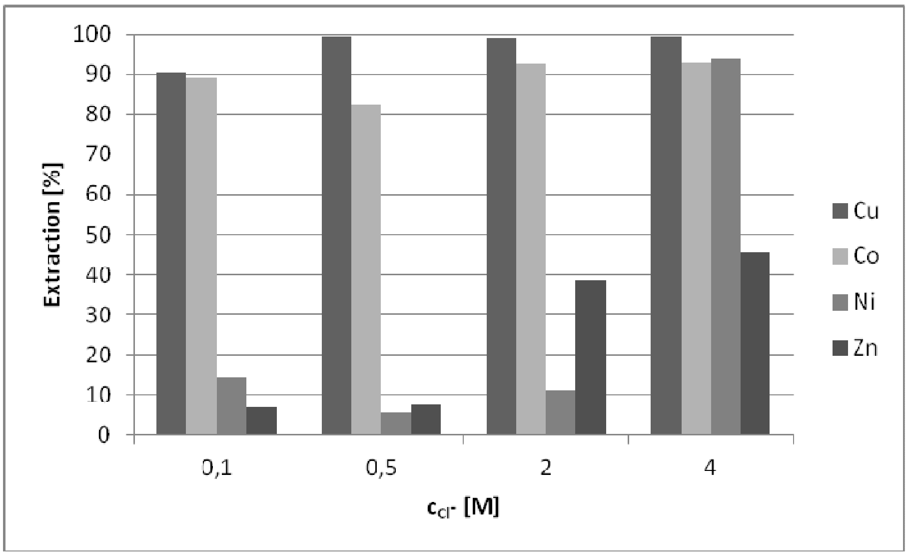


Fig. 2. Influence of chloride ions concentration on copper(II), cobalt(II), nickel(II) and zinc(II) extraction from aqueous chloride/sulphate solutions ($[Me^{2+}]$ 0.01 M; pH = 4, $[SO_4^{2-}]$ = 0.5 M, [oxime] = 0.1 M)

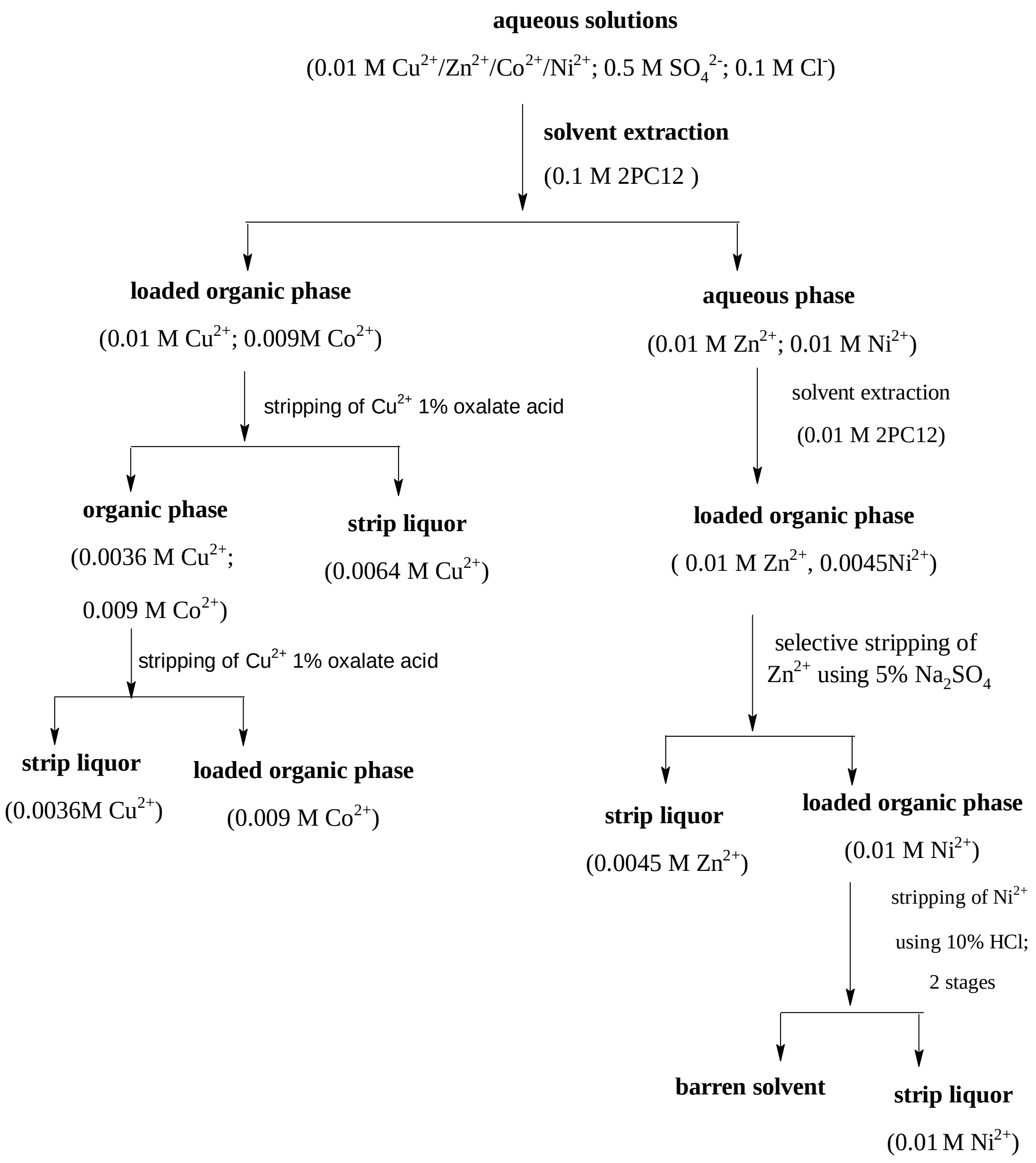
This suggest that the condition of extraction employed here is not able to separate the metals ions from each other. However, the process could be applicable to the separate recovery of copper and cobalt from nickel and zinc.

Selective stripping was also considered to explore the possibility of separating copper(II), cobalt(II), nickel(II) and zinc(II) from chloride/sulphate solutions. As stripping agents aqueous solution of Na_2SO_4 (5%), an aqueous solution of Na_2SO_4 (5%) with oxalate acid (5%), an aqueous solutions of HCl (7% and 20%) and ultrapure water were used. In the first study the organic phase containing copper and cobalt ions was carrying out copper stripping using the aqueous solutions containing oxalate ions. Single stage stripping study carried out at O/W 1:1 resulted in copper stripping to the extent of 64%.

In the second study the loaded organic phase which contained copper(II), cobalt(II) as well as nickel(II) and zinc(II) ions was first washed with the aqueous solutions of sodium sulphate to remove zinc(II) ions (100% re-extraction). Next, the copper ions were stripped from the loaded organic phase with the aqueous solutions of Na_2SO_4 (5%) with oxalate acid (5%). Unfortunately the cobalt, and nickel ions contained in the remaining organic phase could not be stripped selectively.

In case the loaded organic phase contained nickel(II) and zinc(II) ions the metals were separated by selective stripping with the aqueous solutions of sodium sulphate (100% re-extraction of Zn(II)) and next with 10% HCl (70% re-extraction of Ni(II)).

Based on the above results, we can propose a scheme of processes for the separation of copper(II), cobalt(II), nickel(II) and zinc(II) ions from chloride/sulphate solutions.



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EXTRACTION OF ZINC(II) IONS WITH QUATERNARY 3-PYRIDYNIUM KETOXIME

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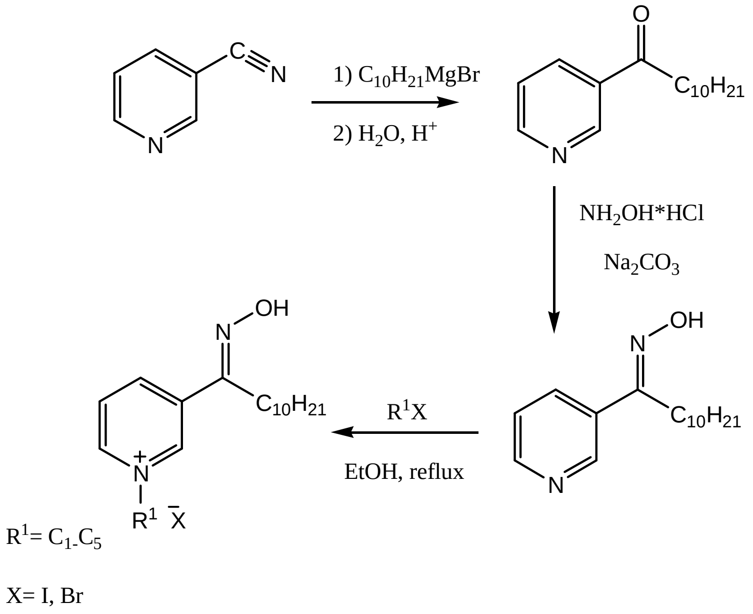
The most promising method for obtaining zinc from solutions is solvent extractions (1). The development of this method has enabled recovery of metals or other inorganic ingredients from industrial wastes especially from galvanic wastewater and solid wastes, which are extremely hazardous for the environment. The recovery of zinc(II) ions from acidic chloride solutions using the solvent extraction method is of particular interest and various extractants have been investigated: organophosphorous extractant – Cyanex 272, Cyanex 301, Cyanex 302 (2,3) and tributyl phosphate (4), tertiary amines (5) and also quaternary ammonium salts or ionic liquids (6). The extraction ability of hydrophobic 2-, 3- and 4-pyridylketoximes towards copper(II), zinc(II), cadmium(II) and iron(III) chlorides from weak acidic aqueous solutions has been broadly investigated (7-9). Although, hydrophobic 3-pyridylketoximes are weaker extractants of copper(II) ions than their 2-isomer, in the case of zinc(II) ions the created complexes are more stable (9). Furthermore, recent studies have indicated that the oxime of 1-(3-pyridyl)undecan-1-one is an effective extractant of zinc(II) ions from hydrochloric acid solutions even in the presence of other metals such as iron(II), iron(III) or copper(II) (10). However, the efficiency of the zinc extraction process by the oxime depends mainly on the contact area, contact time of the two phases and the concentration of a protonated form of the ligand. Moreover, the protonated ligand decomposes after contact with a stripping agent and the next extraction stage also requires high concentration of hydrochloric acid in the aqueous feed. These problems can be overcome by structure modification from 3-pyridyneketoxime to quaternary 3-pyridynium ketoxime.

The aim of the present work was to investigate the effect of 3-pyridynium ketoxime structure and aqueous phase composition on the rate of zinc(II) extraction.

Experimental

1.1. Synthesis of model extractant

The quaternary pyridinium ketoximes (3-[1-(hydroxyimino)undecyl]-1-methylpyridinium iodide (**3PC10-MeI**), 3-[1-(hydroxylimino)undecyl]-1-ethyl-pyridinium bromide (**3PC10-EtBr**), 3-[1-(hydroxyimino)undecyl]-1-propyl-pyridinium bromide (**3PC10-PrBr**) and 3-[1-(hydroxylimino)undecyl]-1-pentyl-pyridinium bromide (**3PC10-PnBr**)) were synthesised in a three stage reaction (Scheme 1) (7). In the first stage 1-(3-pyridyl)undecan-1-one was synthesised by treating 3-pyridylcarbonitrile with decylmagnesium bromide. In the second stage, the synthesised ketone was treated with hydroxylamine hydrochloride in the presence of sodium carbonate (at pH = 7). In the last stage, the synthesised oxime was treated with appropriate alkyl halides to give a quaternary salt (11).



Scheme 1. Synthesis of quaternary pyridinium ketoximes

The yields of the products were 40-60%. NMR (^{1}H, ^{13}C) and FT-IR spectra proved the structure of synthesised compounds.

1.2.Extraction procedure

Basic extraction and stripping studies were carried out in a test tube using equal volumes of both phases O/W = 1. Both phases were shaken for 30 minutes at room temperature (21-23^{o}C) using Bio-mix BWR 04. An aqueous feed solutions were prepared by dissolving appropriate amounts of zinc(II) chloride (5 g/dm^3) in ultrapure water at various hydrochloric acid concentration (from 0 to 4 mol Cl^- /dm^3) and at a constant chloride ions concentrations (4 mol Cl^-/dm^3). The influence of chloride ions concentration on the complexes' formation was studied using aqueous solutions containing a constant mineral acid concentration (0.5 mol/dm^3 HCl or HNO_3), various chloride ions concentrations (from 0.5 to 4 mol Cl^-/dm^3) and at a constant ionic strength I = 4 mol/dm^3 regulated by the addition of appropriate amounts of sodium chloride and sodium nitrate(V). An organic phase used in extraction studies contained the quaternary pyridinium ketoxime (0.05 – 0.15 mol/dm^3) and toluene as a diluent with 10% (v/v) addition of decan-1-ol. The metal concentration in the aqueous phase was analysed by Mettler Toledo T50 titrator using EDTA as a titrant. The metal content in the organic phase was determined by a mass balance between the concentration of a metal in the aqueous phases before and after extraction. The percentage of extraction (E%) was calculated from the contents of metal ions in the aqueous phases before and after extraction. The distribution coefficient (D) was taken as the ratio of the zinc(II) concentration in the organic phase to the concentration in the aqueous phase after extraction.

2. Results and discussion

The extraction studies showed that the synthesised quaternary pyridinium ketoximes (3-[1-(hydroxyimino)undecyl]-1-methylpyridinium iodide, 3-[1-(hydroxyimino)undecyl]-1-ethylpyridinium bromide, 3-[1-(hydroxylimino)-undecyl]-1-propylpyridinium bromide and 3-[1-(hydroxylimino)undecyl]-1-pentylpyridinium bromide) could be applicable in removing zinc(II) ions during solvent extraction from the strong acidic chloride solutions. The extraction process depended mainly on the quaternary salts of 3-pirydylketoxime structure and chloride ions concentration, however zinc(II) extraction by studied ligands did not depend on the concentration of hydrogen ions.

The extraction of zinc(II) ions from acidic chloride solutions depends strongly on the structure of the alkyl halide associated with the pyridine nitrogen atom (Figure 1.). Specifically, an increase in the alkyl chain length accelerated zinc(II) extraction, but the efficiency of the process was not higher than 50% (Figure 2.).

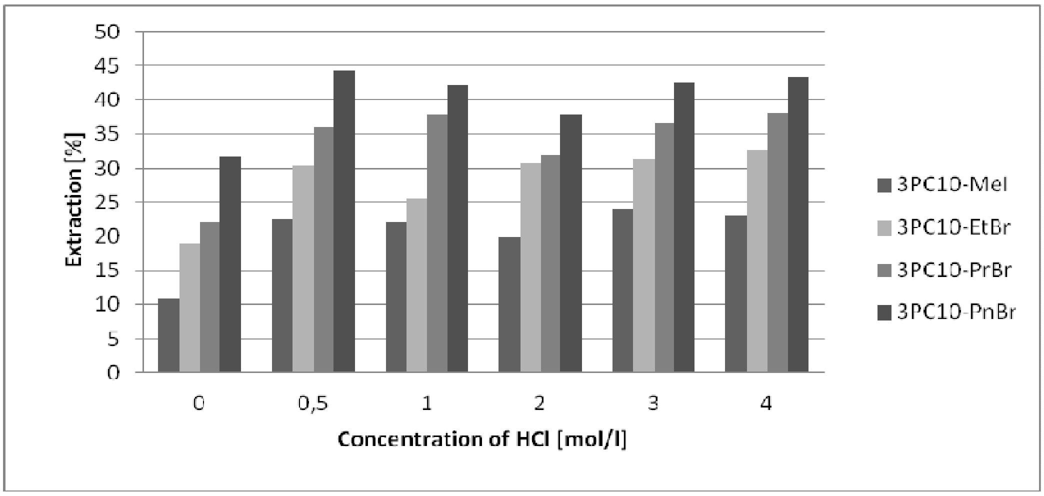


Fig. 1. Extraction of Zn(II) ions from acidic chloride solutions with the quaternary pyridinium ketoximes

The effect of the type of inorganic ions associated with pyridinium nitrogen on the phase separation and the stability of the complex was also observed. The 3-[1-(hydroxyimino)undecyl]-1-methylpyridinium iodide forms stable zinc complexes, which can decompose after contact with 0.5 M NaOH. In case of the 3-[1-(hydroxyimino)undecyl]-1-ethylpyridinium bromide, 3-[1-(hydroxylimino)undecyl]-1-propylpyridinium bromide and 3-[1-(hydroxylimino)undecyl]-1-pentylpyridinium bromide the stripping of zinc(II) ions from the organic phase can be carried out quantitatively with aqueous solution of Na_2SO_4.

The influence of chloride ions concentration in the aqueous phase on zinc extraction was studied by varying the Cl^- concentration from 0 to 4 M. Examination of the results shows that zinc(II) extraction increases sharply with chloride ion concentration up to a maximum of about 1.5 - 2 M Cl^-. Unfortunately, the results were not satisfactory to explain the mechanism of complexation. Further stoichiometric studies of zinc complexes with the quaternary pyridinium ketoximes show that the molar ratio of zinc to ligand in the complex molecule was 1:1.

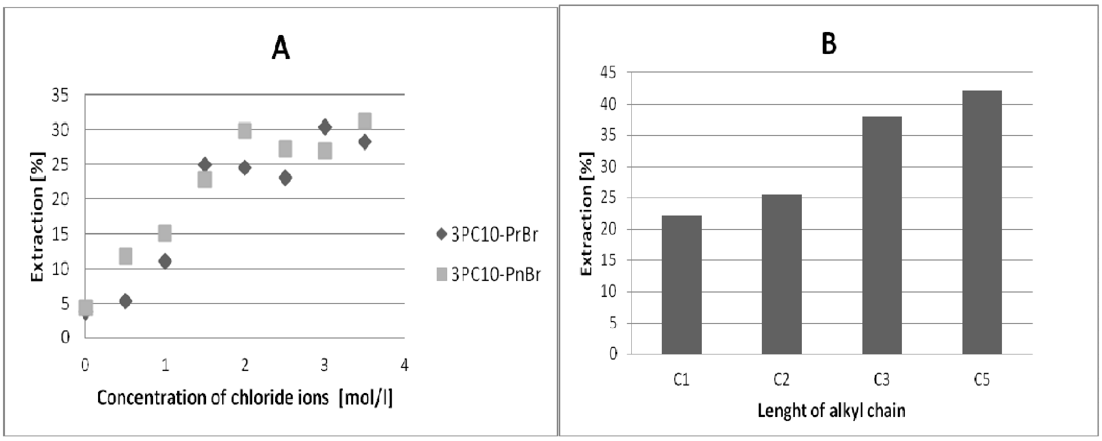


Fig. 2. Influence of chloride ions concetration (A) and length of alkyl chain (B) on the extracion of Zn(II) ions with the quaternary pyridinium ketoximes

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SEPARATION OF NICKEL(II) AND CADMIUM(II) IONS IN SUPPORTED LIQUID MEMBRANES (SLM) USING D2EHPA AS A CARRIER

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Separation of nickel(II) and cadmium(II) ions with use of supported liquid membranes (SLM) from sulphate solution has been studied. Di(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in kerosene was used as the ion-carrier. Obtained data were compared with data from polymer inclusion membranes (PIM) experiments. It was shown that use of SLM membranes enables separation of Ni(II) and Cd(II) ions. Experimental results data show that faster transport and higher recovery factor values were obtained for supported liquid membranes.

INTRODUCTION

Contamination and growing degradation of natural environment are closely connected with human activity. Among many groups of harmful substances one of the most important are heavy metal ions. Nickel and cadmium are used on a mass scale in many branches of industry. Use of different products that contain these metals creates a problem with their utilization. One of such products are Ni-Cd rechargeable batteries. Nowadays they are being replaced with new generation of energy sources, however in some countries they are still manufactured and enter Polish market as equipment of different types of portable electronic devices. The problem of managing these cells is vital because despite abandonment of their production in Poland they are still available on the market and therefore still have an effect on the natural environment and live organisms. In many industrial processes liquid wastes containing ions of these metals are created. Such wastes can also contaminate different types of waters.

There are many different methods of removal and recovery of nickel(II) and cadmium(II) ions from water and wastewater (1-2). Methods such as electrochemical precipitation (3), membrane electrolysis (4), electrodepositon (5) and electrodialysis (6) have been used. Disadvantage of these techniques are high operational costs caused by energy consumption.

Coagulation - flocculation has also been employed for heavy metal removal (7). In recent years, ion-exchange has received interest as one of the most promising methods to purify wastewaters laden with heavy metals (7-8). Another technology which can play an important role in solving ecological problems caused by heavy metals is sorption (7,9). Special form of sorption is biosorption. There are some results showing that agriculture waste or by-products which can be used as a low value sorbents. Different types of biomass like e.g. orange peel (10) have been investigated for biosorption of heavy metals.

Recently membrane separation has been increasingly used for treatment of wastewater (11). There are many different types of membrane processes e.g. nanofiltration, ultrafiltration, and reverse osmosis which can be used to remove heavy metal ions. Supported liquid membranes (SLM) have been applied for recovery nickel(II) and cadmium(II) (12) since they offer good selectivity and high transport rates, therefore they are a very interesting option to overcome the solvent extraction disadvantages. Scientists have also reported other type of membranes, polymer inclusion membranes (PIM) (13), which show good long-term stabilities, although in general lower fluxes can be obtained with this kind of membranes due to their high viscosity.

In this paper, the separation of Ni(II) and Cd(II) ions from sulphate solution with use of supported liquid membranes with D2EHPA as carrier has been studied. There are two part of the study: firstly the study of SLM transport and secondary comparison obtained data with results from polymer inclusion membrane.

EXPERIMENTAL

Solution of known metals ions concentrations was prepared by dissolving an appropriate salt: nickel(II) sulphate hexahydrate and cadmium(II) sulphate 8/3-hydrate in deionized water. The pH was adjusted by the addition of appropriate volume of sulphuric acid or sodium hydroxide. As a support in SLM experiments a PTFE-filter (Whatman) with a pore size of 0.2 or 0.45 µm and diameter 47 mm were used. These filters were soaked in 1 M D2EHPA solution in kerosene.

To synthesize polymer inclusion membranes a solution of cellulose triacetate, the ion carrier (D2EHPA) and the plasticizer, (*orto*-nitrophenyl octyl ether, ONPOE, Fluka) in dichloromethane was prepared. The CTA, ONPOE and D2EHPA solutions were mixed and a portion of this solution was poured into a Petri dish. The organic solvent was allowed to evaporate overnight. Afterwards the membrane was separated from glass by immersion in distilled water. The membrane was conditioned in 0.1 M HCl for 12 hours.

Transport experiments were carried out in a permeation cell in which the membrane was tightly clamped between two cell compartments one with a donor phase (i.e. solution of metal salts) and second with an acceptor solution (0.5 M H_2SO_4). Concentrations of metal ions were measured by atomic absorption spectrometry (SOLAR 939) with an air/acetylene flame and the appropriate hollow cathode lamps. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

The influence of pH on the recovery factor of nickel(II) and cadmium(II) from sulphate solutions is shown in Fig. 1. The pH of the source phase was maintained constant at appropriate value. The results indicate that higher recovery factor was obtained for cadmium on whole range of pH from 0 to 6. It was around 40% for Cd(II) ions at pH = 3 and higher during 4 hours. It was found that recovery factor for Ni(II) ions was only about 10%. Therefore, separation of these ions could be possible. Recovery factors for both metal ions increase with time.

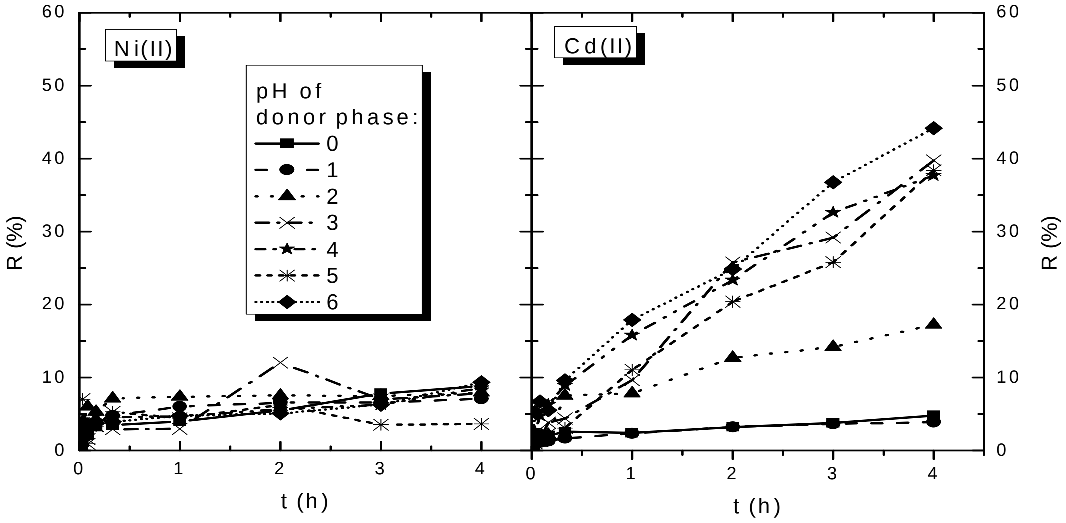

Fig. 1. Recovery factor of nickel(II) and cadmium(II) ions as a function of time in SLM experiments. Transport conditions are described in section: Experimental

Data obtained from supported liquid membranes were compared with data from polymer inclusion membranes experiments. The results obtained for PIM membranes are presented in Fig. 2. Some researches for PIM transport were done in different pH of donor phase. The results for pH = 3 were chosen for comparison with data from supported liquid membranes. Recovery factor of PIM membranes was lower than the one from SLM transport. It was only around 20% of cadmium(II) and 6% of nickel(II).

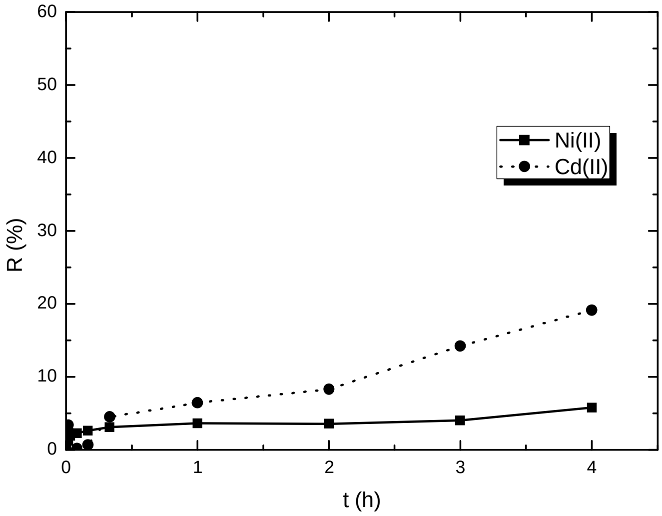

Fig. 2. Recovery factor of nickel(II) and cadmium(II) ions as a function of time in PIM experiments, pH of donor phase = 3. Transport conditions are described in section: Experimental

The effect of PTFE-filter pore size on recovery factor was also studied. Two different pore size were used: 0.2 and 0.45 µm. The results of nickel(II) and cadmium(II) transport through these membranes are shown in Fig. 3. The analysis of obtained data points that there was almost none influence of PTFE – filter pore size on recovery factors for both metal ions.

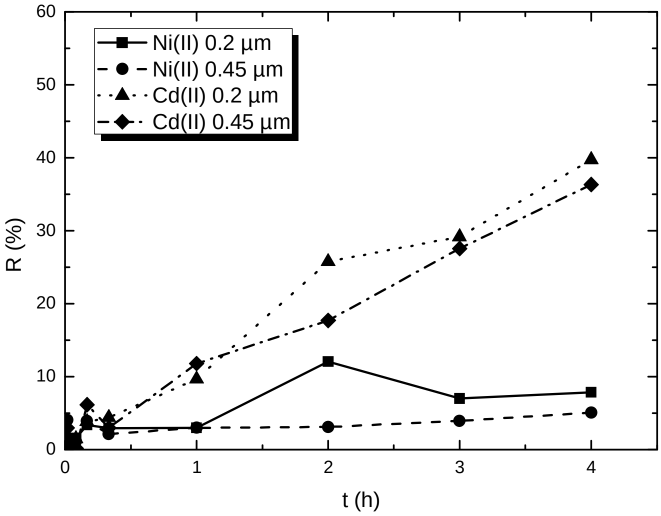

Fig. 3. Recovery factor of nickel(II) and cadmium(II) ions as a function of time in SLM experiments, pH of donor phase = 3. Other transport conditions are described in section: Experimental

CONCLUSIONS

The obtained experimental results of nickel(II) and cadmium(II) ions transport through SLM and PIM membranes prove the possibility of application of this process to selective separation of these metals from sulphate solution. The maximum Cd(II) recovery factor was obtained in 4 h was 44% and 9% of Ni(II) for SLM membranes. Recovery factor of nickel(II) has lower values than for cadmium(II) ions, which suggests that this ion stay in donor phase. Comparison of data from SLM and PIM transport show that faster transport and higher recovery factor values were obtained for supported liquid membranes.

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ON THE MODELLING OF METAL CATION TRANSPORT THROUGH A BULK LIQUID MEMBRANE

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For many years the mathematical modeling of liquid membrane (LM) processes has received considerable attention because of its ability to determine the physico-chemical parameters useful for the prediction of the pertraction processes performance. Generally, one can distinguish three groups of the approaches – the simplified model of consecutive first order reactions (irreversible or reversible) (1), the network thermodynamics approach (2), and the classical approach considering the transport in concentration diffusion layers at the boundaries feed|LM and LM|strip solution (3). In the last one, sometimes the existence of stagnant diffusion layers on the boundaries aqueous|organic phase is neglected and only the diffusion through a liquid membrane is considered. This approach is justified under the condition of efficient stirring.

In the modeling of metal ions transport through LM two assumptions concerning the exchange reaction can be made. The first one, commonly used in the literature (3), locates the exchange reaction directly on the interface between aqueous and organic phases. The second one shifts the place of the reaction to the aqueous phase (4). These approaches are called “Small” and “Big Carrousel”, respectively, (5). In such a modeling, because of simplicity, usually the Fick’s law is applied. It is justified for the strip solution where the electrolyte concentration is much higher than that of metal cation and thus the electric potential term has insignificant effect on the metal cation movement. However, this condition is not satisfied on the feed side, where the metal cation concentration is comparable to that of protons which are used as a stripping agent. Thus, the fluxes of these cations are strongly interrelated by the gradient of electric potential generated by different ion mobilities.

In this presentation, the approach based on the Nernst-Planck equation, applied for the feed and strip solutions, and compare it with the Fick’s law approach, assuming the equilibria located at the boundaries of aqueous/organic phases is presented. Both models are tested using the experimental data on the cadmium permeation from $Cd(NO_3)_2$ solution through BLM (D2EHPA in kerosene) to 1 M H_2SO_4 solution. The effect of the equilibrium constant at the boundary aqueous|organic phase, the thicknesses of the concentration diffusion layers, the form the Cd-D2EHPA complex, the presence of undimerized D2EHPA in BLM, and the ion pair formation (Cd^{2+}-SO_4^{2-}) in the strip solution on the cadmium permeation was investigated. It was found that both tested models yield a similar fit of the experimental data. However, in the case of the Fick’s model, a large dispersion of optimal fitting values of the cadmium mass transfer coefficient and the thickness of aqueous diffusion layer was found, depending on the model assumption. Thus, these parameters do not have a real meaning and can only be treated as fitting parameters.

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INVESTIGATION OF BIPOLAR ELECTRODIALYSIS USEFULNESS FOR DICARBOXYLIC ACIDS SEPARATION FROM FERMENTATION BROTH

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The focus of presented study was bipolar electrodialysis for selective separation of fumaric acid from fermentation broth containing various co-products such as acetic acid, citric acid and mineral salts (1-3).

In our investigation two types of devices were applied i.e. electrodialyser consisting of three-compartments and ten-compartments, each equipped with bipolar *(PCcell, PC200bip)* and anion selective membranes *(PCcell, 250D)*. All processes of EDBM were carried out at room temperature under constant electric current conditions.

In preliminary experiments several model solutions containing fumaric acid, acetic acid, citric acid and mineral salts were tested. Binary, ternary and quaternary model systems were considered.

Based on results experimentally obtained the current efficiency, energy consumption as well as the separation efficiency were calculated and compared for processes occurring in the three- and ten-compartments set-up. Moreover, the influence of the initial feed composition, the current density, the total membrane area of electrodialysis stack on the efficiency of transport of fumaric acid were analyzed (4-5). The presented studies showed that bipolar electrodialysis can be used as one of the purification step for separation of fumaric acid from fermentation broth.

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SEPARATION OF OXALIC, TARTARIC AND LACTIC ACIDS FROM THIER MIXTURES USING POLYMER INCLUSION MEMBRANES WITH 1-ALKYLIMIDAZOLES AS A CARRIER

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1. Introduction

Safe and environmentally friendly fermentation processes are in recent years of broad interest among methods of organic compounds production. This method reduces chemicals production and reduces costs and resulting by-products and impurities. As a result of biotechnological conversion, oxalic, tartaric and lactic acids can be obtained. The final qualitative and quantitative composition of the fermentation broth depends on the type of microorganism and the conditions of the fermentation process. Oxalic, tartaric and lactic acids are widely used in many industries. Lactic and tartaric acids are used primarily in the food industry as preservatives and acidifiers. In addition, thanks to probiotic, exfoliating and cleansing properties they are also used in the pharmaceutical and cosmetic industries. What is more, the latest application of lactic acid the production of biodegradable plastics (1-2). However, oxalic acid is mainly used in the textile industry and in the hydrometallurgy of heavy metals (3).

After the fermentation process, a problem concerning the separation of the desired products occurs. The most commonly used methods are precipitation and extraction. However, these methods are usually associated with the separation of by-products and the necessity of using large amounts of often expensive and harmful solvents. It is therefore important to develop a fully-effective separation method, which allows for the selective separation of high-quality products of fermentation solutions. One of the possibilities are the use of separation techniques using a polymer inclusion membranes. Polymer inclusion membranes are of increasing interest for separating organic and inorganic constituents from aqueous solutions. Research devoted to the theme of inclusion polymer membranes concern mainly the separation of metal ions such as zinc, nickel, cobalt and copper (4). However, recently there have been reports in the literature concerning the transport of organic compounds by polymer inclusion membranes. These studies related to, inter alia, citric and lactic acid (5). Despite this, studies on the separation of organic compounds are still very limited, therefore PIM can be a separation technique with broad research capabilities.

2. Experimental

Transport of organic acids through polymer inclusion membrane was carried out using two glass chambers. One chamber contained feeding phase while second chamber contained the receiving phase. The volume of each phase was 45 cm^3. During the separation process each phase was intensively stirred. Between the chambers a polymer inclusion membrane was placed. The surface of the membranes was equal to 4.15 cm^2. Schematic of the experimental apparatus is shown in the Figure 1.

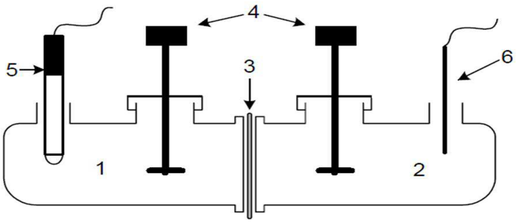

Fig. 1. Experimental apparatus diagram 1 − chamber with receiving phase, 2 − chamber with feeding phase, 3 − polymer inclusion membrane, 4 − stirrers, 5 − electrode, 6 − temperature sensor

During the study of organic acids transport, the feeding phase was used 0.1 M solution of the appropriate acid. However, during the separation process, feeding phase consisted of three-component mixture of oxalic, tartaric and lactic acids as well as a binary mixtures of oxalic and tartaric acids, oxalic and lactic acids, tartaric and lactic acids. The receiving phase in both cases was demineralized water (R ≈ 1.5 MΩ). The separation process was carried out for 24 hours. To determine the concentration of organic acids, conductivity of receiving phase was measured every 7 minutes for the duration of the process. Based the previously determined calibration curve, the conductivity was converted to the molar concentration of organic acid in the receiving phase. However, in the case of mixture separation ion chromatography analysis was applied.

For the synthesis of polymer inclusion membranes cellulose triacetate (CTA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) as a polymer matrix were used. 1-alkylimidazoles were applied as a carrier, where the alkyl chain in the imidazole contained 10, 11, 12, 14 or 16 carbon atoms.

Based on the basic relationship of transport through polymer inclusion membranes, the mathematical model describing the transport of organic acid by polymer inclusion membranes has been proposed:

$$-\frac{1}{2}\ln\left(1-\frac{2\cdot C}{C_0}\right)=\frac{V}{A}\cdot k\cdot t\,, \qquad (1)$$

where C_0 - the initial concentration of the organic acid [mol/dm^3], C - concentration of organic acid in the receiving phase at time t [mol/dm^3], V - volume of feeding/receiving phase [m^3], A - surface of membrane [m^2], k - rate constant [1/s], t - time [s].

Knowing the rate constant *k*, the volume of feed phase and the surface of membrane permeability coefficient can be determined as (P [m/s]):

$$P=\frac{V}{A}\cdot k\,, \qquad (2)$$

from which values of the diffusion coefficient (D [m^2/s]):

$$D=\frac{P\cdot d}{K}\,, \qquad (3)$$

and the initial flux (J_0 [mol/(m^2*s]) can be determined:

$$J_0 = \frac{V}{A} \cdot k \cdot C_0. \qquad (4)$$

In addition, for each of the processes carried out the selectivity coefficient was determined:

$$S_{1,2} = \frac{J_{0Acid1}}{J_{0Acid2}}. \qquad (5)$$

3. Results and discussion

The research of transport of oxalic, tartaric and lactic acids through polymer inclusion membranes were conducted. For each of the processes carried out the characteristics describing transport rate according to Equation 1-4 were determined. Figure 2 present the dependence of flow for transported acids for each of the carrier. Comparing the data presented in Figure 2, the differences in the rate of transport of analyzed acids using cellulose triacetate as the polymer matrix can be observed. For other polymer matrices the similar dependences are observed. The highest flux values were obtained for the transfer of oxalic acid, tartaric acid and then the lowest for lactic acid. Comparing the types of the carrier used, the increase of carbon chain length of 1-alkylimidazole affects positively they rate of transport and reaches maximum value for IMI-14, then decreases. The same dependence was obtained for each of the analyzed acids.

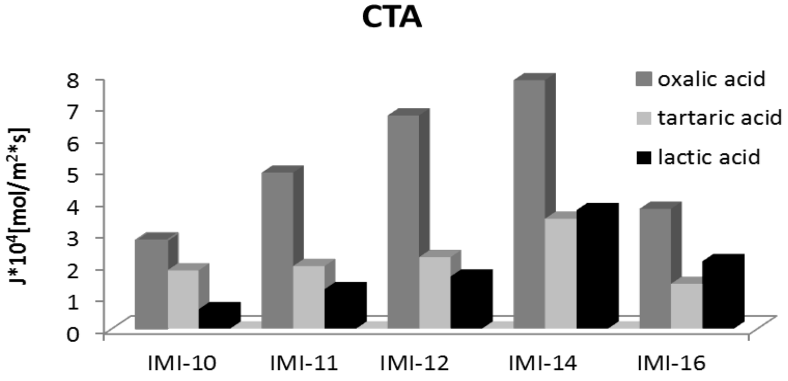

Fig. 2. Comparison of the rate of transport of oxalic, tartaric and lactic acid through the PIM

Due to the notable differences in the rate of transport of oxalic, tartaric and lactic acids according to the equation *5* selectivity coefficients were determined. In Table 1 the values of the coefficients of selectivity of the process with the use of CTA are presented. As it can be seen the highest values for a couple oxalic acid and lactic acid were obtained. The maximum value is obtained in case of IMI-10. For the couple of tartaric and oxalic acids the best results were obtained with IMI-12, and for tartaric and lactic acid for IMI-10.

Table 1. Coefficients of selectivity

	IMI-10	IMI-11	IMI-12	IMI-14	IMI-16
Oxalic acid/Tartaric acid	1.52	2.49	2.98	2.26	2.67
Tartaric acid/Lactic acid	3.00	1.59	1.37	1.08*	1.49*
Oxalic acid/Lactic acid	4.54	3.96	4.09	2.10	1.78
*Lactic acid/Tartaric acid					

In Figure 3 the relationship described using mathematical model *1* is presented. As can be seen, there are significant differences in the initial rates of transport of oxalic, tartaric and lactic acids. Oxalic acid is transported the fastest, then tartaric acid and finally lactic acid. The resulting selectivity coefficients and the relationship shown in Fig. 3 suggest that there is a potential for the selective separation of analyzed acids and thereof mixtures.

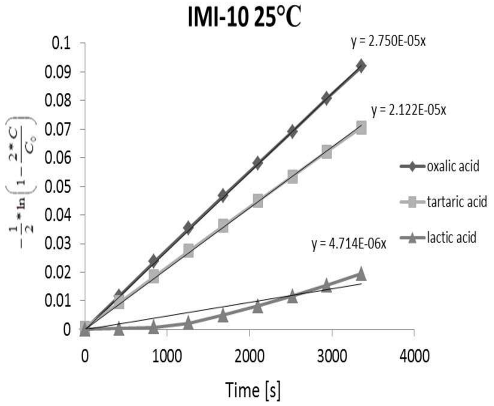

Fig. 3. Dependence of -1/2ln(1-(2*C/C_0)) from the time of transport of oxalic, tartaric and lactic acid

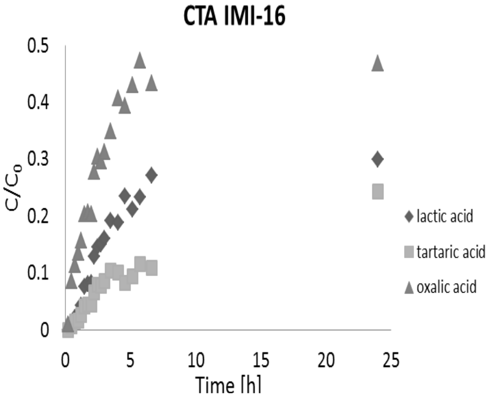

Fig. 4. Change of the concentration of organic acid in the receiving phase during the separation process of the acid mixtures

Based on the results of the differences in the rate of transport of oxalic, tartaric and lactic acids the separation process from the mixture was carried out. Examples of results are shown in Figure 4. As it can be seen a high preference for oxalic acid, using IMI-16 as the carrier and the CTA as the polymer matrix is observed. On the basis of previously determined selectivity coefficients for the IMI-16 the highest value for couples of oxalic and tartaric acids was observed, which is consistent with the results shown in Figure 4. Similar results were obtained for the other systems of the applied research.

4. Conclusions

The rates of transport of oxalic, tartaric and lactic acids is affected by both the type of carrier and the polymer matrix used. These differences are caused by the structure of the active compound and the compatibility of carrier with the polymer matrix used. The studies concerning the separation of the mixture components show that selective separation of oxalic, tartaric and lactic acid by polymer inclusion membranes is possible with the selection of appropriate composition of the membrane.

Acknowledgements: This work was carried out in part the framework of Statutory Research 32-376/2013-DS conducted at the Poznan University of Technology.

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INFLUENCE OF CARRIERS CONCENTRATION (1-ALKYLIMIDAZOLS) ON CITRIC ACID TRANSPORT ACROSS POLYMER INCLUSION MEMBRANES (PIM)

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Introduction

Citric acid is one of the most commonly applied organic acid on the world. He is used mainly as antioxidant, acidity regulator and effervescent agent with hydrogen carbonate in food industry. One of the production steps is releasing of citric acid from fermentation broth (1). This process is realized by precipitation of citric calcium and thereafter salt dissolving in sulfuric acid(VI). In effect of this the pure citric acid and waste gypsum are obtained. This method of citric acid releasing from fermentation broth is expensive and cause production appreciable amount of waste gypsum. Therefore, the new methods of fast and cheap citric acid releasing are searched. For that purpose, the investigation of different separation methods including extraction and membrane processes are carried out.

One of the membrane processes intensively developed during last time is application of polymer inclusion membranes (PIM) (2). This kind of membrane is commonly investigated for separation of metal cations (3,4). But it is possible to find publication showed that they can be applied for organic compounds separation (5-8). Important advantage of PIM is fact that thanks to their specific preparation, it is possible to regulate the parameters of membrane like selectivity or transport rate. It is feasible by chosen appropriate composition of membrane (9).

Polymer inclusion membranes are composed on polymer matrix, plasticizer and carrier. As polymer matrix cellulose triacetate or polyvinyl chloride are commonly applied. As plasticizers wide range of compound like ortonitrophenyl alkyl ethers or oxyethylated alcohols and others are used. As carriers, compounds that are commonly applied in extraction processes like amines, ionic liquids, phosphoric acid derivatives and many others are used. Some of these compounds can play both, the plasticizer and the carrier role. Thanks to appropriate selection of membrane composition it is possible to control their property. Important point of membrane preparation is chosen of type of carrier and plasticizer like also concentration of them. As is shown by many authors, concentration of individual components in membrane has an important effect on the transport parameters.

The subject area of investigation was determined the influence of type and concentration of 1-alkylimidazols as carriers on transport rate of citric acid across polymer inclusion membranes.

Experiment

Membranes were prepared in accordance with standard procedure, described by many authors. As polymer matrix, CTA was used and all produced membranes contain the same amount of polymer - 0.0187 g. As carriers and simultaneously plasticizers 1-alkylimidazols with alkyl chain length from 10 to 16 carbon atoms were applied. The amount of carrier in membranes include from $1.25*10^{-5}$ to $2*10^{-4}$ mol (0.0025 - 0.0584 g).

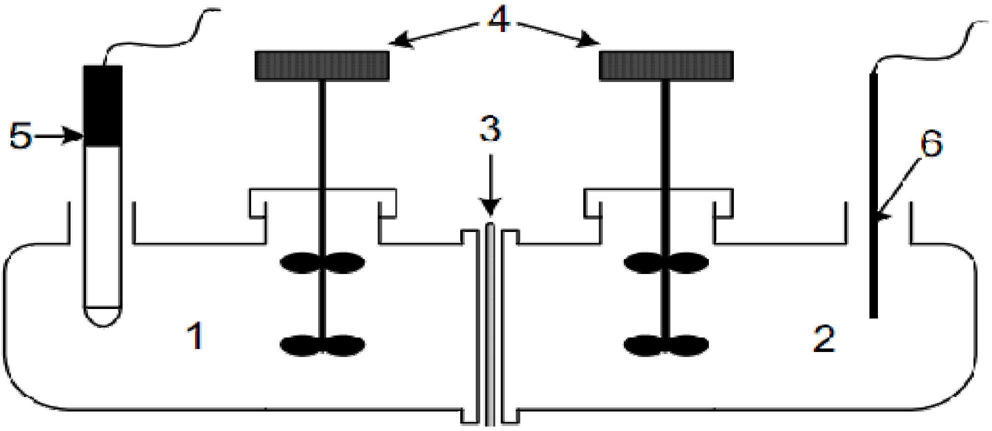

Fig. 1. Experimental apparatus: 1 - feeding phase, 2 - receiving phase, 3 - PIM, 4 - mechanical strirer, 5 - conductometric electrode, 6 - temperature sensor

In research the experimental apparatus consisting of two glass chambers was used. One chamber with feeding phase and second with receiving phase were separated by PIM membrane (Fig. 1). Both feeding and receiving phase were constantly and intensively stirred. Volume of both phases was the same and equal $V = 60$ cm^3. The membrane surface was equal $A = 4.15$ cm^2. Membrane consisted of polymer matrix – cellulose acetate (CTA) and one of the active compounds - 1-alkyl-imidazole (simultaneously carrier and plasticizer) alkyl chain length of 10, 11, 12, 14 and 16 carbon atoms (Imi10-Imi16). 1-alkyl-imidazoles were prepared as described earlier.

Measurement procedure

Solution of citric acid on 0.1 M concentration was used as feeding phase. As a receiving phase applied deionizatied water ($R \approx 1.5$ MΩ). Research was conducted at constant temperature equal $T = 25^{o}C$. Processes run 24h. In order to determined a citric acid concentration during process, conductivity of receiving phase was measured (every 7 minutes). The conductivity was converted to concentration of acid on this phase. Before transport process thickness of all membranes was measured. On the basis of received results, the parameters describing transport rate of citric acid across PIM (permeability - P, molar flux - J, diffusion coefficient - D) were calculated.

Results

In Figure 2A example change of citric acid concentration in receiving phase to the initial acid concentration against research time, for different amount (described as mass fraction) of imi10 in membrane was plotted. As it can be seen, with increasing of 1-alkylimidazol concentration in membrane the transport rate also increase and attain maximum value for mass fraction of imi10 equal $X = 0.53$. Further increasing of imi10 in membrane do not results in rise of transport rate what can be explain that high amount of imi10 bring release of carrier on membrane surface and component is not built-in membrane structure.

Beginning with fundamental relationship (first Fick's law) it is possible derive simplify formula that described transport of citric acid across membrane:

$-\frac{1}{2}\ln\left(1-\frac{2\cdot C}{C_0}\right)=k\cdot t$, slope of the straight line k is equal $k=P\frac{A}{V}$,

where: P - permeability, A - membrane area, V - feeding phase volume, C - acid concentration in receiving phase, C_0 - initial acid concentration if feeding phase.

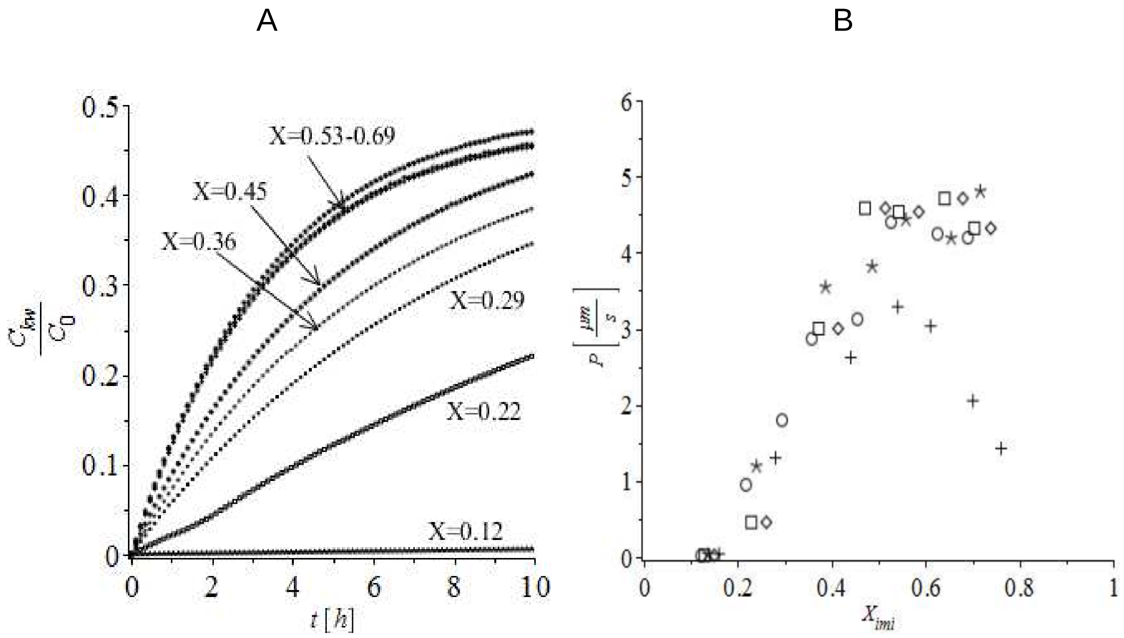

Fig. 2. A - An example dependence of time of process on relative citric acid concentration in receiving phase for different amount of imi10 in membrane. B - The change of permeability coefficient as function of 1-alkylimidazol amount in membrane for individual carrier. ○ - imi10, □ - imi11, * - imi12, ◊ - imi14, + - imi16

In Figure 2B the change of permeability coefficient P as a function of 1-alkylimidazol amount in membrane for individual carrier is plotted. As it can be seen, the imidazols with alkyl chain length from 10 to 14 carbon atoms characterize by similar shape curve. In the case of these compounds it could be observed that maximal value of permeability coefficient is similar and equal $4.5*10^{-6}$ m/s. Also it is possible to see that for these carriers, the maximum of transport speed was obtained for the same amount of imidazol in membrane, equal 0.5-0.6 w/w. Further increase of carrier amount don't influence on transport rate of citric acid across PIM. Probably reason of this behavior is precipitation of imidazols on the membrane surface. It means that this part of carrier is not build-in into membrane structure and can be completely or partially removed by dissolving in water during membrane conditioning. While imi16 characterized by different curve shape (Figure 2B) in comparison with other imidazols. In this case the maximum of transport rate is smaller (P = $3.4*10^{-6}$). Also concentration increasing of imi16 above 0.55 w/w works fast decreasing of transport rate. This behavior is connected with precipitation of imi16 on membrane surface. And because this carrier has low solubility in water and in room temperature is solid it makes difficulty to remove them from surface during membrane conditioning. This carrier precipitated on the membrane surface can produce additional resistance on citric acid transport.

The next characteristic things of investigated membranes are presence of minimal imidazols concentration. Bellow this concentration the citric acid transport not occurs. This minimal amount of carrier in membrane is called percolation threshold. On the basis of obtained results (figure 2B) it is possible to see that this minimal amount of carrier in membrane is similar for all imidazols and equal 0.16-0.17 w/w. Above the percolation threshold very fast increasing of transport rate is observed. Many authors suggest in articles that the presence of percolation threshold is evidence of fixed-site jumping mechanism of compound transport across membrane (7,8).

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SEPARATION OF Zn(II) AND Mn(II) IONS FROM PREGNANT LEACH SOLUTION OF SPENT ZINC HOUSHOLD BATTERIES

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Introduction

In our times economical and environmental requirements force the development of effective and inexpensive methods for recovering of valuable metals from secondary sources. Due to large amount of electrical batteries selling every year they can be thought as a considerable secondary source such metals. Among them zinc-carbon and alkaline zinc-manganese dioxide batteries are widely used as they have good electrical properties/price ratio and they can be consider as a secondary source of Zn and Mn. Recycling processing of spent zinc–carbon and alkaline–manganese batteries should be developed to achieve environmental conservation as well as the effective utilization of these metal resources. Several methods to recover metal values from spent batteries based on pyrometallurgical or hydrometallurgical technologies can be found in the literature (1–12). A hydrometallurgical method of recovering those metals seems to be more attractive than pyrometallurgical. In general terms, pyrometallurgical routes do not require battery dismantling, however operations are very energy consuming and some emissions of dust and gases are expected.

Hydrometallurgical routes are commonly found more economical and more efficient than pyrometallurgicalmethods. Metal separation routes based on hydrometallurgical operations are characterized by lower energy consumption, higher metal selectivity and no air pollution, as there are no particles produced. However, some pre-treatment steps are necessary in order to improve metal dissolution rates in the aqueous phase, like battery classification, dismantling, magnetic separation and leaching (1,4–8). Although few of hydrometallurgical processes of spent batteries are already in use it is steel a need for new methods providing working with higher efficiency and lower operational costs. This paper presents results of separation of zinc(II) and manganese(II) from the leaching liquor (PLS – pregnant leach solution) with use of solvent extraction, ion-exchange or transport through supported liquid membranes.

Experimental

The initial aqueous solution (PLS) was obtained from leaching of spent household zinc batteries with sulphuric acid. It consisted of Zn^{2+}: 0.2, Mn^{2+}: 0.2, K^+: 0.1, NH_4^+: 0.1,H_2SO_4: 0.01 mol dm^{-3}. The competitive solvent extraction as well as transport through supported liquid membranes has been studied with solutions of di(2-ethylhexyl)phosphoric acid (D2EHPA, Fluka), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, Cytec) and bis(2,4,4-trimethylpentyl)ditiophosphinic acid (Cyanex 301, Cytec) in kerosene (Aldrich).

The competitive solvent extraction of Zn(II) and Mn(II) ions has been studied by contacting of the equal volumes (10 cm^3) of the PLS and organic solutions for 30 minutes at constant room temperature. After extraction the liquid phases were left for separation for 24 hours time. After that the metals contents in the aqueous phase have been determined.

Ion-exchange experiments were done with resins: chelating – Lewatit OC-1026 with di(2-ethylheksyl)phosphoric acid group and strongly acidic – Lewatit MonoPlus SP 112 with sulphonic group (both of Lanxes). The sorption of zinc(II) and manganese(II) ions onto resins were carried out by means of the batch method. The wet resin (10.0 g) was contacted with the corresponding volume of PLS for 30 min. using the magnetic stirrer. After stirring, the solution was separated from the resin by filtration, and the concentration of ions was determined.

Competitive transport of metal ions from PLSinto sulphuric acid solution across the SLM was studied using two-compartment cell with flat-sheet membrane of 19.6 cm^2 area. In all experiments the support used for the liquid membranes was microporous, hydrophobic polypropylene Celgard® 2500 film with 25 mm thickness, 0.040 mm effective pore size and porosity of 45%. The support was soaked for 12 h in a 0.1 M solution of an appropriate carrier in kerosene. The volumes of aqueous feed (PLS) and receiving phase (H_2SO_4) were equal to 200 and 50 cm^3, respectively. Both aqueous phases were pumped by peristaltic pump.

In all experiments metal ions concentration in the aqueous phase has been determined by means of the Solaar 939 AAS spectrophotometer (Unicam) while the pH value has beenmeasured with a CX-731 (Elmetron) pH-meter. The pH was adjusted by the addition of an appropriate volume of potassium hydroxide solutions.

RESULTS

The results of the metal ions solvent extraction experiments with 1.0 M solutions ofD2EHPA, Cyanex 272 or Cyanex 301 in kerosene are shown in Fig. 1. In the case of all applied compounds the best extracted ion was zinc(II). The complete extraction of Zn(II) was achieved at pH above 3.0, 2.0 and 1.0 for D2EHPA, Cyanex 272 and Cyanex 301, respectively. Extraction selectivity zinc(II) over manganese(II) was increased in the order: Cyanex 301 <Cyanex 272 < D2EHPA. $pH_{0.5}$ obtained for Zn^{2+} ions were 0.2, 0.3 and 0.8, whereas those obtained for Mn^{2+} ions were 0.7, 1.2 and 2.3, respectively in the same order of extractants. The biggest difference in $pH_{0.5}$ for Zn(II) and Mn(II) was achieved for D2EHPA, what indicates that in the case of this acid the better separation of these metal ions could be obtained. In all the investigated pH range practically did not observe extraction of neither potassium nor ammonium ions.

In this work the influence of pH on the sorption of zinc(II) and manganese(II) ions from the sulphate PLS on strongly acidic (Lewatit MonoPlus SP 112) as well as chelating (LewatitOC-1026) ion exchangers was investigated. The results are shown in Fig. 2 and they indicate that the recovery factor of both metal ions is growing with increase of aqueous solution pH. At higher sulphuric acid concentration better adsorbed ion was zinc(II). The recovery factor was almost 100% for both metal ions at pH above 3 for MonoPlus SP112 and pH above 4 for OC-1026. MonoPlus SP112 allows conducting sorption at lower pH – recovery factor for zinc at pH = 0 gained more than 60 % whereas for OC-1026 was less than 10%. On the other hand the resin OC-1026 was characterized by better separation properties. Separation of the studied ions with this resin could be possible at pH about 2.

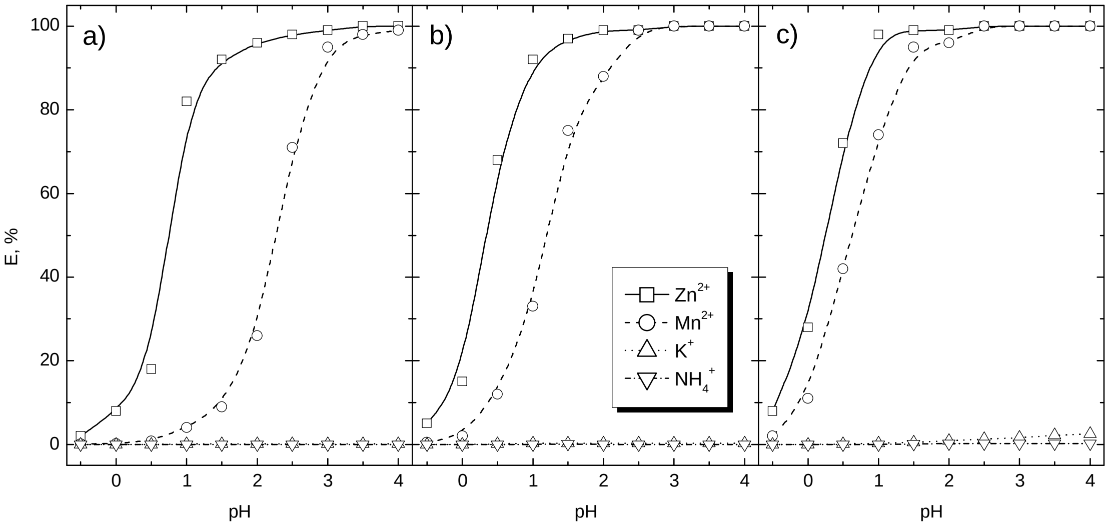

Fig. 1. Extraction percentage as a function of PLS equilibrium pH for D2EHPA (a), Cyanex 272 (b) and Cyanex 301 (c). Conditions of experiments – see Experimental

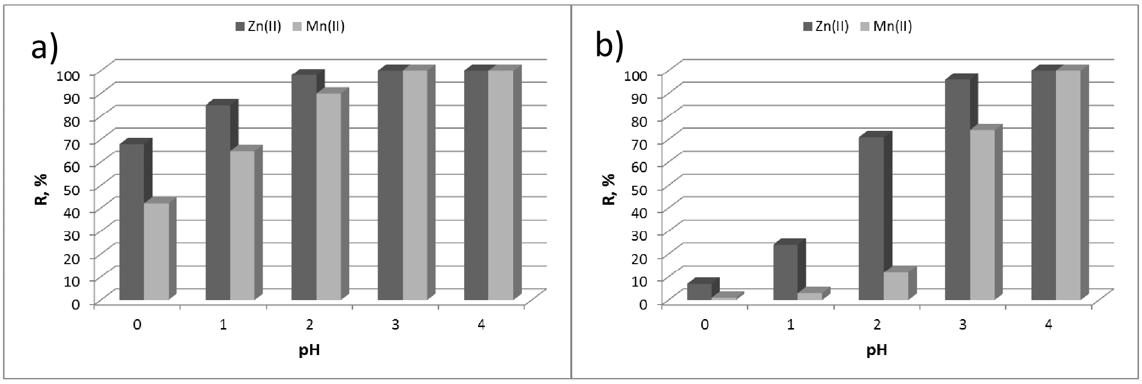

Fig. 2. Recovery factor of zinc(II) and manganese(II) in ion-exchange process with resins LewatitMonoPlus SP112 (a) and Lewatit OC-1026 (b). Conditions of experiments – see Experimental

In this paper a competitive transport of zinc(II) and manganese(II) ions from PLS across supported liquid membranes also is presented. In membranes the same compounds as in solvent extraction processes were used in a role of ionic carrier. It was found that main factor determining metal ions transport rate and selectivity was pH of aqueous feed phase (PLS). The obtained values of initial fluxes of Zn(II) and Mn(II) as a function of pH were presented in Table 1 (12). The fluxes of potassium as well as ammonium cations were at least 100 times lower, what allows to state the they are practically not transported.

Table 1. Initial flux of zinc(II) and manganese(II) as a function of PLS pH in SLM transport of ions(12). Conditions of experiments – see Experimental

pH	**J^0, µmol m^{-2} s^{-1}**					
	D2EHPA		***Cyanex 272***		***Cyanex 301***	
	Zn^{2+}	**Mn^{2+}**	**Zn^{2+}**	**Mn^{2+}**	**Zn^{2+}**	**Mn^{2+}**
0	4,00	0,80	2,00	0,45	5,01	3,20
1	12,1	1,79	8,02	1,49	45,6	15,0
2	22,2	5,91	15,0	4,88	50,0	41,8
3	44,8	14,0	27,9	9,03	55,0	52,1
4	51,9	45,2	34,7	28,8	56,1	53,0
5	52,0	51,5	39,1	32,4	56,0	52,9

It was found that Zn(II) ions were transported faster than manganese(II) ions for all investigated ionic carriers and the rate of transport was increasing with decrease of PLS acidity. Taking into account increasing rate of transport the ionic carriers can be arranged in the order: Cyanex 272 < D2EHPA < Cyanex 301. On the other hand very similar Zn(II) and Mn(II) fluxes observed in the case of Cyanex 301 indicate that separation of both metal ions is impossible. The highest differences of metal ions transport rates were found for D2EHPA in the pH range from 0 to 2.

CONCLUSIONS

Due to a large amount of zinc-carbon and zinc alkaline batteries selling every year they are promising secondary source of zinc and manganese. This paper discusses and demonstrates the possibility of zinc and manganese ions separation from sulphate Pregnant Leach Solution with use of solvent extraction, ion-exchange or transport through supported liquid membranes. The obtained results show that such separation is possible in each of applied method with D2EHPA as the extractant or ionic carrier or with resin Lewatit OC-1026.

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MATHEMATICAL MODELING OF TWO-STAGE EXTRACTION KINETICS USING THE SINGLE DROP TECHNIQUE

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The main methods of investigating the kinetics of extraction include stirred tanks, constant interfacial area cells, moving drops and the short time phase contact methods (1). All of these methods posses various hindrances in regard to determining the extraction kinetics. Many simplifications can be applied in order to create coherent mathematical models of extraction kinetics and draw conclusions concerning the extraction mechanism, extraction rate constants and the possible resistances limiting the extraction rate. This work is deals with the mathematical models of metal ions extraction from chloride solutions using the rising drop method taking into account an often neglected step of drop formation.

The rising drop method of investigating the rate of extraction is very useful when it comes to using the evaluated constants and correlations in the design equations of extraction columns. The main problem though is the level of complexity of such a technique. Many processes should be taken into consideration for fully describing the extraction in such a system, including the fluid motion inside the originating drop, adsorption processes at the interface from both outside and inside of the droplet, reactions at the fluid-fluid interface, diffusional processes occuring at the outside of the drop, the motion of fluids during the stage of droplet travel etc. Thus, it is almost impossible to describe all of the occuring phenomena and derive a mathematical model for extraction in the techniques conditions. Some simplifications have to be used in order to create a model that can be solved and used to describe the process.

One of the very often assumed simplifications is the one saying that the flow inside the drop can be considered turbulent (2). The easiest implication of this assumption is that the distribution of all components inside the drop is uniform, thus no diversities of concentrations or density take place. The diffusional and convective processes may be neglected and the average values of concetrations inside the drop may be used.

When examining the reactions taking place at the interface of the drop it is also convenient to neglect the diffusional processes occuring on the outside of the drop. It can be justified by using high concentrations of the components in the continuous phase introducing thus time-independent quantities into transport equations.

The rate of reactions occuring during the extraction can be described using some rate constant and the bulk concentrations of components influencing the extraction process. Two parameters that are of great importance when describing rising drop extraction are the drops volume and surface. During the stage of drop travel through the continuous phase these values are approximately constant, but during the drop formation both of them are highly time-dependent. The forward rate of metal ions extraction from chloride solutions can be described using a simple differential equation:

$$\frac{d[K]}{dt} = k_f \frac{A}{V}[M]^a[Ex]^b[Cl]^d - \frac{[K]}{t}, \tag{1}$$

where *[K]* is a concentration of extracted complex inside a drop, *[M]* and *[Cl]* are, respecitvely, a concentration of metal cations and chloride anions outside the drop, *[Ex]* is an extractant concentration inside a drop, *A* – drops surface, *V* – drops volume, k_f – extraction rate constant, *t* – time.

The first term at the right side of the equation (1) describes the rate of chemical reaction at the interface of the drop, while the second one takes into account dillution of the complex concentration with the extractant solution, which the drop is being made of. Even with *[M]* and *[Cl]* considered as constants, equation (1) has many time-dependent quantities. The surface and volume of the drop can be approximated assuming that the drop has the shape of a spherical cap. To solve the equation (1) the time dependence of *[Ex]* is needed, and can be described as:

$$\frac{d[Ex]}{dt} = -k_f \frac{A}{V}[M]^a[Ex]^b[Cl]^d - \frac{[Ex]}{t} + \frac{[Ex]^0}{t}, \tag{2}$$

where $[Ex]^0$ denotes the concentration of extractant solution being pumped into the drop. Third term on the right side of the equation (2) describes the change of the extractant concentration inside the drop caused by the initial extractant solution supply into drop during the drop formation step. Equations (1) and (2) can be solved together numerically assuming simple initial conditions. Hypothetical graph of the solution can be seen in Figure 1.

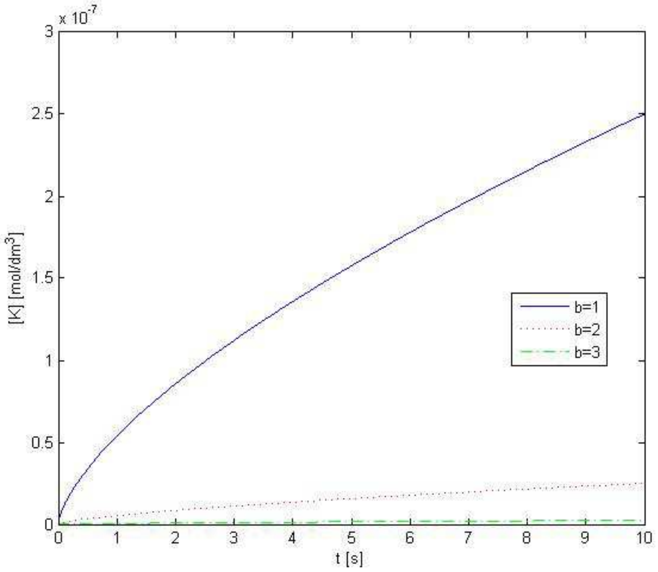

Fig. 1. Concentration of the extracted complex vs time during the drop formation stage for different values of *b*. *[M]* = 0.1 M, $[Ex]^0$ = 0.1 M, *[Cl]* = 2 M, *a* = 1, *d* = 2, $k_f = 10^{-7}$

The investigation of the stage of drop formation can give information about both the mechanism of the reaction occuring during extraction process and the rate constant used in the equations (1) and (2). Though, very often drop formation is being neglected and only the stage of drop travel through the continuous phase is being considered (3-6). For this case equations similar to equation (1) and (2) have been used ignoring the terms describing the flow of extractant solution into the drop. The analytical solutions found dependent on the value of the constant *b*, which denotes the reaction order in relation to the extractant:

$$[K]=[K]_{df}+[Ex]_{df}\left(1-\exp\left(-k_f\frac{A_d}{V_d}[M]^a[Cl]^d\left(t-t_{df}\right)\right)\right), \tag{3}$$

$$[K]=[K]_{df}+[Ex]_{df}-\left([Ex]_{df}^{-b+1}+(b-1)k_f\frac{A_d}{V_d}[M]^a[Cl]^d\left(t-t_{df}\right)\right). \tag{4}$$

In all cases index *df* denotes the values of variables during the drop detachment from the nozzle. Equation (3) is used, when *b* = 1 and equation (4) describes the complex concentration in other cases. The drops volume and surface are assumed constant during the drops travel through the column. Combining one of the equations from (3-4) with the numerical solution for equations (1) and (2) grants the full description of the forward reaction during the single drop extraction (figures 2-5).

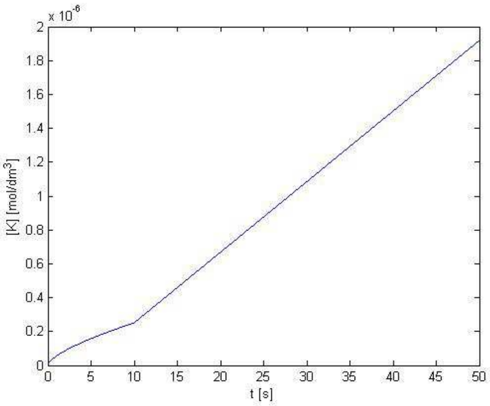

Fig. 2. Concentration of the extracted complex vs time for the two-stage extraction assuming *b = 1* (*[M]* = 0.1 M, *[Ex]*^{0} = 0.1 M, *[Cl]* = 2 M, *a* = 1, *d* = 2, t_{df} = 10s, k_f = 10^{-7})

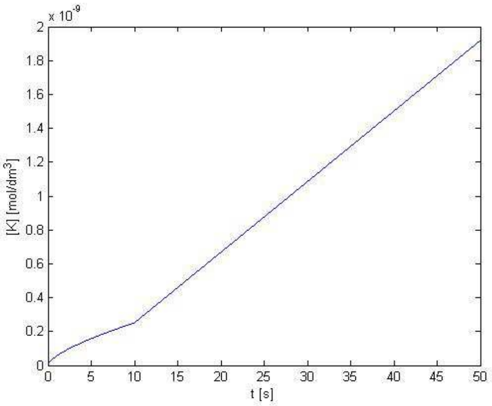

Fig. 3. Concentration of the extracted complex vs time for the two-stage extraction assuming *b = 2* (*[M]* = 0.1 M, *[Ex]*^{0} = 0.1 M, *[Cl]* = 2M, *a* = 1, *d*=2, t_{df} = 10s, k_f = 10^{-7})

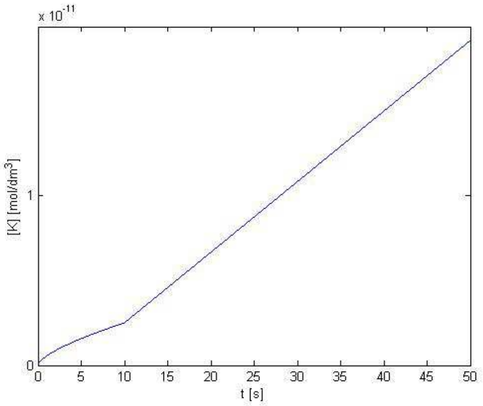

Fig. 4. Concentration of the extracted complex vs time for the two-stage extraction assuming *b = 3* (*[M]* = 0.1 M, *[Ex]*^{0} = 0.1 M, *[Cl]* = 2 M, *a* = 1, *d* = 2, t_{df} = 10s, k_f = 10^{-7})

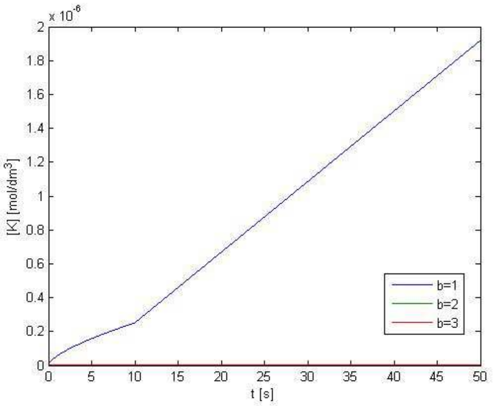

Fig. 5. Concentration of the extracted complex vs time for the two-stage extraction assuming various *b* values (*[M]* = 0.1 M, *[Ex]*^{0} = 0.1 M, *[Cl]* = 2 M, *a* = 1, *d* = 2, t_{df} = 10s, k_f = 10^{-7})

Presented figures show how big of an influence can the drop formation stage have on the extraction process using the single drop technique. Investigating two stages of the single drop extraction instead of only the travel step can in fact yield better results having in mind that the main assumption behind using forward rate extraction is that an initial stage of the extraction is considered. Omitting the drop formation stage can actually be the cause of big errors when determining the values of rate constants. Proposed solutions deal with this problem and can be used for any extraction that can be described using presented rate equation (1).

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APPLICATION OF ELECTRODIALYSIS TO THE TREATMENT OF SPENT COPPER AND ZINC INDUSTRIAL ELECTROLYTES

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Zinc electrolyte (ZE) obtained from zinc smelting process and copper electrolyte (CE) obtained during electrorefining process were treated by means of electrodialysis (ED). Three anion exchange membranes: ACM from Neosepta, PC Acid 60 and PC Acid 100 from PCCell were tested. All of the mentioned were combined with CMS cation exchange membrane from Neosepta, which enables monovalent/bivalent cation separation. In addition influence of electric current densities and flow rate on process parameters were examined. Studies were carried out with application of PC ED200 electrodialyser manufactured by PCCell, containing five membrane cells and four hydraulic circuits: the diluate, concentrate, anolyte and catholyte. Size of membranes is 125 x 262 mm with active area equal to 0.021 m^2. Flow rate of streams was controlled at constant level by set of rotameters. Voltage was applied by DC regulated power supply. Configuration of a system is presented in Fig. 1.

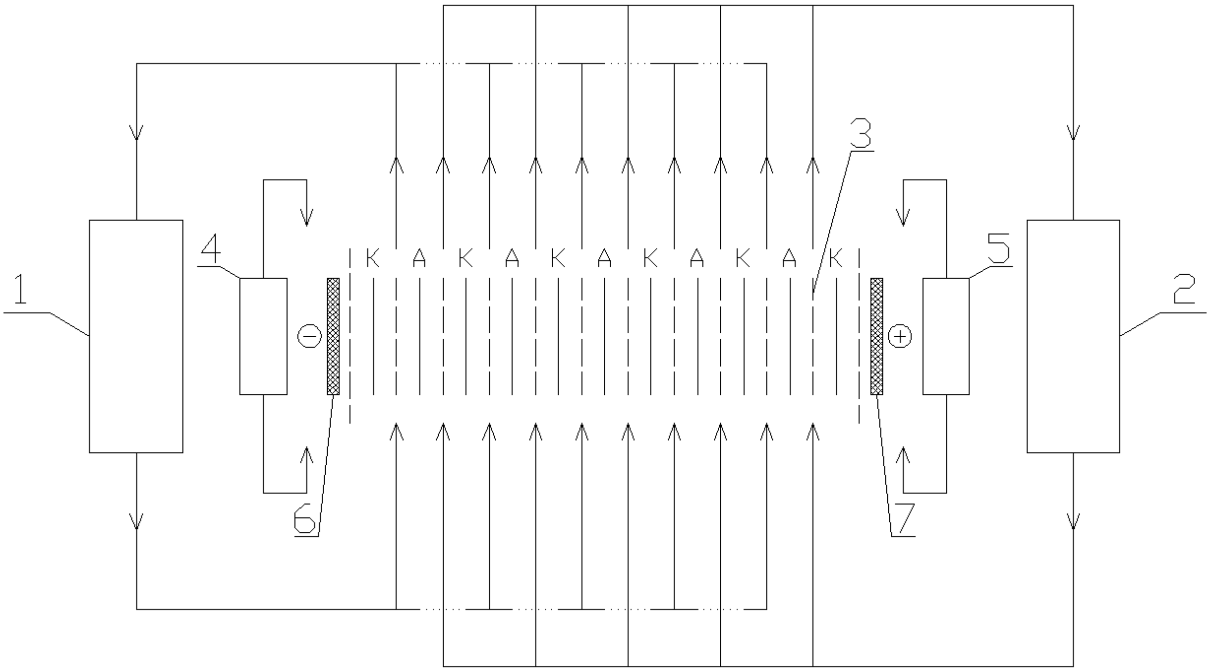

Fig. 1. Electrodialysis system scheme: 1 - diluate stream; 2 - concentrate stream; 3 - membrane spacer; 4 - catholyte stream; 5 - anolyte stream; 6 - cathode; 7 - anode; A - anion exchange membrane; K - cation exchange membrane

Compositions of treated zinc electrolyte and copper electrolyte components are presented in Table 1 and Table 2.

Table 1. Zinc electrolyte composition

H_2SO_4 [g/dm^3]	Zn [g/dm^3]	Mg [g/dm^3]	Mn [g/dm^3]	Cl [mg/dm^3]
150	56.8	14.4	3.60	580

Table 2. Copper electrolyte composition

H_2SO_4 [g/dm^3]	Ni [g/dm^3]	As [g/dm^3]	Sb [g/dm^3]	Cu [g/dm^3]	Fe [g/dm^3]
215	8.2	4.0	0.30	0.20	0.14

Zinc electrolyte

Initial membrane comparison was performed with a usage of synthetic solution of composition similar to industrial zinc electrolyte. During the tests one was able to reduce acid concentration up to 20 g/dm^3, successfully retaining most of metal ions in diluate stream. After that point, process had to be stopped due to rapid increase of required voltage in order to keep constant value of electric current. This caused warming of streams, what could damage membranes. Best results were obtained with application of CMS ACM membrane set. Comparison of average obtained process parameters is presented in Table 3.

Table 3. Results of zinc electrolyte electrodialysis

No.	Current efficiency [%]	Energy consumption [Wh/mole]	Zn retention [%]	Mg retention [%]	Mn retention [%]	Cl concentration in diluate stream [mg/dm^3]	
						initial	final
1.*	42.2	131.4	96.4	97.9	96.8	581	168
2.*	47.8	129.8	97.6	98.0	97.2	626	113
3.*	54.3	117.2	97.7	98.3	97.6		
4.*	54.5	114.7	97.9	98.5	97.8	676	164
5.*	58.0	99.0	97.5	99.1	98.6	588	210
6.*	49.3	122.0	96.9	98.4	97.8	544	118
7.*	58.2	192.7	97.9	98.3	97.9	609	252

1* - Acid 60, synthetic solution, 70 dm^3/h, 570 A/m^2
2* - Acid 100, synthetic solution, 70 dm^3/h, 570 A/m^2
3* - ACM, synthetic solution, 30 dm^3/h, 570 A/m^2
4* - ACM, synthetic solution, 100 dm^3/h, 570 A/m^2
5* - ACM, synthetic solution, 70 dm^3/h, 570 A/m^2
6* - ACM, industrial zinc electrolyte, 70 dm^3/h, 570 A/m^2
7* - ACM, industrial zinc electrolyte, 70 dm^3/h, 1140 A/m^2

Obtained results during test with a usage of industrial zinc electrolyte show similarity to that obtained with synthetic solution The difference is 20% higher energy consumption. Regardless of current density applied, the ratio of mass of analyzed component (Zn, Mg and Mn) transferred to concentrate stream to mass of removed acid, remains approximately the same. The flow rate 70 dm^3/h is optimal for conducted processes. Obtained retention coefficients value for each analyzed metal ion is of high value (above 99% in most cases) till the 60% acid removal. After that point, retention coefficient starts to decline for each tested membrane. Irrespective of current density applied, or membrane type chosen, majority of chloride ions are being removed from diluate stream during the course of the process.

Copper Electrolyte

Results obtained during initial comparison tests of three membranes sets were calculated at the point of 70% acid removal, due to rapid decrease of retention coefficient of ion metals as the experiment continued. All tests were conducted with application of industrial electrolyte, flow rate of streams equal to 70 dm^3/h and constant current throughout the whole experiment equal to 570 A/m^2. Increased current density during following tests caused enhancement of separation efficiency of tested membranes, hence results at the point of 80% acid removal are presented. Obtained data is given in Table 4.

Table 4. Results of copper electrolyte electrodialysis

	Current efficiency [%]	Energy consumption [Wh/mole]	Ion retention [%]				
			Ni	As	Sb	Cu	Fe
PC Acid 60 570 A/m^2 (70%)	44.8	110.7	96.0	83.9	94.3	91.3	97.7
PC Acid 100 570 A/m^2 (70%)	59.9	78.2	94.5	79.4	97.6	90.2	97.1
ACM 570 A/m^2 (70%)	57.7	102.7	94.1	79.6	98.8	92.5	98.7
ACM 860 A/m^2 (80%)	53.3	139.3	96.3	73.6	98.1	89.1	98.1
ACM 1140 A/m^2 (80%)	52.4	167.7	96.8	73.6	97.7	90.4	98.3

The retention coefficient of arsenic is reduced compared to other analyzed elements (Ni, Sb, Cu and Fe). For each analyzed membrane set. Amount of remaining arsenic at the end of the process in diluate stream is around 80% and around 74% during the tests with increased current density (860 and 1140 A/m^2). Higher current density caused reduction of transport rate of Ni, Sb, Cu and Fe through the membrane and enabled additional reduction of acid concentration in comparison to obtained results during test with application of 570 A/m^2 current density.

REMOVAL OF LOW-MOLECULAR CARBOXYLIC ACIDS FROM AQUEOUS SOLUTIONS VIA DIFFUSION DIALYSIS

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Nowadays there is a strong interest in renewable energy sources due to dwindling fossil fuels and increasing environmental pollution (1-3). One of such sources is biodiesel, which is a biofuel produced from vegetable oils and animal fats in transesterification reaction. Besides, this reaction is also the main source of glicerol - a by-product in the process (4). To avoid additional costs of glycerol purification, a bioconversion of glycerol to other required compounds is applied (5). This process, however, has some limitations applied to the production of acids. Always provides a good yield of more end - products, which involves the need to find a suitable method of separation and recovery from the fermentation broth (6). As it turns out, the separation and purification of the products is often as much as 50% of the cost (4,5).

During the conversion of glycerol to polyols and dicarboxylic acids (such as succinic acid, fumaric acid) in the fermentation broth other low molecular weight organic acids, such as acetic, lactic, citric acid, are formed. They also can be isolated and used in various industries such as pharmaceutical, chemical and food processing (e.g. as acidity regulators and preservatives). These compounds are particularly attractive because of the possibility of their further conversion to esters, acid chlorides, amines, amides, ketones, aldehydes, etc. (5). It is necessary to improve the manufacturing processes and the recovery of these acids, also from waste streams. There are many methods for separation of the acids from fermentation broths, including electrodialysis, nanofiltration, adsorption, ion exchange or precipitation. Some of these methods generate relatively high costs and in addition are not always environmentally friendly because they produce large amounts of solid waste (7).

One of technological methods of recovery of this acids from fermentation broth is precipitation of calcium salts and then decomposition of these salts using sulphuric acid, and finally crystallization of the product. This technological method is inconvenient and produces a large amounts of solid waste (calcium sulphate). Recovery of organic acids from the aqueous solution can be also obtained using the sorption on an anion exchange bed. The studies show the possibility of retention of succinic acid on the weak anion exchanger (Lewatit MP64) with the efficiency of 0.86 mol/dm^3 (8). The disadvantage of this method is the need to regenerate the bed using 4% NaOH solution and getting the product in the form of sodium salt. The next step is then electrodialysis with bipolar membranes, where sodium succinate solution is splitted into two separate streams of succinic acid and NaOH solution. For the separation of dicarboxylic acids from fermentation broth a reactive extraction may be used involving basic extractants, and physical extraction with suitable solvents. Distribution ratio of succinic acid between the organic phase (e.g. ethyl ether, butanol and butyl acetate) and aqueous phase equals 1.2-1.5. This makes the continuous removal of the fermentation product from the fermentation broth possible. Purified extracts after evaporation of a solvent can be crystallized to obtain a pure acid.

Another effective method of separation of acids from aqueous solutions is a diffusion dialysis with the use of anion exchange membranes. The membrane constitutes a diffusion barrier for salts due to the Donnan exclusion of cations from positively charged matrix. The effect of exclusion does not apply to hydronium ions, which are subject to facilitated diffusion by Grotthuss mechanism (9). The feed, which is a mixture of salt and acid, flows counter currently to the dialysate solution. Ions are moving from the feed solution to the dialysate obtaining a gain of concentration gradient, which is the driving force for the process. Anions can easily pass through the membrane and cations are retained (except for protons). More than 95% of an acid can be recovered from a mixture of salts using countercurrent flow streams (10). Diffusion dialysis is also well known for recovery of spent mineral acids such as HCl, H_2SO_4, HF. Carboxylic acids are weak acids (pKa of succinic acid equals 4.21 and 5.64 (11) and their separation is based on the sorption mechanism in the membrane material in form of undissociated species. Partition coefficients of carboxylic acids such as lactic acid, propionic acid, acetic acid are in the range of 1.0-1.4, and the separation factors obtained for these acids and their salts are in the range of 20-37 (8,12).

It is the aim of our work to study transport of some low molecular acids in the presence of glycerol or 1,3-propandiol by means of diffusion dialysis.

Diffusion dialysis of low molecular organic acids (monocarboxylic – acetic acid and dicarboxylic – fumaric and succinic acids) was carried out at room temperature in a flat membrane module by Osmonics (shown in Fig. 1) with the anion-exchange membrane FAD (FumaTech, membrane area of 150 cm^2). The model feed solution (V_f = 230 cm^3) was composed of acetic, succinic or fumaric acid (Fluka) with additives such as 1,3-propandiol and glycerol (Sigma Aldrich). Distilled water was used as a receiving solution (V_s = 120 cm^3). The two aqueous phases flowed across the membrane in a closed loop at a rate of 20 cm^3 /min (peristaltic pump Unipan).

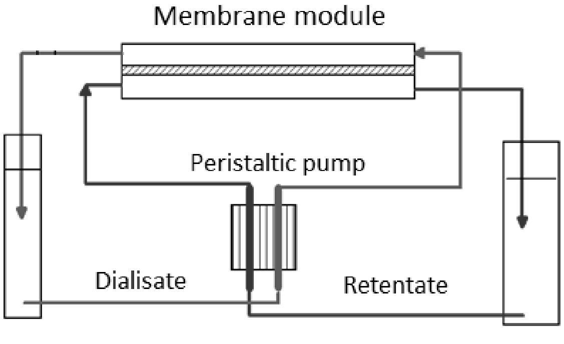

Fig. 1. A scheme of the membrane module used for diffusion dialysis studies

Effect of change of the carboxylic acids concentration, changes of the flow rate and pH of model solutions on the efficiency of the diffusion dialysis were examined. The studies showed that with the increase of pH the efficiency of the process decreases. The presence of glycerol also reduced the efficiency of an organic acid transport by diffusion dialysis. Addition of 1,3-propandiol did not affect the transport of acids across the membrane. For each process retention and the selectivity of the membrane were calculated.

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SIMULATION OF POWER PLANT FLUE GAS DESULPHURIZATION USING CHEMCAD PROGRAMME

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Abstract

In this paper simulation of the SO_2 removal by absorbing and reacting SO_2 with limestone slurry, and limestone scrubbing was realized by application of a spraying reactor in ChemCad programme. Simulation investigations for effects of different operating variables on the SO_2 removal from flue gases are presented.

Because of high SO_2 removal efficiency, reliable and low utility consumption the wet method of flue gas desulfurization (FGD) in power plants is temporarily the most widely used (1-5). There are numerous problems in the prediction of the SO_2 removal from flue gases because efficiency of the reaction system depends on a wide range of variables.

Experimental

The proposed technological scheme of flue gas desulphurization (FGD) plant made in ChemCad programme is presented in Fig. 1.

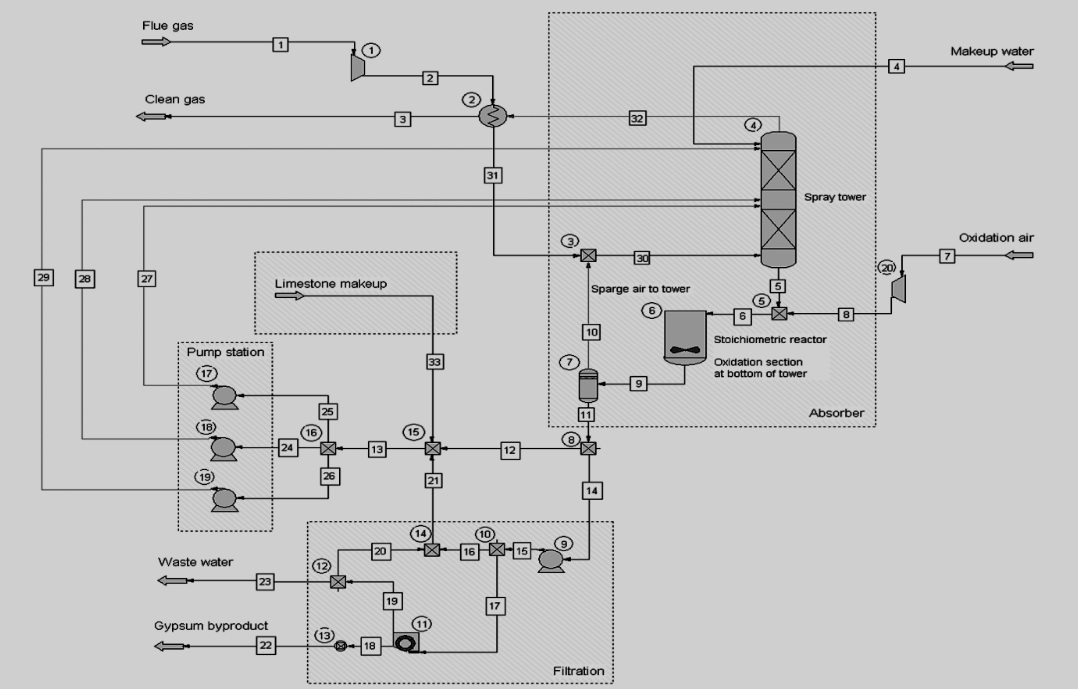

Fig. 1. Technological scheme in Chemcad programme of the flue gas desulfurization plant

Hot flue gases from power plant boiler (stream 1) after preliminary cooling were flowing (stream 31) to the lower part of absorption tower (4) while calcium stone ($CaCO_3$) slurry with additional water was sprayed at the top part of the tower (streams 27-29, Fig. 1). (1, 19) - Flue gas compressor, (2) - Heat exchanger of and heating of purified flue gases and cooling of raw flue gases before absorption tower, (3) - Flue gas and air from apparatus of sulfates oxidation mixer , (4) - Mixer of absorption slurry with air stream (oxidation reagent), (5) - Oxidation reactor, $CaSO_3$ to $CaSO_4$, (6) - Gas-liquid separator, (7) - Absorption slurry stream divider, gypsum separation and slurry recirculation streams, (8) - Slurry pump, (9) - Absorption slurry stream divider, absorption slurry to gypsum separation and slurry recirculation streams, (10) - Gypsum slurry filter, (11) - Sewage stream divider, to absorption slurry preparation and sewage treatment plant, (12) - Gypsum quality and stream divider 10 controller, (13-14) - Mixers, (15) - Absorption slurry stream divider, (16-18) – Pumps.

The desulfurization reactions are presented below. Reaction 1 and 2 take place in the absorption tower (4) while reaction 3, oxidation step with using air stream is realized in the bottom part of absorption tower presented here by stoichiometric reactor (6).

$SO_2 + 2H_2O \rightarrow H_2SO_3 + H_2O$ 1

$CaCO_3 + H_2SO_3 \rightarrow CaSO_3 + CO_2 + H_2O$ 2

$CaSO_3 + ½O_2 \rightarrow CaSO_4 + 2H_2O \rightarrow CaSO_4 \bullet 2H_2O \downarrow$ 3

The produced sorbent- gypsum slurry was partially recycled to the FGD process (stream 16 and 21) while part (stream 17) was transported to filtration step (11). The product of the plant is gypsum and sewage (streams 18 and 19). Part of the sewage was directed to preparation of calcium stone slurry (streams 20, 21 and 33). The sorbent slurry produced in mixer 15 is divided for three streams (24, 25 and 26) and next it is delivered to absorption tower in order to spray at three or five levels and to absorb sulfur dioxide.

In the simulation process “Electrolite Module” and ‘true species model” from ChemCad System library were applied.

The following process parameters were accepted for the flue gas desulfurization process:

- ✓ fuel - brown coal, fuel heating value 7,3 MJ/kg, water and sulfur content W_r=52,9 %, S = 0,69 %, respectively.
- ✓ Sorbent – the milled calcium carbonate (calcium stone).
- ✓ The average SO_2 content in dry flue gases 6000 mg/Nm^3.
- ✓ Temperatures of flue gases before the absorption tower: 120, 140, 158ºC,
- ✓ Three volume sorbent slurry to flue gas ratio i.e. 10, 15 and 20 dm^3/Nm^3,
- ✓ Spray levels: 3 and 5.

The selected simulation results of flue gas desulfurization are presented in Tables 1 -2 and Fig. 1.

The data in Table 1 presents changes in temperature and the contents of the two major impurities, sulfur dioxide and hydrogen chloride during the desulfurization process. Gas temperature is lowered in the heat exchanger 2 before the absorber tower to 120ºC and in the absorber due to evaporation of water in the slurry to about 66ºC. The content of sulfur dioxide was decreased in absorption tower by more than 97 % wt and hydrogen chloride by about 99 %

wt. Before discharge of flue gas into the chimney chilled in the absorber exhaust gas is heated in the same heat exchange (2) to more than 100º.

Table 1. Example of simulation data for the selected process parameters, temperature of flue gases 120ºC, 3 spray levels, 15 dm^3 slurry/Nm^3 of flue gas

1. Flue gases before heat exchanger and desulfurization	
1a. Temperature of raw flue gas before heat exchanger	163ºC
1b. Sulfur dioxide content in raw flue gas before heat exchanger	14348 kg/h
1c. Hydrogen chloride content in raw flue gas	35.86 kg/h
2 a. Temperature of raw flue gas after heat exchanger	120ºC
3 a. Temperature of slurry in absorption tower	66.3ºC
4 a. Temperature of gypsum	66.6ºC
5. Flue gases before heat exchanger and after desulfurization	
5 a. Temperature of flue gas before heat exchanger	64.2ºC
5 b. Sulfur dioxide content in flue gas before heat exchanger	422 kg/h
5 c. Hydrogen chloride content	0.38 kg/h
6 a. Temperature of the purified flue gas after heat exchanger	104.4ºC

The data in Fig. 2 show that the decisive factor in terms of efficiency flue gas desulfurization has a number of slurry spray levels, much lower exhaust gas temperature entering the absorption and the amount of the circulating suspension (L/G).

Changing the flue gas temperature entering the absorber influence mainly impact on the temperature of flue gases discharged to the chimney (Table 2). Regardless of the FGD process parameters slurry pH changes in a small range, 5.5-5.8. Similarly is in the case of temperature desulfurization absorption tower. Regardless of the temperature of the flue gas entering the absorber (120 to 158ºC), the temperature in the tower is relatively stable in a range of 65.9-68.9ºC.

Table 2. Influence of process parameters on temperature of absorption and flue gases before the chimney and pH of absorption slurry

Spray levels	Flue gas before absorption, ºC	L/G ratio	Flue gas temp. after absorption,ºC	Flue gas temp.after heat exchange,ºC	pH in absorption slurry
3	120	10	66.6	105.3	5.6
3	120	15	66.9	105.4	5.7
3	120	20	67.1	105.5	5.8
3	140	10	66.8	87.4	5.6
3	140	15	66.9	84.6	5.7
3	140	20	67.2	84.7	5.8
3	158	10	68.9	71.3	5.6
3	158	15	67.0	714	5.7
3	158	20	67.2	74.6	5.8
5	120	10	65.9	105.8	5.5
5	120	15	67.1	105.5	5.7
5	120	20	67.4	105.5	5.8
5	140	10	66.1	87.1	5.6
5	140	15	67.2	87.7	5.7
5	140	20	67.4	87.9	5.8
5	158	10	66.4	70.8	5.6
5	158	15	67.2	71.6	5.7
5	158	20	67.4	71.8	5.8

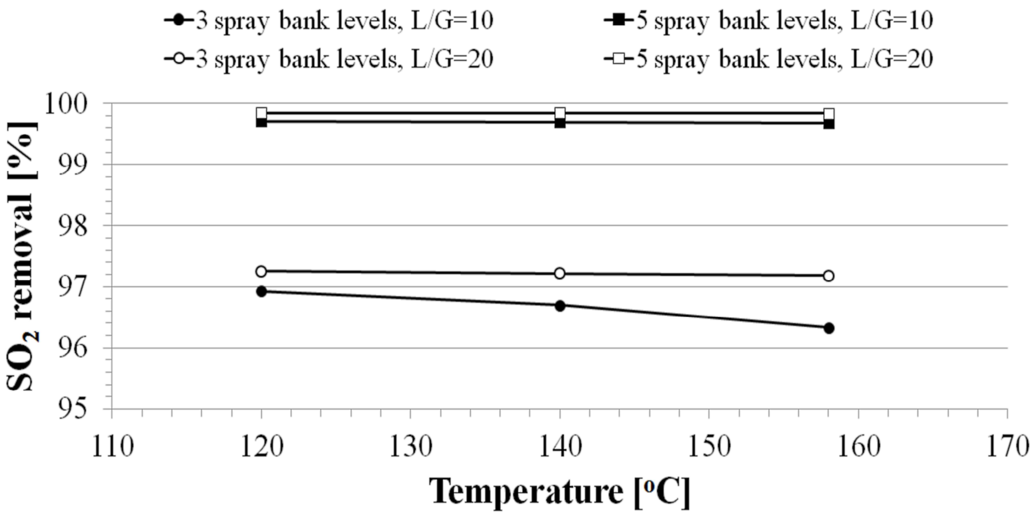

Fig. 2. Influence of FGD process parameters on desulfurization level

It is a result of automatic regulation of absorption temperature as a result of varying of the degree of evaporation of water. In a case of introduction of exhaust gas to the absorber at a higher temperature more water is evaporated. This affects both the energy loss of exhaust gas and increase the cost of fresh water supply to the process.

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III. POSTERS

HYDRODYNAMICS AND KINETICS OF BIOLEACHING

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Bioleaching is a new technology to extract metals from the minerals, which utilizes bacteria to break down the mineral matrix, liberating the useful metals from the raw minerals into solution for subsequent solvent extraction and recovery processing. The technology is especially suitable for dealing with low-grade ores, waste ores, sub-marginal ores and refractory mineral resources (1,2). Most important chemolithotrophic bacteria, using in bioleaching, are *Acidithiobacillus ferrooxidans,* which can convert insoluble sulfides into soluble sulfates. These bacteria are able to oxidize ferrous(II) ions to ferric(III) ions and extract metals (for example copper) to solutions (3).

In the present work, the results of bioleaching of copper wastes from Lubin was studied. The bioleaching processes with different amounts of polyethylene fittings were carried out in glass column.

In the present work, a material in the column can be classified as porous material. The permeability (k) is the most important parameter for the study of flows in porous media. The porosity (φ) is other important parameter for porous material. There is the relationships between porosity and permeability $k = f(\varphi)$. The macroscopic property of porous material in the column was correlated with the bioleaching efficiency (the concentration of Cu^{2+} ions in leaching solution).
The kinetic of bioleaching was monitored by measuring the values such as: pH, Eh, the concentration of ferrous and ferric ions (complexometric method). The protein concentration (Lowry method) was also investigated. It is related to the amount of microorganisms and their metabolic activity. The described process gives an opportunity to use the bioleaching of copper wastes for industrial application.

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REMOVAL OF ACIDIC AND BASIC DYES FROM WATER USING CROSSLINKED POLYSTYRENE BASED QUATERNARY ETHYL PIPERAZINE RESIN

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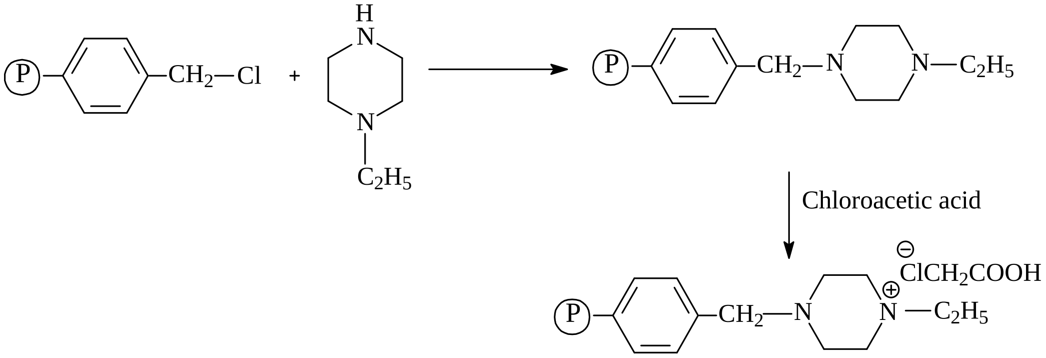
Dyes usually have a synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to biodegrade (1). Dye removal techniques can be divided into three categories: biological, chemical and physical. All of them have advantages and disadvantages. Because of the high cost and disposal problems, many of these traditional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries.

In this study, a beaded polymer with quaternary amine functions were prepared in two steps, starting from poly(vinyl benzyl chloride-ethylene glycol dimethacrylate) based beads, according to the synthetic protocol; modification of ethyl piperazine and quaternization with chloroacetic acid.



Scheme 1. Preparation of the sorbent

Dye extraction experiments were carried out simply by contacting resin samples with aqueous dye solutions at room temperature. Capacities were determined by colorimetric analysis of the residual dye contents.

The adsorption conditions (initial dye concentration and pH) were varied to evaluate the mechanism of adsorption of both basic dyes and acidic dyes on the prepared sorbent. Kinetic studies and regeneration of the sorbent were also investigated.

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CHARACTERIZATION OF GLASS BEADS SURFACE MODIFIED WITH SURFACTANTS

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Knowledge of solid surface properties is an important aspect in many industrial processes like oil agglomeration or flotation. Both methods are called “colloidal method” and can be used for selective separation of one mineral from mixture. In such type of method the properties of solid surface play a crucial role in adhesion of oil droplets to mineral surface or adhesion of solid to bubble air (1). Literature data revealed that the most important factor, which affects the efficiency of agglomeration or flotation, is hydrophobicity. This parameter can be estimated by contact angle measurements and surface free energy components calculation (2). Direct contact angle measurements used for planar solid surface cannot be applied for finely dispersed solid materials, which are used in oil agglomeration or flotation processes. In such cases the determination of this parameter is more problematic and not well described in literature (3). In our experiments we used a capillary method, where the contact angle can be calculated from Washburn equation. In this method the solid material was manually placed in a small column plugged at the bottom by a piece of material to support the bed. During experiment an increase in weight of the bed due to a wetting liquid penetration was recorded every second. In such method the problem is to obtain repeatable packing density, therefore the glass spherical beads with smooth surface were used as solid to eliminate the effect of roughness and heterogeneity of the surface. The material was washed with acid, dried and used in experiments. The surface of the solids was modified using anionic (sodium oleate and sodium dodecylsulphate) and cationic surfactants (dodecylammonium hydrochloride, cethyltrimethylammonium bromide) commonly used in mineral processing. The contact angle was determined for liquids such as n-heptane, water, ethylene glycol, formamide and 1-bromonaphtalene. These data were used to estimate the surface free energy components using van Oss’s equation. To confirm obtained data, the flotation experiments of treated and untreated glass beads were performed in a Hallimond tube.

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KINETIC AND THERMODYNAMIC ASPECTS OF BORON ADSORPTION ONTO POLYMERIC ION EXCHANGERS

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In the present study, two kinds of polymeric beads were produced using atom transfer radical polymerization technique. Boron removal from aqueous solution by synthesized polymeric ion exchangers (GMA-PVC, VBC) was investigated. The effects of pH (3, 6.5, 10) and initial boron concentration (10, 20, 30 mg·L^{-1}) on boron removal were studied. Thermodynamic studies were conducted at different temperatures (25, 45, 65ºC) with 20 mg·L^{-1} initial concentration. Maximum capacities of GMA-PVC and VBC were determined at pH 10 as 1.668 and 3.261 mg·g^{-1}, respectively. With decreasing pH, maximum adsorption capacity of GMA-PVC was reduced to 0.964 mg·g^{-1} at pH 3.0 while that of VBC was observed as 2.456 mg·g^{-1}. The adsorption affinity of GMA-PVC was increased from 1.668 mg·g^{-1} at 25ºC to 3.302 mg·g^{-1} at 65ºC. However for VBC sample, adsorption decreased with increasing temperature indicating exothermic process.

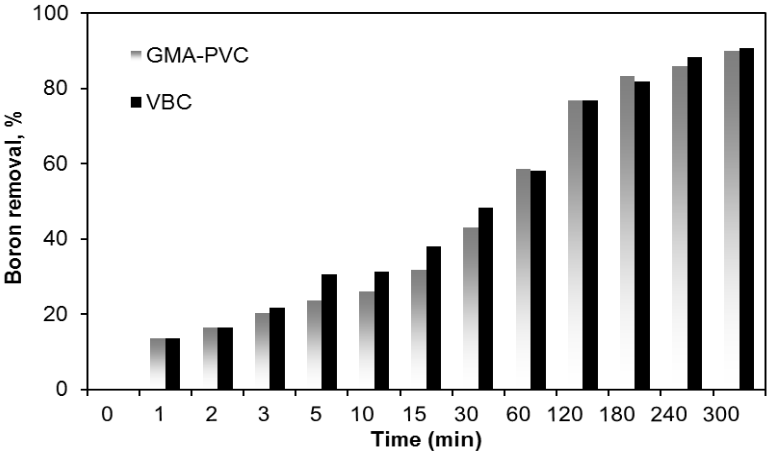

Fig. 1. Effect of contact time on boron removal by GMA-PVC and VBC samples

Approximately 58% of B was removed by GMA-PVC in 1 h and after 6 h, removal efficiency of B was 95% (Fig. 1). The controlling mechanism of the adsorption process was investigated by fitting the experimental data with kinetic models. The results were found to obey the second-order kinetic and intra particle diffusion. The second order model provides better correlation coefficients, which is 0.999 and 0.998 for VBC and GMA-PVC, respectively. The theoretical capacity values estimated from the first-order kinetic and Elovich models gave significantly different values compared to experimental values indicating these models might not be sufficient to describe the adsorption mechanism.

THE STUDY ON LIQUID-LIQUID EXTRACTION OF URANIUM(VI) IN THE SYSTEM WITH THE MEMBRANE CONTACTOR

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Extraction with use of membrane modules represents a new approach to the concentration and purification of uranium solutions, which are obtained after leaching of uranium ores. In the first step of experiments the selection of extracting agents appropriate for the membrane process was carried out. The experiments were performed using model solutions of uranyl nitrate ($UO_2(NO_3)_2 \cdot H_2O$) in 5 % sulfuric acid. After preliminary experiments test of membrane resistivity and determination of extraction efficiency, di(2-ethylhexyl)phosphoric acid (D2EHPA) were found to be most favorable for the membrane extraction process. The next step of the work were experiments with use of real solutions of uranium originating from leaching uranium ores (sandstones of the Lower and Middle Triassic from Perybaltic Syneclise and brown shale from Podlasie Depression) with use of sulfuric acid or alkaline solutions of $NaOH/Na_2CO_3$. The experiments of membrane extraction were performed with the small installation equipped with the membrane contactor Liqui-Cel® Extra-Flow 2.5 x 8 produced by CELGARD company. The flow of two phases in the module was arranged in co-current mode and relationship of the average linear velocities of these phases were determined from the Bernoulli equation. Back extraction (stripping) from organic phase to aqueous phase was conducted in the same membrane module with use of solutions of sodium or ammonium carbonate. The extraction efficiency was in the range of 74.22 – 98.07 % for the model solutions; 52.46 – 92.23 % for the real acidic solutions and 79.89 – 93.80 % for the real alkaline solutions. Based on the results of experiments the installation integrating processes of membrane extraction/re-extraction was built. Such process involved two membrane modules, one for extraction and the other for back extraction. It is advantageous because allows to carry both process in one apparatus. The benefit of the integrated membrane process over one-stage installation with one single membrane module may also rely on the fact that the overall mass transfer coefficient resulting from the integrated process can be greater than the coefficient of mass transfer obtained in a single membrane module (1). The results of this research will be used for development of methods for the extraction of uranium from Polish uranium ores (sandstone, shale) and the secondary raw materials, such as phosphoric acid. The membrane method can be considered an interesting alternative to traditional extraction methods applied for the production of uranium oxide U_3O_8 for the NPPs (Nuclear Power Plants).

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MOLECULAR DYNAMICS IN CITRIC ACID EXTRACTION

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Molecular modelling methods are widely used to analyse and describe effects that proceed during the extraction process. Molecular modelling simulations allow to research behaviour of the extraction solvents, analytes and extractants (1). With the intention of examination molecular modelling usefulness in describing extraction process, several molecular computational technics were used. Citric acid is an important ingredient of pharmaceuticals and cosmetics products. However, the dominant use of citric acid is as a flavoring and preservative in food and beverages. Typical extractants that are used in extraction of this acid are: tributhyl phosphate (TBP), trioctylamine (TOA) and 1-decyl-imidazole (IMID10).

The behaviour of liquid-liquid extraction system was researched during molecular dynamic simulation preformed using Amber 10. On Gaussian09, quantum-mechanic simulations were applied in order to describe interaction between analytes and extractants molecules. Extraction solvent consisted of mixture: solvents molecules (373 chloroform and 1645 water), 36 analyte molecules (citric acid) and 30 molecules of extractants (TBP, TOA, IMID10). As described in (2) computational techniques correctly describe behaviour of the extractat and analytes in pure solvent system or at the organic/water interface. Presented work describes behaviour of these compounds in chloroform/water mixture system. Obtained results indicate that solutes molecules separated from each other and formed two-phase system while extractants molecules, due to amphiphilic structure, adsorbed at the interface. Position of the extractants is strictly specified: polar part is pointed towards aqueous phase while alkyl chains are immersed in organic phase. Calculated concentration value of TBP, TOA and IMID10 at the interface is equal as follows: $1,47\text{x}10^{-6}$ mol/m^2, $1,06\text{x}10^{-6}$ mol/m^2, $1,47\text{x}10^{-6}$ mol/m^2 and it is related to the experimental one. Moreover molecular dynamic simulations without extractant shows that analyte molecules are adsorbed at the water/chloroform interface or moved deep into aqueous phase. Addition of extractant molecules to the system results in the presence of citric acid in organic phase. In interfacial area occurrence of H-bonds between TBP, TOA or IMID10 and citric acid could be observed. As shown by quantum-mechanic analysis, extractant/analyte interactions are strong (approximately 15 kcal/mol) and organic complex structures, which migrate deep into organic phase, depend on free energy of solvation. Obtained results correspond to the experimental ones.

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CITRIC ACID TRANSPORT ACROSS POLYMER INCLUSION MEMBRANES (PIM) WITH OXYETHYLATED ALCOHOLS AS PLASTICIZERS AND 1-ALKYLIMIDAZOLES AS CARRIERS

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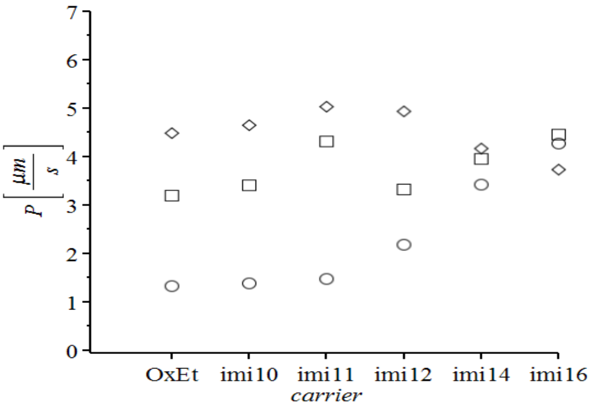
Citric acid is one of the most commonly applied organic acids in the world. It is usually produced in the fermentation process (1). Because of the high costs of acid precipitation from fermentation broth, new methods for this production step are being searched for. One of the methods that can be used is the application of polymer inclusion membranes (PIM) (2). The important parameters that influence compounds transport through PIM are the proper choices of adequate plasticizer and carrier (3,4).

The research were carried out applying oxyethylated alcohols as plasticizers (Genapol® X20, X60, X150 - Clariant Corporation), that contained 2, 6 and 15 oxyethylated groups. As a carrier 1-alkylimidazoles with alkyl chain length from 10 to 16 carbon atoms were used. Cellulose triacetate was used as a polymer matrix. Also, the transport abilities of membranes containing no carrier were researched.



Process parameters:

Feeding phase – 0.1 M citric acid,
Receiving phase – DI water,
Phases volumes – 60 cm^3,
Membranes surface – 4.15 cm^2,
Temperature – 25 ºC,
Experiment duration – 24 h.

◊ - Genapol® X150
□ - Genapol® X60
○ - Genapol® X20

On the basis of obtained results, the values of transport parameters: permeability coefficient - *P* and molar flux - *J* were calculated. As it can be seen in the presented figure, for the carriers with alkyl chain length from 10 to 12 carbon atoms citric acid transport increases with the increment of oxyethylated groups number in plasticizer. But for imidazoles with 14 and 16 carbon atoms there is no significant difference between them.

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HYDROMETALLURGICAL TREATMENT OF SULPHIDE COPPER CONCENTRATES AS A PROCESS OF METALS SEPARATION

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The subject of presented study is a copper sulphide concentrate from Lubin Concentrator, KGHM Polska Miedź S.A. The material is highly complex in terms of mineralogical and chemical composition both of barren and metal-bearing components. The concentrate contains carbonate phase as a dominating rock material and various sulphide minerals of copper and accompanying metals: silver, cobalt, nickel, vanadium, molybdenum and zinc. Due to high content of organic carbon, lead and arsenic the concentrate cannot be accepted, for technological and ecological reasons, as a feed to pyrometallurgical processing.

The concentrate contains large amounts of carbonates that most frequently form polymineral intergrowths with metal sulphides (1). In order to liberate metal-bearing minerals prior the atmospheric or pressure leaching, controlled decomposition of carbonates with sulphuric acid in non-oxidative conditions has to be applied. It is a selective separation of magnesium and calcium from sulphide copper concentrate.

During atmospheric leaching in oxygenated solutions of sulphuric acid and ferric ions, copper and other valuable and toxic metals are transferred from solid phase into solution, by oxidation of sulphide minerals (2). This unit operation can be described as a metals separation process in which sulphides of copper, zinc, cobalt, nickel, arsenic and molybdenum are digested. Silver and lead remain in the solid phase and can be recovered by a separate process, using chloride or pressure leaching.

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BIPOLAR NANOFILTRATION MEMBRANES OBTAINED BY PLASMA DEPOSITION

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Track-etched membranes were used as support for deposition of plasma polymerized layers and formation of bipolar nanofiltration membranes. The 75 KHz plasma reactor was applied for deposition of plasma-polymers on the poly(ethylene terephthalate) microfilter with pores of 0.2 µm. Three kinds of monomers were polymerized: n-butylamine, allylamine and acrylic acid. For each monomer the polymerization parameters were optimized. It was found that acrylic acid deposited at the highest rate, allyloamine slower and finally n-butylamine. Among the electrodes, the powdered one appeared to be the best for membrane modification. The investigated plasma-polymers were deposited at various sequences on one or both sides of the porous support.

The obtained membranes showed good rejection properties towards sulfate and carbonate ions with still large permeate flux. It was shown that the sequence of deposited layers did not affect the separation properties. For some investigated membranes bivalent ion rejection reached 50-80% value.

Acknowledgment: The research was supported by Wrocław Research Centre EIT+ under the project "The Application of Nanotechnology in Advanced Materials" - NanoMat (POIG.01.01.02-02-002/08) financed by the European Regional Development Fund (Innovative Economy Operational Programme, 1.1.2).

INFLUENCE OF TEMPERATURE AND MATERIAL STABILIZATION ON PRECIOUS METAL SORPTION BY THE IMMOBILIZED EGGSHELL MEMBRANE

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In this study we present the use of immobilized eggshell membranes for the sorption (reduction) of gold, platinum and palladium. Also, the influence of temperature and material stabilization in hydrochloric acid were studied.

Eggshell membranes (ESM) were prepared by suspending raw eggshells in hydrochloric acid. The biomass was washed in distilled water, dried, grinded, sieved and mixed with polysulfone or polyacrylamide dissolved in *N*,*N*-dimethylformamide. The mixture was stirred at room temperature, and then, dripped into water/acetone mixture, where beads were formed by a phase inversion process. The beads were then washed and dried and subsequently used for gold, platinum and palladium sorption.

Sorption and sorption kinetics were compared for the room and 50ºC temperatures. Sorption was also compared for the stabilized and non stabilized beads. Beads stabilization was carried out in 0.5 M hydrochloric acid for 24 h, washed with distilled water and dried.

The biosorption experiments were carried out in batches as follows: known weight of immobilized ESM were added to 50 mL solutions of gold, platinum or palladium and shaken at RT or 50ºC for 48 and 192 hours.

Material stabilization in hydrochloric acid increase the sorption nearly twice. Increasing the temperature also increases the sorption results.

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EQUILIBRIUM AND KINETICS OF CHROMIUM(III) EXTRACTION WITH ALIQUAT 336 FROM CHLORIDE SOLUTION

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Compounds of chromium are widely applied in many industrial processes, e.g. in metal electroplating, glass coloring, in preservation of wood, and in the leather processing. Effluents and solid wastes containing chromium(III) create an environmental hazard and a risk for the human health. Therefore, recovery and removal of Cr(III) from solid and liquid wastes is crucial for environmental protection and economic reasons. Different methods have been proposed to recover chromium(III) from aqueous solutions, industrial floats and wastewaters. As it comes from literature data the solvent extraction is one of the most efficient method for concentration and separation of various metal ions and it can be used for removal of Cr(III) from aqueous solutions.

The aim of our studies was a comparison of the rate of chromium(III) extraction with commercial reagent Aliquat 336 from alkaline solutions of different compositions, prepared from the chromium(III) chloride.

The kinetics experiments of Cr(III) extraction have been investigated by a Lewis-type stirred transfer cell with constant interfacial area. The same volumes of the aqueous and organic phases were also used. The rotation number of the stirrers were kept in the range of 30÷120 rpm, because above 120 rpm the interfacial area was not flat and stable. Chromium(III) concentration in the aqueous phase was measured by atomic absorption spectroscopy using a Varian SPECTR AA800. The metal concentration in the organic phases was measured by the stripping of chromium(III) into 0.5 M sulphuric(VI) acid and measured by atomic absorption spectroscopy.

The obtained results allowed to compare the rate of Cr(III) extraction from aqueous solutions of different concentration of NaOH. The effect of stirring speed in the Lewis cell on the initial rate of the chromium(III) extraction from aqueous phases was shown. It was found that the rate of extraction is dependent upon stirring speed up to 120 min^{-1}. The initial extraction rate of chromium(III) ions is affected by the concentration of Aliquat 336 in the organic phase, composition of aqueous phase and stirring speed. It is known that structure of chromium compounds in aqueous solution is changing with time. The effect of ageing of aqueous solutions on equilibrium and kinetics of chromium(III) extraction was also shown.

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REVERSE OSMOSIS OF SINGLE SALT SOLUTIONS - EVALUATION OF THE TRANSPORT MODELS

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The filtration of single salt solutions (NaCl, NH_4Cl, $NaNO_3$, NH_4NO_3, Na_2SO_4, $(NH_4)_2SO_4$) through a commercial reverse osmosis membrane was investigated. The dead-end SEPA ST cell (Osmonics, USA) was used. The applied pressure difference was 10-30 bars, the initial feed concentration was 0.1 and 0.2 M, the final feed concentration in the cell reached even 0.4 M, depending on the kind of experiment. The following order of observed retention coefficients was found:

$$1 > (NH_4)_2SO_4 = Na_2SO_4 > NaCl > NH_4Cl > NaNO_3 > NH_4NO_3 > 0.8$$

which means that the investigated RO membrane better differentiates anions Cl^- and NO_3^- than Na^+ and NH_4^+. As expected, the divalent anion SO_4^{2-} is better rejected by the membrane than the monovalent anions.

The experimental data were fitted using the Spiegler-Kedem-Katchalsky model of salt filtration based on the transport equations of non-equilibrium thermodynamics. It was assumed that the model parameters a) are constant, b) they depend on the concentration according to the charged membrane model, c) they are a power function of concentration. In the case of NH_4NO_3, only a slight improvement of the data fit was obtained when assuming the concentration dependence of parameters (Fig. 1).

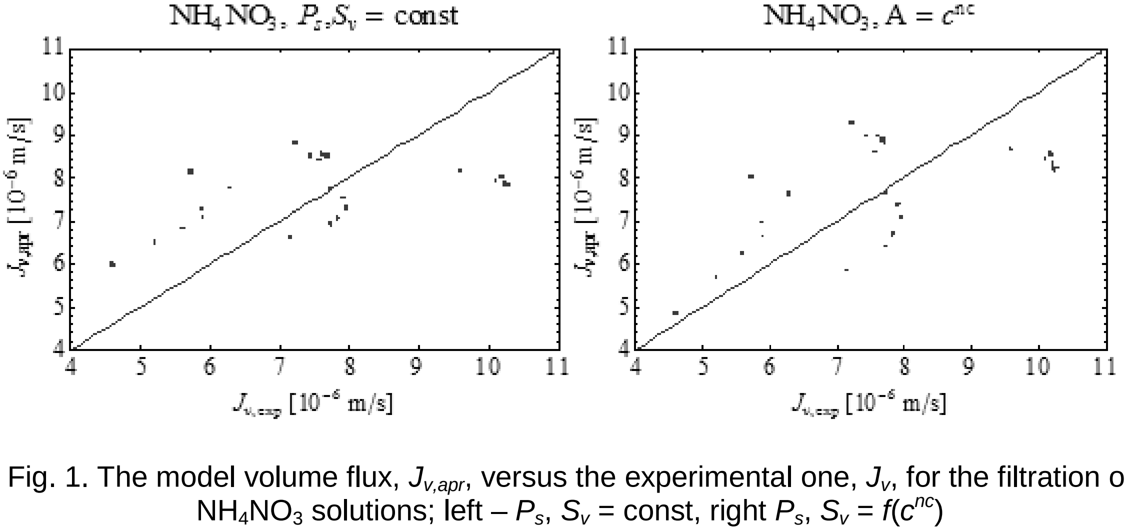

Fig. 1. The model volume flux, $J_{v,apr}$, versus the experimental one, J_v, for the filtration of NH_4NO_3 solutions; left – P_s, S_v = const, right P_s, $S_v = f(c^{nc})$

CHARACTERIZATION OF MEMBRANE SURFACE BY THE STREAMING POTENTIAL MEASUREMENTS

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The streaming potential measurements are widely used to characterize the membrane surface being in contact with an electrolyte solution. The potential is related to the membrane surface charge, thus its measurement supply the information about the interactions of solutes with the membrane (1).

In this work, the results of the tangential flow streaming potential measurements made for a commercial RO membrane and five types of ultrafiltration membrane synthesized at INCD ECOIND are presented. The UF membranes were obtained in a steady-state process, using an inversion phase technique. The studied membrane types were: membranes obtained from polysulfone solutions (concentration 10 and 12% Psf, solvent N-methyl-pyrrolidone), composite membranes polysulfone–polyaniline (PANI) obtained from polysulfone solutions (concentration 10 and 12% Psf, dissolved in a mixture of N-Methyl-pyrrolidone (NMP) and aniline), and composite membrane polysulfone – polyetheretherketone (SPEEK). The cell was made in our workshop. It was equipped with three pairs of electrodes – the SCE, silver-silver chloride and platinum electrodes. The Keithley 2700 multimeter equipped with the 7710 multiplexer card was applied for gathering the data. The pressure difference was measured with the Validyne pressure transducer. The influence of kind of electrolyte and of pH on the membrane surface charge was discussed. The differences in the streaming potential measured with the above mentioned electrodes were shown.

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FUNCTIONALIZED RESINS FOR NOBLE METALS SORPTION

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Precious metals, next to food and energy, are considered as the most important commodities. Their role is so significant that the economical and geopolitical situation of many countries depends on it (1). Need for development and restrictive environmental protection legislations causes growing global demand for noble metals and there is no doubt that evolving human society will need even more of them (2,3). That fact forces us to develop new, efficient ways of precious metals sourcing. Ion exchange is one of these methods.

The objective of present work is investigation of sorption potential of Au(III), Pt(IV) and Pd(II) on VBC/DVB resin modified with piperazine and pyridine moieties. Sorption tests were proceeded with batch method from multicomponent 0.1M HCl solutions that contained equivalent molar amounts of chlorocomplexes of gold, platinum and palladium in concentration range of 0.1-4.7 mmol/dm^3.

Suspension VBC/DVB copolymer was modified with 1-(2-aminoethyl)piperazine (resin 1a), 1-amino-4-methylpiperazine (resin 1b), 1-methylpiperazine (resin 1c), 4-aminopyridine (resin 2a), 2-(aminomethyl)pyridine (resin 2b) and 2,6-diaminopyridine (resin 2c).

Piperazine resin 1c revealed the greatest total sorption capacity (5.9 mmol/g), that result was far better than maximum sorption capacity on pyridine resins (3.1 mmol/g for resin 2a). The best for uptake of Au(III) was resin 1b (2.0 mmol Au/g), for Pt(IV) resin 1c (2.1 mmol Pt/g) and for Pd(II) resin 1a (1.5 mmol Pd/g). Pyridine resins showed lower uptake values and were as follows: 0.9 mmol Pt/g for resin 2a, 1.0 mmol Pd/g and 1.5 mmol Au/g for resin 2b, respectively. Resin 1b showed great affinity towards gold (partition coefficient reached 70 000). All of the pyridine resins during sorption tests preferred palladium (partition coefficients were up to 100 000).

Based on the results, we found obtained functional piperazine and pyridine VBC/DVB resins suitable for noble metals recovery.

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BIOMIMETICS OF METALLOENZYMES PREPARED BY MOLECULAR IMPRINTED TECHNIQUE – THEIR CATALYTIC ACTIVITY AND STABILITY

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One of the most promising method for preparation of materials with high recognition ability is molecular imprinting technique (MIT). Molecularly imprinted polymers (MIP) found applications in various areas such as: separation science, biosensors, drug delivery, chromatography, extraction and catalysis (1-4). The catalytic systems being a combination of transition metal ions with imprinting materials were found to be very similar to those existing in metalloenzymes. Thus, such enzyme analogues were successful used in: hydrolysis reactions, Diels-Alder aldol condensation, isomerization, stereoselective reactions, regioselective reactions (1,2,5-8).

This work presents the catalytic activity and stability of metalloenzyme biomimetics. The MIP were obtained by suspension polymerization of functional monomers (4-vinylpyridine, acrylonitrile) with TMPMA as a cross-linker in the presence of 4-methoxybenzyl alcohol (template) and transition metal ions (Cu^{2+}, Co^{2+}, $Mn^{2+,}$ Zn^{2+}). Additionally, two kinds of the cavities were obtained: in the volume and on the surface of the polymer matrix. The catalytic activity was compared for of metal ions inside of the cavities and imprinting method (volumetric and surface method). The catalysts imprinted with Cu^{2+}, Co^{2+} and Zn^{2+} were successfully used towards oxidation reaction of hydroquinone in the presence of the hydrogen peroxide solution in buffer acetate (pH 5). The Mn^{2+}-imprinted catalyst showed no activity due to the insufficient metal loading. Cu^{2+}-MIP showed the highest efficiency. Stability studies of Cu-, Co- and Zn-MIP catalysts were also performed. Both KO-Co(II) and KP-Co(II), did not show the catalytic activity after 10 months from the synthesis. For catalysts obtained with zinc and copper ions both sorption and catalysis process were successfully carried out in 10 and 18 months after polymerization.

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THE FUNDAMENTAL STUDIES OF REACTIVE FLOTATION OF SERPENTINITE AND MAGNESITE

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Serpentine and magnesite particles were used in the reactive flotation tests due to the potential of using pure minerals. Serpentinite describes a group of common rock-forming hydrous magnesium iron phyllosilicate ($(Mg, Fe)_3Si_2O_5(OH)_4$) minerals. Serpentinite can be used in the process of CO_2 capture and mineral storage. However, this process requires removing impurities such as silica and magnesite. Magnesite is a mineral with the chemical formula $MgCO_3$ (magnesium carbonate) and the main source of magnesium oxide. The deposits contain various minerals gangues, mainly carbonates, silicates and oxides. To obtain high-quality products based on magnesite beneficiation process is necessary.

Reactive flotation is defined as a flotation related to the chemical reaction. In case of magnesite and serpentinite separation, reactive flotation is associated with leaching of mineral particles under acid conditions. The leaching is preceded by the coating of the particle with a layer of polymer – poly(vinyl alcohol) (PVA). The acid penetrates the PVA membrane and reacts with carbonate minerals particles. The carbonate based minerals dissolution in an acidic medium generates CO_2 bubbles. The CO_2 accumulate between the particle and polymeric membrane. Capturing the CO_2 gas at the mineral particle surface into bubbles using a coating agent (PVA) can be used to intensification of the selective flotation process (1,2).

Fundamental studies of possibility of using the reactive flotation as a method of selective separation of magnesite and serpentinite was performed. The present work aims to determine the interaction of collector (sodium oleate) and a protective polymer (PVA) in the reactive flotation of investigated minerals under acidic conditions.

The leaching kinetics were studied under constant temperature and acid concentration. To describe the dissolution mechanism of serpentinite and magnesite particles Shrinking Core Model was proposed (3).

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ETHANOL-WATER PERVAPORATION ON MAGNETITE LOADED CHITOSAN MEMBRANES

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The industrial and economic importance of volatile liquids has considerably increased in recent years (1-7). In this operation, membranes are powerful tools for separation of liquid and offer in many cases a cheaper, less energy consuming and eco-friendly alternative to classical processes (1). In membrane pervaporation process separation of a liquid mixture at the feed side to a vapor at the permeate side of the membrane by differences in sorption and diffusion of liquids with simultaneous evaporation of the permeating compounds takes place (8). A useful strategy for improving the separation efficiency of polymeric films is the incorporation of inorganic materials into the polymer matrix. In composite membranes inorganic components are dispersed in a polymer matrix (1-3). These membranes benefit in the selectivity of active components and the simplicity of polymeric membrane processing. Recently, in our group poly(2,6-dimethyl-1,4-phenylene oxide) composite membrane containing different amount of nano-sized magnetic iron oxide (magnetite) was used in gas separation (N_2/O_2) experiments and vapor permeation (ethanol/water) studies (1-2). Presence of the magnetic particles additive has an impact on the separation properties of the polymer matrix. Using this type of membranes in separation of gaseous mixtures restrains permeation of paramagnetic constituent and promote diffusivity of the diamagnetic component. In case of the vapor permeation studies increase both of the flux and diffusivity of the less polar component is observed.

In this article, a new type of the composite membrane made of chitosan filled with iron ferroferric oxides (Fe_3O_4) is investigated. Impact of the magnetic particle content in chitosan matrix on the transport and separation properties of investigated membranes in pervaporation (water/ethanol mixture) processes is discussed.

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KINETICS OF COPPER(II) TRANSPORT THROUGH PIM WITH TRIAZOLE DERIVATIVES AS CARRIERS

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Extraction of metals through polymer inclusive membranes can be used as an alternative process for solvent extraction. The harmful impact of the former process is lower than that of the latter. The PIM process also decreases the amount of solvents consumed during the process. Furthermore, a smaller quantity of extractant (in the function of a carrier) is used with the PIM process. Thus, the use of more expensive, higher quality extractants becomes a possibility.

Triazole derivatives are a new type of carriers in separation process of copper(II). They are used in industrial chemistry as antifungal, antimould substances, fungal grove inhibitors and as drugs in medicine (1,2). In this paper 1,2,4-triazoles with the following configuration of alkyl chains: R = C_8H_{17}; C_9H_{19}; $C_{10}H_{21}$, $C_{11}H_{23}$; $C_{12}H_{25}$; $C_{14}H_{29}$ and $C_{16}H_{33}$ were used. The structure of typical 1,2,4-triazole is shown in Figure 1.

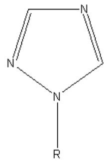

Fig. 1. The structure of 1,2,4-triazoles

The feeding phase consisted of 0.1M $CuCl_2$ and of the required amount of NaCl and HCl which regulate the concentration of chloride anions (0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 3.5; 4.0; 4.5 and 5.0 mol/L solutions were used). The receiving phase consisted of demineralized water. In the structure of membrane cellulose triacetate was used as the matrix, 2-nitrophenyloctyl ether was used as the plasticizer and triazoles were used as carriers. All of the solutions were prepared using methylene dichloride as the solvent. The process of copper(II) ions transport was conducted in a spiral module. The analysis of hydrodynamic conditions present in the process was also conducted.

Acknowledgments: This work was carried out in the framework of NCN grant no. 7441/B/T02/2011/40.

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SELECTIVE RECOVERY AND PURIFICATION OF PLATINUM GROUP METALS FROM SPENT AUTOMOTIVE CATALYST

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Platinum group metals (PGMs), such as palladium (Pd), platinum (Pt), and rhodium (Rh), are mainly used as automotive catalyst, because they have effective catalytic characteristics. Separation and recovery of PGMs from spent automotive catalysts is therefore an active issue. In our group, separation and recovery of PGMs from spent automotive catalysts has been investigated, using ion exchange process (1). Considering distribution route, the PGMs should be metallic state. In the present work, therefore, metalation of the PGMs from the eluents of the ion exchange process of previous work (1) is investigated.

Metalation of PGMs is conducted by precipitation, followed by calcination. Precipitation of PGMs was conducted by adding HCl or NaOH solution to each eluent at room temperature in the cases of Pd and Pt and at 80ºC in the case of Rh. Figure 1 shows the effect of pH on the precipitation yield of PGMs. In the case of Pd, precipitation yield increases with decrease in the pH, and quantitative precipitation is achieved at pH = 1. $(PdCl_2)(NH_3)_2$ is a possible species of the precipitates. In the cases of Pt and Rh, precipitation yields increase with increase in the pH, and quantitative precipitation is achieved at pH = 10. $Pt(OH)_4$ and $Rh(OH)_3$ are possible species of the precipitates.

Calcination of the precipitates obtained was conducted under air, N_2, and H_2 atmosphere. In the case of air and N_2 atmosphere, parts of the compounds exist as oxides. This is likely caused by the O_2 existed in the electric oven. Metallic PGMs can be therefore obtained when calcined under H_2 atmosphere in all cases.

Purities and recovery rate of the PGMs were determined, followed by dissolution the products with aqua regia, as summarized in Table 1. In the cases of Pd and Pt, purity and recovery rate are high. However, purity and recovery rate of Rh is still low, due to the incomplete dissolution with aqua regia. Purity and recovery rate of Rh will be improved in future works.

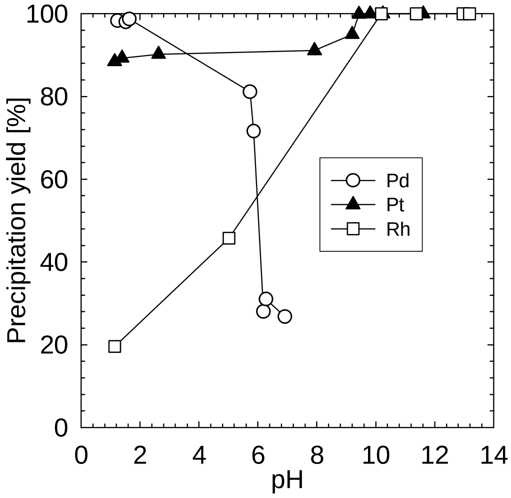

Figure1 Effect of pH on the precipitation yield of PGMs

Table 1. Purity and recovery rate of PGMs

	Pd	Pt	Rh
Purity [%]	100	100	97
Recovery rate [%]	95	96	70

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TRANSPORT OF NICKEL(II), COBALT(II), CADMIUM(II) AND ZINC(II) IONES THROUGH POLYMER INCLUSIVE MEMBRANES WITH 1-ALCOXYMETHYLOIMIDAZOLES AS A CARRIER

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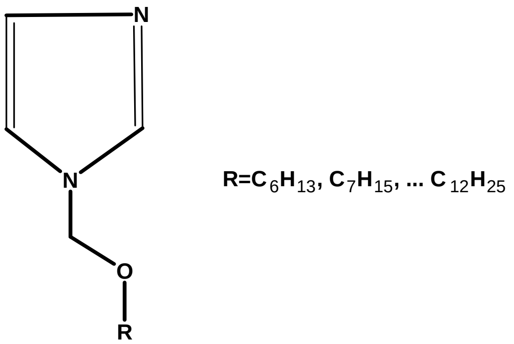
Nickel, cobalt, cadmium and zinc belong to a group of metals with a significant industrial meaning. All of them are acquired in various processes utilizing the, so called, wet processes, in which one of the stages includes resource leaching and afterwards, separation of metal ions from the polymetalic solution using extraction. Hydrometallurgical methods are also applied in the processing of wastes containing heavy metal ions.

Lately, the increase of interest in membrane processes as an alternative to extraction process of separation and precipitation of metal ions can be noticed. From the various membrane techniques processes including polymer inclusive membranes are getting more and more significant. These membranes are more resilient and chemically resistant than polymer supported membranes. The built-in carrier is much more difficult to rinse than the carrier in supported membranes and its presence improves the selectivity of separation process in comparison to other membrane processes.

The aim of this work is to study 1-alkoxyimidazoles as a prospective metal ions carrier in polymer inclusion membranes. Membranes consisting of cellulose triacetate as a polymer matrix, 2-nitrophenyloctyl ether as a plasticizer and the proper amount of a carrier were used in the studies.



Feeding phase consisted of nickel(II), cobalt(II), zinc(II) and cadmium(II) chloride solution with various concentrations of chloride anions. As a receiving phase demineralized water was used. In the studies conducted, a glass unit consisting of two cells with 50 cm^3 of solution each and divided by a membrane (surface equal to 4.12 cm^2) was used.

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INFLUENCE OF SOLVENT TYPE AND CONCENTRATION OF ACTIVE COMPOUND (TOA) ON CITRIC ACID EXTRACTION

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Citric acid is one of the most commonly applied organic acids in the world. It is usually produced in the fermentation process (1). Because of the high costs of acid precipitation from fermentation broth, new methods for this production step are being searched for. One of the methods that can be used is extraction process. On this method the type and concentration of active compounds (2) as well type of solvent (3) play important role.

The influence of active compound concentration - trioctylamine (from 0.025 to 0.1 mol/dm^3) and type of solvent: methyl-isobytyl ketone - MIBK, diethylcarbonate - Et_2CO_3 and toluene on extraction process of citric acid was investigated. Initial concentration of acid in water phase was equal 0.01 to 0.3 mol/dm^3. Equal volumes of both phases (10 cm^3) were shaking in Erlenmeyer flask (1 h) in order to obtain state of equilibrium. After it the solutions were left in order to phase separation and the concentration of citric acid in water phase was measured.

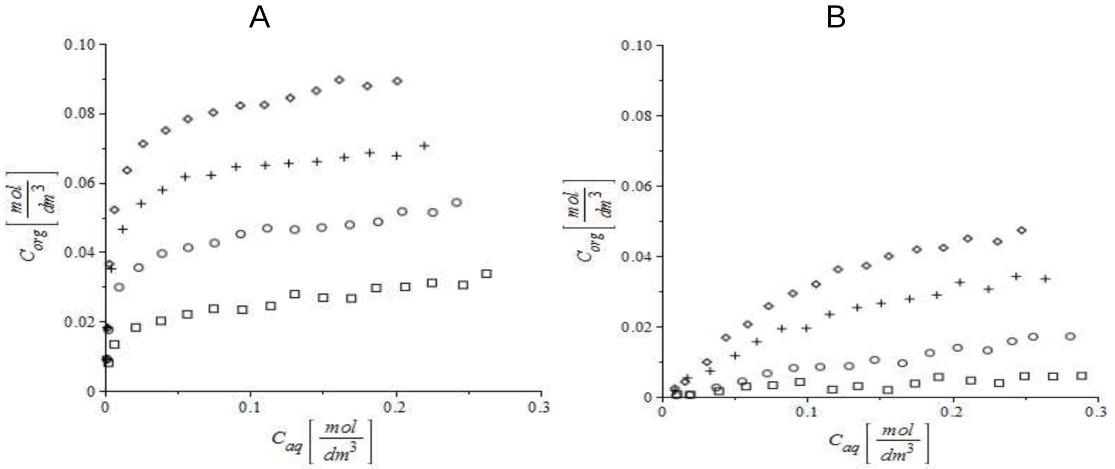

Fig. 2. The dependence of citric acid concentration in organic phase on concentration in water phase for MIBK (A) and toluene (B) as solvent. The initial concentration of TOA in organic phase: □ - 0.025 M, ○ - 0.05 M, + - 0.075 M, ◊ - 0.1 M

As it can be seen (fig. 1A,B) the concentration of TOA in organic phase as well the type of applied solvent are influenced on extraction process of citric acid. The active solvent - MIBK provide better results in comparison with toluene.

Acknowledgements: This work was carried out in part the framework of Statutory Research 32-376/2013/DS, conducted at the Poznan University of Technology.

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MODIFICATION OF CROSSLINKED GLYCIDYL METHACRYLATE-BASED POLYMERS FOR COPPER(II) IONS EXTRACTION

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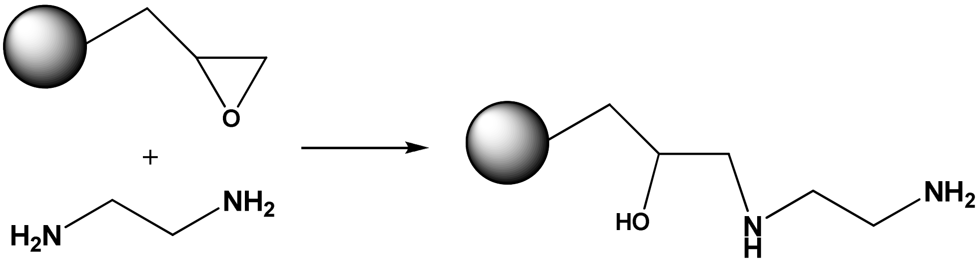
The terpolymer beads were prepared by suspension polymerization of GMA (0.4 mol), MMA (0.5 mol) and EGDMA (0.1 mol) (1). Epoxide content was determined as 3.40 mmol g^{-1} by pyridine–HCl method. Reaction of ethylenediamine with crosslinked terpolymer beads of glycidyl metacrylate–methyl methacrylate–ethylene glycol dimethacrylate yields corresponding polymers with epoxyamine functions (Scheme 1). Reaction with excess of ethylenediamine gave almost quantitative conversion as has been inferred from titrametric analysis of the amine content (6.4 mmol g^{-1}) of the product. The resulting polymer resin having epoxyamine functions is high capacity (3.1 mmol g^{-1}) copper(II) sorbent and useful for extraction of trace Cu(II) ions (100 ppm) from aqueous solution.



Scheme 1. Synthesis of epoxyaminated GMA-based polymers

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REMOVAL OF Cu(II) IONS FROM AQUEOUS SOLUTION BY PULLULAN-BASED SEMI-IPN POROUS HYDROGELS

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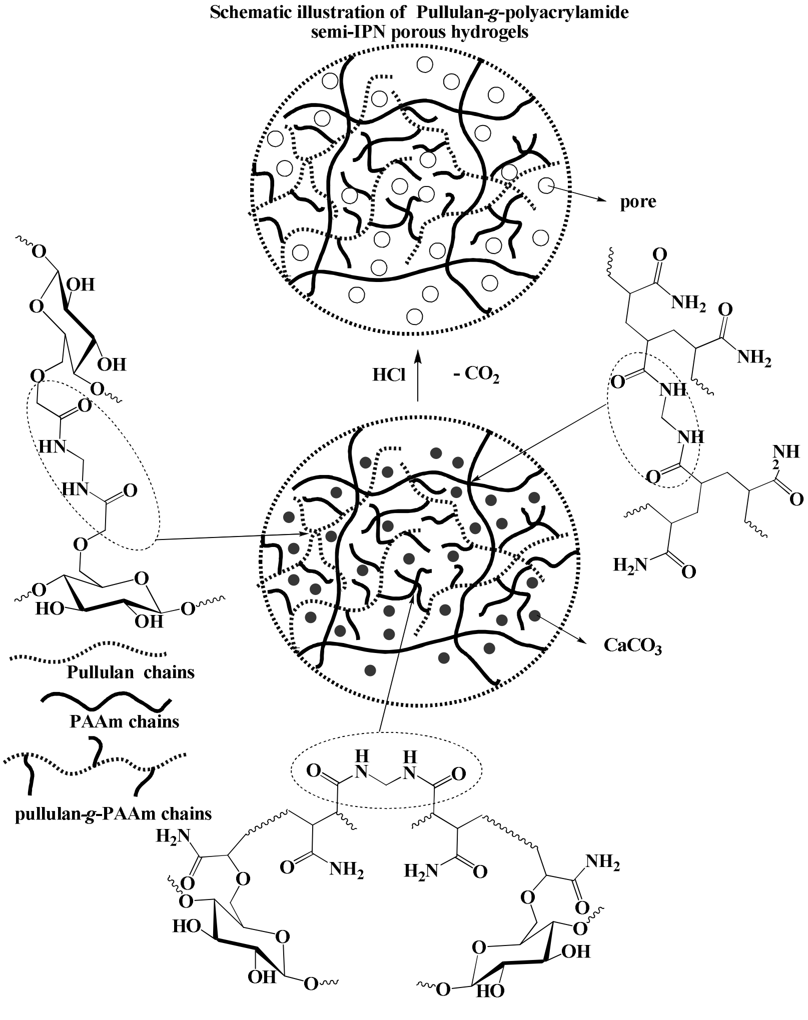
Pullulan-graft-polyacrylamide semi-IPN porous hydrogels were prepared through a radical polymerization method. Physical and chemical characteristics of the hydrogel were investigated by Fourier transform infrared spectroscopy, thermal gravimetric analysis and scanning electron microscopy. The swelling behaviors of the hydrogels were investigated under varying conditions of time, temperature and pH. The optimized swelling capacity under standard conditions was found to be 2630% per gram of the hydrogel. The prepared hydrogel has the potential to be used for metal ion adsorption in water treatment. Such a possibility was examined through adsorption of copper(II) ions from an aqueous solution.



REVERSE OSMOSIS OF TERNARY IONIC MIXTURES

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The filtration of ternary ion solutions (Na^+-NH_4-Cl^-, Na^+-NO_3^--Cl^-, and Na^+-Cl^--SO_4^{2-}) through a commercial reverse osmosis membrane in the dead-end mode was performed. The total retention coefficient and individual ion retention coefficients were determined. The influence of the presence of one ion on the retention of another ion was investigated.

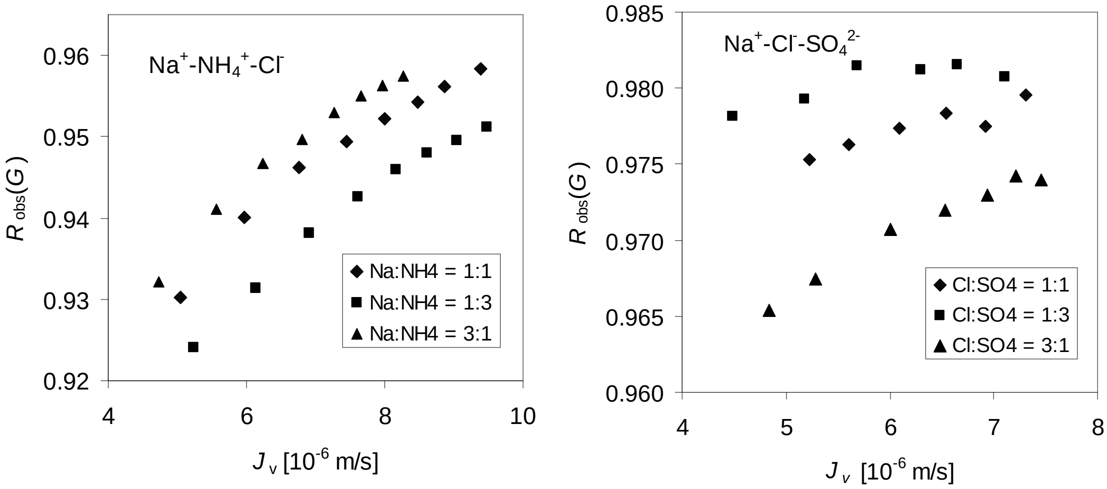

Fig. 1. Changes of the observed total retention coefficient, R_{obs}, and volume flow during the filtration of NaCl-NH_4Cl (left) and NaCl-Na_2SO_4 (right) mixtures; Jv decreases with time, c_{total} = 0.2 M, Δp = 30 bar

The experimental data were fitted using the Spiegler-Kedem-Katchalsky model of salt filtration adapted to the ternary ion solutions. The applicability of such a model was verified. The concentration dependence of the ion transport coefficient was discussed.

PERTRACION OF p-NITROPHENOL – A KINETIC MODEL

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The effect of the feed phase concentration and liquid membrane volume on the p-nitrophenol (PNP) pertraction efficiency was studied. The two consecutive irreversible first order reaction model was applied for description of the transport kinetics, according to the kinetic scheme (1):

$$M_f \xrightarrow{k_f} M_{LM} \xrightarrow{k_s} M_s \tag{1}$$

where M is the concentration [mol/dm^3] of solute in the feed (f), liquid membrane (LM) and stripping (s) phase, k_f, k_s denotes apparent mass transfer coefficients for the feed (f) and stripping (s) phase [cm/s].

The experiments were performed in the H–type bulk liquid membrane system (BLM). As the feed phase, the PNP solution ($c_f = 1\times10^{-5} \div 2\times10^{-4}$ M, V = 200 cm^3) was applied. As the stripping phase a 200 cm^3 of 0.01 M NaOH was used. The liquid membrane volume (toluene) was 50 cm^3. The contact area between the liquid membrane and the aqueous phases (f/LM and LM/s) was 17 cm^2. The concentration of the PNP solutions were determined from the absorbance values measured by a UV-Vis spectrophotometer (UV-2101PC Shimadzu).

The results indicated that the transport of PNP in the BLM system occurs under nonstationary conditions and can be described using a kinetic model of two consecutive irreversible first order reactions. In such a case, a maximum flux (J_{max}) is a characteristic value describing the pertraction efficiency. The dependence between the volume of the liquid membrane and J_{max} is nonlinear as it was found by one of the authors (2). From the relationship between the feed phase concentration(c_f) and J_{max} :

$$J_{max} = k_{ov} \cdot c_f \tag{2}$$

the overall mass transfer coefficient k_{ov} = 2.34 (±0.07)$\times10^{-4}$ cm/s was also evaluated.

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KINETIC STUDY OF Cu^{2+} SORPTION ONTO SOME COMPOSITE SORBENTS BASED ON CHITOSAN

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In recent years, the attention of researchers was focused on the environmental pollution with heavy metal ions because of their high toxicity and non-biodegradability (1). Among the conventional techniques used for the removal of these pollutants from the wastewaters the sorption process is mainly preferred. Chitosan (CS), the only cationic polysaccharide, has attracted numerous scientists due to its chelating properties against heavy metals (2). Recently, CS composites with inorganic compounds showed even higher sorption capacities than CS alone (3-5).

The purpose of this study was to modulate CS sorption capacities by obtaining new composites with a synthetic polycation having reactive primary amine groups. Poly(vinyl amine) (PVAm) has been selected for this purpose because it has not been so intensively investigated for the composites preparation. The composites have been prepared as microspheres by an ionic/covalent cross-linking. The influence of the covalent cross-linking strategy and of the ratio between CS and PVAm on the sorption kinetics of Cu^{2+} has been evaluated. It has been noticed that the composites in which the covalent cross-linking with epichlorohydrin (ECH) was performed in tandem with the ionotrop gelation in sodium trypolyphosphate (TPP) have higher sorption capacities compared to the composites post cross-linked with ECH, in basic medium. The ratio between CS an PVAm is also important, it was found an enhancement in the amount of Cu^{2+} sorbed by the composites having the molar ratio between CS and PVAm 90:10 compared with the composites having the molar ratio 60:40. In order to examine the controlling mechanism of the adsorption process, the experimental data obtained have been fitted by some kinetic equations (pseudo-first order, pseudo-second order and intraparticle diffusion). The sorption mechanism of Cu^{2+} ions obeyed on the pseudo-second order kinetics, supporting though that chemisorption as the rate-determining step. The reusability of the composite beads was also tested and it was found that the sorption capacity is increasing in the second cycle of sorption.

Acknowledgements: This work was supported by CNCSIS-UEFISCSU by the project PN-II-ID-PCE-2011-3-0300 and also by research fellowship within project "Enhancing Educational Potential of Nicolaus Copernicus University in the Disciplines of Mathematical and Natural Sciences" (project no. POKL.04.01.01-00-081/10.)

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SYNTHESIS AND CHARACTERIZATION OF SOME ICE-TEMPLATED METHACRYLIC ACID BASED HYDROGELS

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Hydrogels are hydrophilic systems that are composed of water-insoluble three-dimensional polymer network stabilized by physical or chemical crosslinks (1). Between different type of hydrogels, macroporous hydrogels are now in the centre of interest. Their advantage over conventional hydrogels consists in the improved mechanical resistance and fast response rate at small changes in the external stimuli (2). Among different techniques of formation of macroporous hydrogels, cryogelation is one of the most versatile (2-4). Cryogelation is a technique of synthesis of materials at temperatures below the freezing point of water. The ice crystals constitute a template for the reaction that takes place between concentrated soluble substances (monomers, initiator, polymers) in non-frozen zones (2,4).

The aim of this work was to synthesize novel cryogels, based on cross-linked poly(methacrylic acid-*co*-acrylamide) (P(MAA-*co*-AAm)). N,N'-methylene-bisacrylamide (BAAm) has been used as cross-linker, ammonium persulfate (APS) as initiator and N,N,N',N'-tetramethylethylenediamine (TEMED) as polymerization activator. The effect of changing the synthesis parameters (the molar ratio between MMA and AAm and the initial concentration of monomers, C_o) on swelling kinetics and state of water was evaluated. It was found that both initial monomer concentration and monomer ratio strongly influenced equilibrium swelling ratio, SR_{eq}. DSC analysis revealed that in all analyzed cryogels there are several metastable states of water due to the water being bound with different binding sites. The maximum amount of non-freezing water considerably varied with molar ratio of monomers and reaches The highest value of 1.269 was found for cryogels with MAA:AAm molar ratio equal with 70:30.

Acknowledgements: This work was supported by CNCSIS-UEFISCSU by the project PN-II-ID-PCE-2011-3-0300 and also by research fellowship within project "Enhancing Educational Potential of Nicolaus Copernicus University in the Disciplines of Mathematical and Natural Sciences" (project no. POKL.04.01.01-00-081/10.)

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4VP-14DMB POROUS MICROSPHERES AS HPLC PACKINGS

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Seed polymerization is one of the techniques which can be used for preparation of porous polymeric microspheres with uniform diameters (1). It starts with already polymerized particles, often referred as seed polymer or start polymer, characterized by the narrow particle size distribution. The start particles are dispersed in the reaction medium, new monomer and initiator are added so that the original particles grow into larger ones in the controlled process. Depending on the size of start polymer and its ability to absorb a new monomer, this technique produces particles in the diameter range 5 to 100 µm with a narrow size distribution. To obtain 4VP-14DMB microspheres, this technique have to be modified by adding the special type of surfactant.

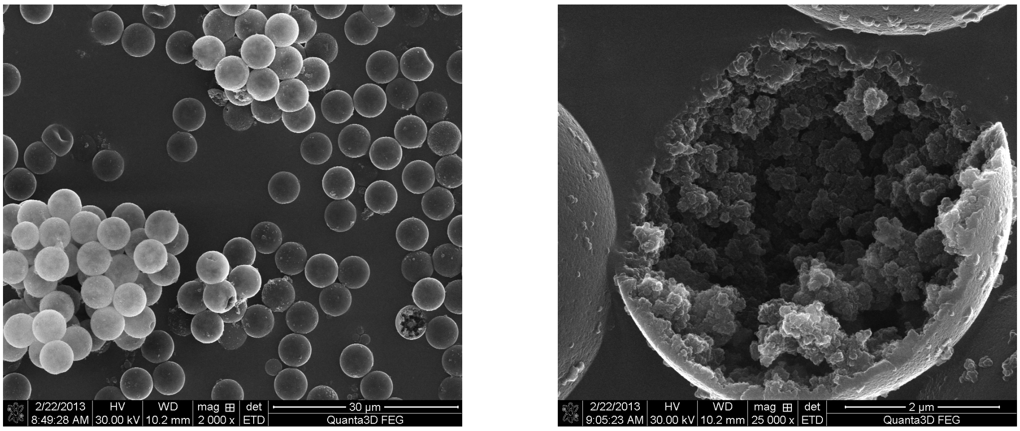

Fig. 1. SEM images of 4VP-14DMB particles

Our aim of this study was to obtain uniform polar polymeric microspheres of 4-vinylpyridine crosslinked with 1,4-dimethacryloiloxybenzene (14DMB) using seed polymerization and polystyrene beads as a core. Conventional polymerization procedure was modified since there were problems with dispersing of new crosslinking agent, 14DMB. By changing molar ratio of monomers and polymerization conditions we obtained 4VP-14DMB composite materials in the form of porous microspheres with diameters about 7 µm (Fig. 1). They were used as packing materials for HPLC. The Smith's method was used in selectivity studies. The retention indices of five homologous series and test compounds were calculated to determine the selectivity of the new composite packings. Prepared columns were tested in the determination of fungicides: carbendazim and thiophanate methyl.

Acknowledgements: This research was supported by National Science Centre of Poland (Grant No NN204354140).

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STUDY OF THE INFLUENCE OF TIME OF ADDITION OF COMPONENTS TO THE ADSORPTION SYSTEM ON THE ADSORPTION OF CARBOXYMETHYLCELLULOSE AND SELECTED SURFACTANTS ON THE ALUMINA SURFACE

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The influence of time of addition of components to the adsorption system (polymer/surfactant/electrolyte/alumina) on the adsorption of anionic polysaccharide carboxymethylcellulose (CMC) and the selected surfactants (anionic SDS and non-ionic TX-10) on the alumina surface (Al_2O_3) was studied. The background electrolyte was 0.01M NaCl. In the case of CMC adsorption, the components were added to the adsorption system in the four different ways a) only polymer b) polymer and surfactant simultaneously c) polymer first, surfactant added after 0.5 h d) polymer first, surfactant added after 4 h. In the case of surfactants adsorption the experiment was planned analogically: a) only surfactant b) surfactant and polymer simultaneously c) surfactant first, polymer added after 0.5 h c) surfactant first, polymer added after 4 h. The amount of CMC adsorption on Al_2O_3 as well as the amount of surfactant adsorption on alumina was measured using colorimetric methods (1-3) on spectrophotometer Cary 100, Varian.

The amount of CMC adsorption on Al_2O_3 is the lowest in the absence of surfactants and also the amount of surfactant adsorption is the lowest in the absence of polymer. When the second component is added simultaneously to the adsorption systems the adsorption of the first one increases, what is the evidence for formation of complexes between CMC and surfactants. The amount of adsorption of the first component is also higher when the second one is added to the adsorption system after some time (0.5 h or 4 h). The reason for that is a formation of a multilayer polymer-surfactant-polymer-surfactant. This process causes the increase of these components adsorption on the alumina surface. Moreover, in the case of SDS the amount of its adsorption depends on time of CMC addition but in the case of TX-100 there is not such dependence. This fact is the consequence of the setting up the adsorption equilibrium of these surfactants.

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THE STRUCTURE OF THE ELECTRIC DOUBLE LAYER IN THE SYSTEM: GUAR GUM/0.001M NaCl/MnO_2

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The adsorption of nonionic polysaccharide – guar gum (GG) on the surface of MnO_2 in the presence of 0.001M NaCl as the background electrolyte was measured at the pH range from 3 to 9. The amount of GG adsorption on MnO_2 was measured using colorimetric method: phenol-sulphuric acid (VI) described by Dubois et al. (1). The absorbance was measured at a wavelength of 490 nm using a spectrophotometer (Cary 100, Varian). Two other methods: potentiometric titration and the zeta potential measurements were used to analyse the structure of the created adsorption layer. The measurements were performed in the presence and absence of the GG macromolecules at the pH range from 3 to 9. The potentiometric titration was conducted automatically and a thermostated, teflon vessel with a shaker, an automatic burette (Dosimat 665, Methrom) and a pH-meter were the parts of the measurement set. The process was controlled by a computer. The electrophoretic mobility was measured using a zetameter (Zetasizer 3 000, Malvern Instruments) and then the zeta potential (ζ) was calculated from the Smoluchowski equation.

The obtained results show that the polymer easily adsorbs on the surface of the metal oxide and its adsorption is poorly influenced by pH changes. The reason for that is non-ionic character of this polymer, but the small differences obtained in these measurements result only from the changes of a kind and the concentration of the surface active groups from the metal oxide surface. The adsorption of guar gum on the MnO_2 surface does not influence the surface charge density in the whole measured pH range, which means that the charge of the compact part of the electric double layer does not change in the presence of this polymer. Also the shifting of the pH_{pzc} (point of zero charge) is not observed in the presence of guar gum. However, this adsorption of GG on the MnO_2 surface strongly influences the diffused part of the electric double layer. The decrease of the zeta potential obtained in the presence of this polymer is observed. The reason for that is the shift of the slipping plane towards the bulk solution. This shift is induced by the polymer adsorption. Another consequence of the changes in the slipping plane position is the shift of the pH_{iep} (isoelectric point) towards lower pH values.

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METHOD OF EXTRACTION OF ACTIVE SUBSTANCES FROM CABBAGE JUICE

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The research carried out concerned the opportunity and effectiveness of application of ionic resins for the selective sorption of heavy metals, organic pollutants and active substances from the cabbage juice and the elaboration of a method of desorption from these resins what was related to retrieval of sorbed substances, mainly active substances. The final effect of work was obtaining a biopreparation with fungicidal and germicidal properties containing active substances in the concentrated form.

It is the most favourable to apply strongly acidic cation resin IR120(H) to eliminate the heavy metals from the cabbage juice, strongly alkaline resin IRA-900(OH) to the organic pollutants and nonionic resin XAD16N to the sorption of the active substances. The examinations of sorption capacity of the resin appointed to the sorption of active substances proved that the sorption effectiveness was dependent on pH of solution dosed to a column and extent of solution clarity related to this. The best effect of the sorption of the active substances was observed at pH of 4.5-5, what was achieved by adding 1.25 mL of 20% lactic acid per 1 L of initial solution. After passing about 200 volumes of the cabbage juice per resin volume through the system of three columns filled with the selected resins, the presence of the active substances in the juice after the column was observed. After passing the juice through the column filled with IR 120(H) sorbing the heavy metals and the column filled with IRA900 (OH) sorbing the organic pollutants in amount of 200 volumes, there were no metals or organic pollutants present in the juice from the columns. It means that sorption capacity of the appointed resins is too big and concentration of the heavy metals and organic pollutants is small when comparing to concentration of the active substances.

The method of desorption for each selected resin was elaborated; it is the most advantageous to conduct desorption of strongly acidic cation resin IR120(H) with 4% hydrochloric acid in amount of 3 volumes as converted to the resin volume in the column. This is the most favourable to conduct desorption of strongly alkaline resin IRA-900(OH) with methanol in amount of 2 volumes as converted to the resin volume in the column, as well as to conduct desorption of nonionic resin XAD-16N with aliphatic alcohol C1-C3 in amount of 5 volumes converting to the resin volume in the column. In order to obtain aqueous solution of biopreparation in concentrated form, it is needed, after adding water, to distillate alcohol off at lowered pressure.

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SORPTION OF Cd(II)-MGDA COMPLEXES ON ACRYLIC ANION EXCHANGERS

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Cadmium is a metal which causes serious toxicological concern. An important source of human exposure to cadmium is food and water, especially for the population living near industrial centers, from which cadmium is emitted to the air (1). In natural water its typical concentration is below 0.001 mg/dm^3, whereas the upper limit recommended by the EPA (Environmental Protection Agency) is less than 0.003 mg/dm^3 (2). Cadmium modifies the metabolism of the elements necessary for the body, such as zinc, copper, iron, magnesium, calcium and selenium. It accumulates in kidneys, pancreas and glands. The main harmful effects in humans exposed to cadmium compounds are damage of the respiratory tract and kidneys. In humans exposed to fumes and dusts chronic toxicity of cadmium compounds is usually found after a few years (3).

Methylglycinediacetic acid (MGDA), patented by BASF and marketed under the brand name Trilon M, is a strong, readily biodegradable complexing agent. Its most important property is ability to form complexes with metal ions (calcium, magnesium, copper, lead, zinc, cadmium, mercury, manganese and iron) soluble in water in the large pH range 2-13, in the 1:1 molar ratio (4).

This paper deals with the development of the acrylic anion exchangers Amberlite IRA 458 and Amberlite IRA 958 that can remove cadmium(II) ions in the presence of methylglycinediacetic acid (MGDA) from water solution. A novel approach to these investigations is connected with the effect of the biodegradable chelating factor MGDA and the possibility of formation of anion complexes with ions. Owing to that these metals can be removed by means of numerous anion exchangers of various types. This method allows easy and effective purification of wastewaters from heavy metal ions without additional hazard for the environment.

The influence of initial concentration of Cd(II) and complexing agent, pH of the solution, phase contact time on the percentage uptake was determined in the batch experiments. The cadmium(II) concentration in the rafinate was determined by the AAS method.

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PREPARATION OF PECTIN-BASED BIOSORBENTS FOR CADMIUM AND LEAD IONS REMOVAL

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Biosorbents are commonly used in heavy metals removal. For this purpose dead microorganisms, algae, fungi or natural polyelectrolytes such as alginates and pectins are utilized. Recently, attention has been focused on byproducts or wastes of biological origin, which are characterized by their availability, high efficiency and low cost. Pectin as well as guar gum-based biosorbents are well known to be applicable for heavy metals ions removal. Various materials under various conditions have different metal ions uptake capacities and metal ion affinity (1-4).

The aim of this work was to prepare biosorbents containing both mentioned materials – guar gum immobilised by pectin gelled by calcium ions. This should increase the effectiveness of heavy metals ions sorption by extension of the optimal conditions range.

Amide pectin was kindly supplied by Zakłady Przemysłu Owocowo-Warzywnego "PEKTOWIN" S.A. w Jaśle. The polysaccharides were dissolved in deionized water and dropped into 1 M calcium chloride solution using peristaltic pump. Biosorbents were kept in 4ºC for at least 24 h and then were filtered and washed for complete removal of free calcium ions. Next, the obtained materials were dried at 35ºC.

Our studies showed that for guar gum immobilization, mixed guar gum-pectin solution should contain at least 3% of pectin. Obtained biosorbents of various composition (guar gum:pectin ratio) were then tested in batch studies for cadmium and lead ions sorption under various conditions.

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DECOMPOSITION OF ZIRCONIUM OXALATE – IMPORTANT STEP IN SEPARATION OF HAFNIUM FROM ZIRCONIUM ON DIPHONIX® RESIN

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Zirconium and hafnium are widely used in the nuclear industry. However, due to their opposing nuclear characteristics, reactor grade Zr must contain less than 100 ppm of Hf. This requirement is very tryingly attainable, as hafnium occurs in all zirconium ores and both elements are exceptionally difficult to separate due to their extremely close chemical properties. Complicated chemistry of their aqueous solutions causes additional problems in the separation.

In our previous work (1,2) we proposed a method for removal of hafnium from zirconium by ion exchange using Diphonix® resin. The hafnium content in zirconium decreased from 2.4% to 0.24%. After the separation, zirconium of increased hafnium content ("hafnium concentrate") is stripped from the resin using ammonium oxalate solution (3,4).

The aim of this work was to decompose zirconium (hafnium) oxalate complexes in order to obtain "hafnium concentrate" in the form suitable for further Hf/Zr separation by ion-exchange. There is no information concerning such decomposition in literature. The following possible methods of oxalate ions decomposition were employed:

- heating with mixture of sulfuric and nitric acid,
- heating with mixture of hydrochloric and nitric acid
- heating with acidified hydrogen peroxide solution,
- heating with ammonium persulfate,
- heating with sodium nitrite,
- passing the gaseous chlorine,
- passing the gaseous oxygen in acidic solution
- electrochemical oxidation

Only heating with ammonium persulfate was found to be applicable for oxalate ions removal. Obtained in this way solutions of zirconium (hafnium) in sulfate form were then investigated in column studies on Diphonix® resin.

Acknowledgements: This work was financed by Polish Ministry of Science and Higher Education, grant No. N N209 231838.

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MOLECULARLY IMPRINTED POLYMERS MODIFIED INSIDE THE ACTIVE CENTERS AS CATALYSTS FOR PHENOLS OXIDATION

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Among all enzymes oxidases, especially with copper ions inside the active centers, constitute one of the most important class of biocatalysts operating in chemical processes (e.x. industrial phenols oxidation) due to their ability of dioxygen activation during redox reactions and biological properties of resulting compounds. This unique property as well as other properties: remarkable regio- and stereoselectivity, high specificity and great reaction acceleration result from structure and peculiarities of their active centers. Most of them contain Cu(II) ions coordinating imidazole nitrogen from histidine ligands (His) - crucial in the electron transport during oxidation, oxygen from water molecules and sometimes sulfur from cysteine (Cys). It is well-known that apart from the structure of catalytic centers, important role in enzymatic reactions plays the environment resulted from other ligands situated near catalytic ones (1).

Our studies focus on the creation of synthetic equivalents of copper oxidases with particular catalytic ligands inside the active centers. To design and synthesize polymeric biomimics, molecular imprinting technique (MIT) was used. The main idea of this approach is formation of assembly of a crosslinked polymer matrix around templating moieties and after removal of the templates the creation of binding cavities complementary in functionality and shape to the original analyte (2). As a main functional monomer able to create Cu(II) active centres, 1-vinylimidazole (widely accepted as a histydyl ligand analogue) has been chosen. Obtained imprinted polymers were subsequently modified on imidazole ligands to introduce new ligands constituted ionic liquids analogues providing favourable environment for tested reactions of various aminophenols oxidation (3). The aim of these modifications was to combine the advantages of ionic liquids such as high polarity, reactivity towards transition metal ions and ability to work in two-phase systems with those of heterogeneous carriers of catalytic metal complexes (4).

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RECOVERY OF NOBLE METALS USING MICROWAVE-ASSISTED FUNCTIONALIZED RESINS

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Vinylbenzyl chloride/divinylbenzene copolymer has been functionalized with ethylenediamine by using microwave irradiation. The *Microwave - Enhanced Chemistry* is a young field of chemistry dating its origins to 1986 and includes the microwave-assisted organic synthesis and the microwave sample preparation technique (1). This environmentally friendly technology creates new opportunities in research, especially in the field of organic synthesis the microwaves caused a veritable revolution in increasing the rate of some reactions by several orders of magnitude (2).

The resulting resins has been characterized by FTIR, content of N and Cl, water regain and gold, platinum and palladium sorption capacity. Various parameters of modification like time, microwave power, choice of appropriate solvent have been studied. All microwave experiments were performed using microwave *Ertec Magnum Open* microwave reactor from ERTEC-POLAND (3) working in the open system at atmospheric pressure.

Tests were carried out using solvent like DMSO, DMF, NMP and mixtures of these solvents. The experiments were performed with output power regulated in the range of 0 - 400 W and a period of 5 to 20 minutes. Obtained resins showed amino groups content in the range 1.2 – 3.6 mmol/g. The best loading capacity of noble metals, 98%, from multicomponent solution of (Au + Pt + Pd + Cu + Fe + Ni) in 0.1 M HCl revealed resin 1 prepared in DMF solution.

The resulting ion exchangers offer opportunities for recovering of precious metals from dilute solutions.

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SYNTHESIS OF TEMPLATED POLYMER ADSORBENT USING STRUCTURED MODIFIED SILICA

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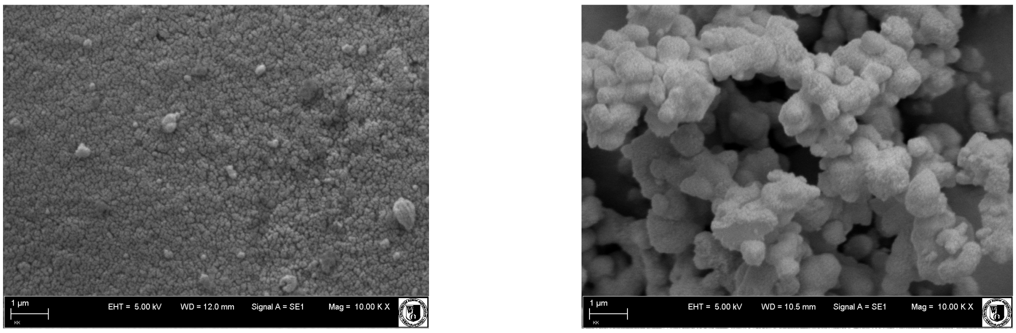
Template synthesis is well-known and commonly used tool in the synthesis of porous materials. In the case of polymers this procedure is based on synthesis of the template, polymerization and subsequent dissolution of template. This results in obtaining polymer network of interconnected pores with precisely defined size and shape coresponding to template structure, so that specific functionality can be imparted (1).

The aim of the work was to synthesize polymer adsorbent using modified structured silica as a template. Surface modification of silica offers numerous possibilities of value-adding property changes and it was recently reviewed (2). Due to large variety of possible subsequent reactions, most modifications are based on reaction between silanol group (Si-OH) on the silica surface and various silanes, such as (3-glycidyloxypropyl)trimethoxysilane. Obtained glycidyl ether easily reacts with amines, what is widely used in drug synthesis. In order to obtain appropriate silica template, strained oxirane ring was opened using isopropylamino-3-(1-naphthyloxy)-2-propanol and 1-(Isopropylamino)-3-[*p*-(β-methoxyethyl)phenoxy]-2-propanol. By using mesoporous materials: MCM-41 and MSU-F, which are characterized by uniform and regular arrangement of pores and channels widths, material properties such as pore volume and surface area were designed. Scanning electron microscopy images of silicas are presented in Figure 1. After performing polymerization the template was removed by dissolution in hydrofluoric acid.



a b

Fig. 1. SEM images of structured silicas: a - MCM-41, b - MSU-F

Due to designed structure, polymer materials prepared using modified silica template can be applied as useful sorbents for selective extraction of pharmaceuticals based on glycidyl ethers, such as β-blockers, especially propranolol and metoprolol.

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DOWEX M 4195 AND LEWATIT TP 220 IN HEAVY METAL IONS REMOVAL FROM ACIDIC STREAMS

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The major environmental problem of primary copper metallurgy is related with the emission of sulphur dioxide into air as well as wastewaters production during the metallurgical treatment of copper concentrates (1,2). Wastewaters from a copper refinery, or any electrolytic metal/acid refinery, are unique in that they contain large concentrations of acid that must be neutralized before metals are removed. Additionally, they contain large quantities of heavy metals such Cu(II), Ni(II), Co(II), Pb(II), Zn(II), Fe(III), etc. as well as arsenic, antimony, bismuth, and other hazardous substances.

Recently the ion exchange (IX) method has been successfully used for heavy metal ions removal from hydrometallurgical streams. To this aim the chelating resins with bis(2-pyridylmethyl)amine also known as the bispicolylamine functional groups are used. The most common examples are Dowex M 4195 and Lewatit TP 220. It was found that the sorption capacity of Dowex M 4195 for Ni(II) was equal to 2 mol/kg. Cu(II) and Ni(II) are effectively adsorbed on this resin even at very low pH while the adsorption of Al(III) is almost negligible. Therefore, the order of the selectivity of the metal ions was as follows: Cu(II) > Ni(II) > Co(II) > Zn(II) > Al(III). It was also proved that the series of affinity for metal ions determined from the one-component solutions for Dowex M-4195: Cu(II) > Ni(II) > Co(II) > Pb(II) > Fe(III) > Mn(II). Dowex M-4195 is characterized by maximal sorption capacity towards Cu(II) ions for pH in the range 1–4. Sorption effectiveness of Cu(II) ions is affected not only by pH but also concentration of sulfate ions and temperature. On a commercial scale DowexM4195 was used for removal of Ni(II) in the presence of Co(II) from sulphate solutions in the refinery INCO's Port Colborne in Canada.

The aim of the presented paper is to develop and optimize a simple and economical method to separate heavy metals from acidic streams in industrial and environmental operations using Dowex M 4195 and Lewatit TP 220 as well as detailed characterisation of these resins.

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ADSORPTION OF Cr (III,VI) FROM AQUEOUS SOLUTION ONTO FLY ASH COATED WITH CHITOSAN

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Fly ash is an environmental pollutant generated in a great amount during the combustion of coal for energy production. It is known as an efficient adsorbent for the heavy metal ions removal. The adsorption capacity of fly ash can be increased by both physical and chemical activation as well as modification. In this study fly ash was activated by high temperature and coated with chitosan powder (1,2).

Chitosan is a cationic aminopolysaccharide copolymer of N-acetylglucosamine prepared through the deacetylation of chitin. Chitin is one of the polymers which is produced from the waste of fishery industry. Chitosan is also known as an excellent adsorbent for metal. This is attributed to: high hydrophilicity (due to a large number of hydroxyl groups of glucose units and the presence of a large number of functional groups - acetamido, primary amino and/or hydroxyl groups), high chemical reactivity of these groups and flexible structure of the polymer chain.

In this study fly ash activated by high temperature and modified by chitosan powder was used in the adsorption process of chromium. The investigated parameters included contact time, initial concentration, sorbent dosage and temperature. The experimental equilibrium parameters were obtained by fitting the experimental data by the Langmuir and Freundlich models. The process kinetics was evaluated by the pseudo first-order, pseudo second-order and intraparticle diffusion models.

The results of these studies show that fly ash coated chitosan is an efficient adsorbent for chromium ions removal. The use of fly ash along with chitosan for removal metal ions from water can increase effectiveness, decrease costs and help of utilize some waste materials.

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ELECTROCHEMICAL PROPERTIES OF A ZWITTERIONIC ION-EXCHANGE MEMBRANE

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The electrochemical properties of a zwitterionic ion-exchange membrane (ion transport number and electric conductivity) were investigated in the aqueous solutions containing mono- and divalent ions (HCl, NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$) in a wide range of concentration (0-1.5 M). The membrane was obtained according to the procedure described in (1). It was formed from a poly(styrenesulfonic acid-*co*-4-vinylpyridine) copolymer which was crosslinked with 1,10-dibromodecane. The copolymer was synthesized using 4-styrenesulfonic acid sodium salt and 4-vinylpyridine through a free radical polymerization in a distilled water.

The electric conductivity was determined by the standard AC current method, the ion apparent transport number was determined from the emf measurements at room temperature. In the case of HCl solutions two pairs of electrodes were used – the SCE electrodes and the Ag|AgCl ones – to check the applicability of the SCE electrodes.

It was found that at low concentrations (≤ 0.1 M) the membrane conductivity in HCl solutions is ca. 1 order higher than that in NaCl and $MgCl_2$ solutions. At higher concentrations this discrepancy decreases which indicates that the proton mobility is more hampered than that of metal cations. The change of Cl^- for SO_4^{2-} substantially decreases the membrane conductivity in the presence of Mg^{2+}, whereas in the presence of Na^+ this effect is only seen at concentrations above 0.5 M.

The transport numbers of H^+ and Na^+ are close to one at low electrolyte (HCl, NaCl) concentrations which means that the cation-exchange character of membrane prevails. At 1-1.5 M these transport numbers significantly decrease, however still, are higher than those in a free solution. The transport number of Mg^{2+}, $t_{Mg2+,app}$, is only 0.57 in the membrane equilibrated with a dilute solution of $MgCl_2$ which means that the transport of divalent cations is substantially hampered compared to Cl^-. At high concentrations $t_{Mg2+,app}$ decreases to 0.24 ($< t_{Mg2+} = 0.41$ in a free solution) which shows the anion-exchange property of the membrane.

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HYBRID MATERIALS MODIFIED WITH IRON OXIDE NANOPARTICLES IN Cr(VI) IONS REMOVAL

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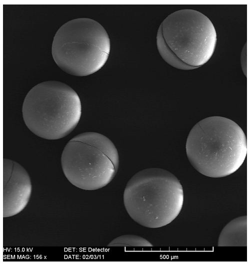
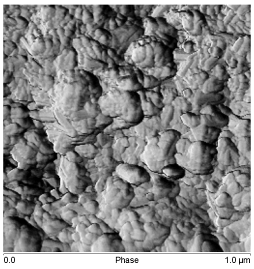
Development of industry causes formation of large amounts of wastewater which increases the natural environment contamination and high toxicity of heavy metal ions is particularly hazardous for human health and life. One kind of hazardous ions are Cr(VI) ions which must be removed from the natural environment due to their high toxicity. They get into the environment as a result of chromating, etching of various metals and as a by-product of electroplating. Large doses of Cr(VI) ions can cause tumorous diseases (1-2).

Lately, hybrid materials modified with nanoparticles of oxides or hydrated iron oxides, have become common for Cr(VI) ions removal. These are organic-inorganic materials prepared based on cation exchangers and anion exchangers. They are formed due to stable dispersion of molecules of oxides and hydrated metal oxides especially iron oxide in their internal structure. They are characterized by very good sorption properties, high selectivity, good hydraulic and magnetic properties as well as high mechanical and thermal strength (3).

The aim of the paper were the studies of Cr(VI) ions sorption on hybrid materials including nanoparticles of iron oxides in their structure. The studies were carried out using the static method with different phase contact time, Cr(VI) ions concentration, pH of initial solutions. The photos show the hybrid materials used for the studies by means of scanning electron microscope (SEM) and atomic force microscope (AFM).





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SEPARATION OF Ag^+ and Cu^{2+} BY POLYMER INCLUSION MEMBRANES WITH *N*-(DIETHYLTHIOPHOSPHORYL)-AZA[18]CROWN-6

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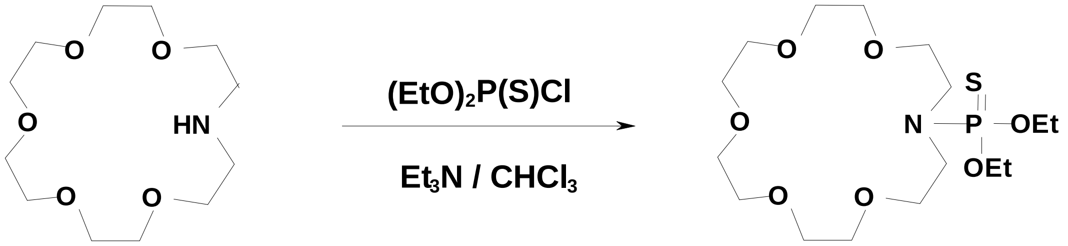
This work presents the synthesis functionalized monoaza crown ether i.e. *N*-(diethylthiophosphoryl)-aza[18]crown-6 and application as the ion carrier in competitive transport of Ag(I) and Cu(II) across polymer inclusion membranes with this lariat ether. The synthesis of thiophosphorylated aza[18]crown-6 was performed in good yield. These membranes with lariat have been successfully developed for selective transport of Ag(I) over Cu(II) from nitrate aqueous solution as feed phase into various receiving phases. The optimal PIMs content was as follows: 20 wt.% of cellulose triacetate as the support, 15 wt.% of the ionic carrier, and 65 wt.% of *o*-nitrophenyl pentyl ether as the plasticizer.



aza[18]crown-6 N-(diethylthiophosphoryl)-aza[18]crown-6

The lariat ether, *i.e.* N-(diethylthiophosphoryl)-aza[18]crown-6 used as ion carrier for competitive transport of silver(I) and copper(II) give preferential selectivity order: Ag(I) >> Cu(II) but with high recovery for lower pH values of aqueous solution. At 0.25 mol dm^{-3} concentration of N-(diethylthiophosphoryl)-aza[18]crown-6 (based on plasticizer and carrier) the ion carrier causes the polymer inclusion membrane saturation and the transport rate is maximal; the fluxes for Ag(I) and Cu(II) equal to 5.5 μmol m^{-2} s^{-1} and 0.2 μmol m^{-2} s^{-1}, respectively.

The stripping agent in the receiving phase plays an important role in removal of metal ions from the membrane phase. So, the influence of different stripping agent in the receiving phase on the transport of Ag(I) and Cu(II) using N-(diethylthiophosphoryl)-aza[18]crown-6 was studied. The experiments were performed under different types of stripping agents, *i.e*. nitric acid or sodium tiosulfate or EDTA in the concentration range 0.1-0.5 mol/L.

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RECOVERY OF ACETONE, BUTANOL AND ETHANOL FROM BINARY AND MULTICOMPONENT AQUEOUS MIXTURES

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Nowadays butanol, the main product of the bacteria fermentation process (so called ABE fermentation), is more often considered as a potential bio-fuel, because of its greater similarity to petrol (1). Currently, research focuses on improving ABE process, as well as on the application of alternative methods to ABE fermentation products recovery – hydrophobic pervaporation included (2, 3).

Pervaporation is a separation process of binary or multicomponent liquid mixtures. In pervaporation, separation of mixture is achieved thanks to the differences in the solubility of the components in the membrane and due to the differences in the diffusivity of these components through the membrane (4).

In our previous work it was found that pervaporation process conducted on PDMS membranes is an efficient technology for butanol recovery from fermented broth (5). In this work we will present results of pervaporative removal of acetone, butanol and ethanol from aqueous solutions (both quaternary and binary aqueous mixtures) by applying the PERVAP 4060 membrane. The effect of feed composition was investigated by using binary aqueous mixtures of acetone, butanol and ethanol, followed by experiments with quaternary ABE-water mixture. The hydrophobic pervaporation process was performed at 40ºC and 60ºC. It was found that investigated PDMS membrane exhibited higher selectivity towards butanol at temperature of 60ºC and higher selectivity towards acetone at temperature of 40ºC for the binary mixtures. Selectivity factor (α) ratios (A:B:E) at temperature 40ºC and 60ºC were 4.2:3.7:1.0 and 3.5:4.2:1.0, respectively. Additionally, the obtained results were compared with results achieved for Pervatech membrane (5) and other literature data (6).

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CHARACTERIZATION OF MODIFIED CERAMIC MEMBRANES BY PERFLUOROALKYLSILANES IN AIR-GAP MEMBRANE DISTILLATION AND PERVAPORATION

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Ceramic membranes can be prepared from metal oxides like alumina, zirconia, and titania. These materials originally possess a hydrophilic character due to the presence of surface hydroxyl (-OH) groups. The hydrophilic surface of the ceramic membrane can be modified by a grafting process. Such modification changes substantially the separation and transport properties of membranes. Perfluoroalkylsilanes (PFAS) are the group of compounds, which are efficiently used for the surface modification of ceramic membranes.

The aim of this work was to characterize hydrophobic grafted ceramic membranes in pervaporation process of aqueous binary mixtures (water-ethyl acetate/EtAc/) and in air-gap membrane distillation (AGMD) of sodium chloride aqua solutions. Titania (TiO_2) and zirconia (ZrO_2) membranes with MWCO of 5kDa were modified by grafting with $C_6F_{13}C_2H_4Si(OEt)_3$ (denoted as C6).

In both processes (PV and AGMD) the influence of membrane material on transport and selective properties was observed (Fig. 1). In PV, higher selectivities were observed for TiO_2 membrane, than for ZrO_2 one (Fig. 1A). In AGMD, titania membrane was characterized by better transport properties (Fig. 1.B1). On the other hand, slightly higher retention coefficient of NaCl was observed for ZrO_2 membrane (Fig. 1.B2). However, for both membranes retention coefficient of NaCl was high and close to 100%.

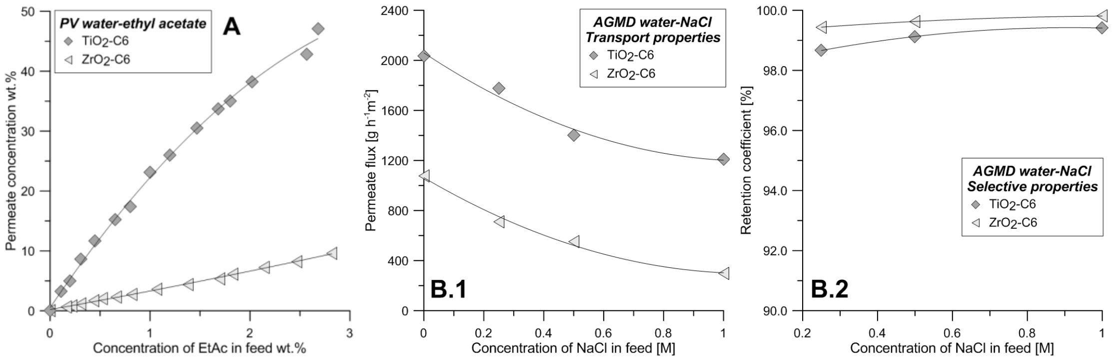

Fig. 1. Characterization of TiO_2 and ZrO_2 membranes in PV (A) and AGMD (B.1 and B.2)

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NITRIC OXIDE REMOVAL OVER CARBON SUPPORTED CATALYST

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In this paper the study of activity of carbon aerogels supported Fe, Cu and bimetallic Cu-Mn catalyst in the selective catalytic reduction of NO are presented.

The nitric oxides (NO_x) are one of the major and most harmful pollutants. There are many methods of reducing nitrogen oxides emission. Currently commonly used is selective catalytic reduction (SCR) with ammonia which uses vanadium and molybdenum or tungsten oxide supported on titanium oxide as a catalyst (1). Many other materials have been reported to be active for this reaction. One of them is catalyst supported on active carbon and carbon aerogels which are characterized by higher activity in lower temperature, than commonly used catalyst (2).

As supports resorcinol-formaldehyde spherical carbon aerogels (SCA) were used. Obtained results for Fe/SCA catalysts were compared with active carbon (WG 12) supported catalyst and monolithic catalyst prepared by co-gelation of resorcinol-formaldehyde sol with ferric acetylacetonate. Obtained results indicate that there is no essential influence of specific surface area and porosity on activity of tested catalyst. However presence of the micropores affects on sorptive properties of materials, which improves the efficiency of NO removal at relatively low temperatures.

All types of iron catalysts are characterized by high (above 80%) nitric oxide conversion at 100 ^{o}C, which in most cases decreases rapidly with temperature increase. The only exception is catalyst prepared on activated carbon with 5 wt % of iron loaded (5% Fe/AC).

In contrast, copper, manganese and mixed Cu-Mn catalysts show relatively high activity in the entire range of tested temperatures. These results allow to consider copper and manganese as an suitable active phase of catalysts supported on carbon aerogels which will be tested in the near future.

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STUDIES ON SYNTHESIS AND SORPTION PROPERTIES OF VP-DMN POROUS COPOLYMERS

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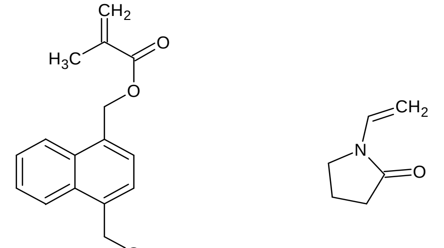
Sorption properties of porous materials depend on many factors such as porosity, impurity, chemical nature of the surface and adsorbate molecules. Among porous polymers synthesized in Department of Polymer Chemistry of Maria Curie-Skłodowska University one can find a huge diversity of porosities, functional monomers and crosslinkers. They are successfully used as packing in high performance liquid chromatography, solid phase extraction, gas chromatography and as specific sorbents in other fields. These applications are strongly connected with the internal structure and physico-chemical properties of the polymeric materials.

Herein, we present the synthesis, characterization of porous structure and sorption properties of copolymers 1-vinyl-2-pyrrolidone-*co*-di(methacryloxymethyl)naphthalene. They were obtained by suspension copolymerization in the form of microspheres. During the copolymerization the toluene was used as a pore-forming diluent. The structural characteristics of synthesized polymer sorbents were determined from the nitrogen adsorption/desorption isotherms. The adsorption data were used to evaluate the BET specific surface area and the total pore volume. The pore size distributions were obtained from desorption branches of isotherms using BJH method.



1,4-di(methacryloxymethyl) naphthalene

1-vinylo- 2-pyrrolidone

Fig. 1. Chemical structures of the monomers

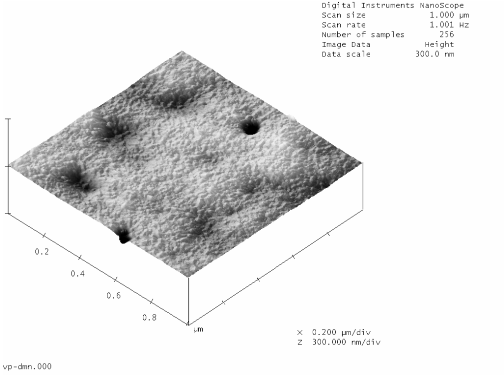


Fig. 2. AFM micrographs of the copolymer surface

The sorption properties of 1-vinyl-2-pyrrolidone-*co*-di(methacryloxymethyl)naphthalene copolymers were determined on the base of isotherms for *p*-chlorophenol sorption from dilute aqueous solution on the investigated copolymers. The influence of molar ratio of the used monomers on the parameters of porous structure and sorption properties was studied in details.

Acknowledgements: This work was supported by National Science Centre of Poland (Grant No NN 204354140).

SYNTHESIS AND CHARACTERIZATION OF MONOLITIHIC POLYMERIC SORBENTS

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One of the significant trends in modern chromatography is searching for new materials as adsorbents to improve the mass transfer, allow fast separation and provide column stability in the whole range of pH. The packing base on porous polymers can meet these requirements. Additionally, they provide a huge variety of functional groups available on the surface. Over the past years the major attention of scientists and producers was focused on particle-packed columns with smaller and smaller microspheres. Nowadays, porous polymeric monoliths become more popular. Comparing with particle-packed, monolithic columns possess several considerable advantages: the final product has the desired geometry and there is no waste; almost any material can be used including water soluble monomers that can not be used in suspension polymerisation and no tedious sieve and packing operations are required. Therefore, development of the monolithic columns with conventional analytical dimensions for the separation of small molecules is desirable.

Herein, we present the synthesis of porous monoliths based on 4-vinylpyridyne (4VP) and trimethylolpropane trimethacrylate (TRIM). They were synthesised directly in chromatographic columns of standard ID (4.6 mm). The formation of porous structure was controlled by adjusting the independent variables of the synthesis (temperature, pore-forming mixture and content of the crosslinking monomer). As a result monoliths well developed internal structures were obtained (Fig. 1). Their chromatographic properties were evaluated on the basis of the standards introduced by Smith (1).

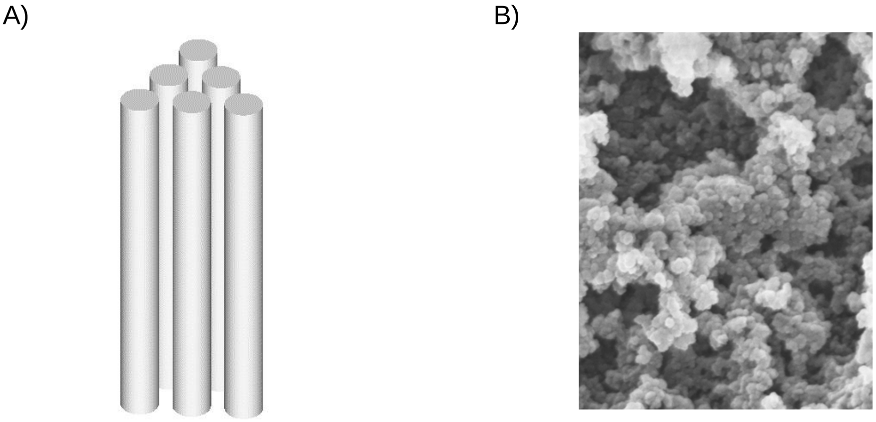

Fig. 1. 4VP-TRIM monolithic HPLC columns (A) and their internal structure (B)

Acknowledgements: This work was supported by National Science Centre of Poland (Grant No NN 204354140).

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DESALINATION OF 1,3-PROPANEDIOL BY ION EXCLUSION

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1,3-propanediol can be effectively produced from the waste glycerol by a fermentation process using e.g. *Clostridium butyricum*. Besides the main product (5.2%) the fermentation broth contained important amounts of carboxylic acids such as lactic acid (0.8%), acetic acid (0.3%), formic acid (0.07%) and succinic acid (0.03%). They were continuously neutralized with NaOH to maintain the desired pH level of 6-6.5.

Prior to desalination the raw fermentation broth was centrifuged and ultrafiltered in order to remove any microorganisms and crude particles. Then the little hazy solution was coagulated at 60ºC by $Al_2(SO_4)_3$ in the amount of 5 g/L. Almost all the organic acids were put into sediment, whereas the salt content (mostly Na_2SO_4) increased to 1.8%.

Ion exclusion was performed on the strong cation exchanger in sodium form at elevated temperature of 60ºC, at moderate flow rate of 2 h^{-1} and bed loading of 0.35V_B. As a result, three elution fractions can be separated: waste salt with only small product lost, cross-contaminated recycle, and strongly desalinated product solution (Fig. 1).

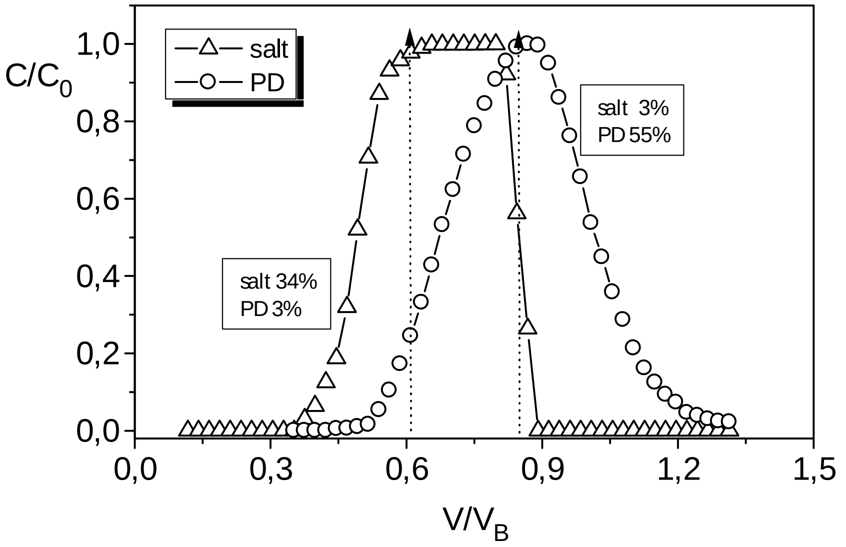

Fig. 1. Separation of 1,3-propanediol (5.2%) and salt (Na_2SO_4, 1.8%) in ion exclusion process (AmberJet 1200Na, 60ºC, 0.35V_B, 2 h^{-1})

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TRANSPORT OF SELECTED BORON SPECIES ACROSS RO MEMBRANES

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Removal of boron from waters meets serious limitation as the result of high rate of boric acid transport across reverse osmosis (RO) membranes. To mitigate the above, methods that involve boric acid conversion into monoborate or borate complexes are proposed (1-3). In this work the effectiveness of transport of boric acid, monoborate and dichelate complex with D-mannitol across selected reverse osmosis membranes was examined. The effect of membrane type on permeability (P) and reflection coefficient (σ) was presented in Table 1. It was observed that the membranes applied differ the most in the effectiveness of transport of H_3BO_3: dense BW-30 and SW-30 membranes reflects H_3BO_3 to a much greater extent than TW-30 and XLE. In addition, since SW-30 membrane indicate the lowest H_3BO_3 permeability, its superiority in boron rejection regardless of its concentration and permeate flux can be understood. On the other hand BW-30 membrane boric acid permeability was considerably larger that of other membranes. Such a behaviour of BW-30 suggests considerably high diffusive flux of boric acid, however, accompanied by good reflection properties. Therefore BW-30 membrane should be the most effective in boron rejection when operated at high permeate flux and low boric acid concentration. Similar trends were observed in the case of monoborate and dichelate complex.

Table 1. H_3BO_3, $[B(OH)_4^-]$ and dichelate complex with D-mannitol transport coefficients

Species	Membrane	$P \cdot 10^{10}$, m/s	σ
Boric acid, H_3BO_3	TW-30 (Filmtec)	22000 ± 5000	0,689 ± 0,008
	XLE (Filmtec)	15000 ± 2000	0,516 ± 0,002
	BW-30 (Filmtec)	31000 ± 9000	0,892 ± 0,004
	SW-30 (Filmtec)	11000 ± 4000	0,944 ± 0,004
Monoborate, $[B(OH)_4^-]$	TW-30 (Filmtec)	360 ± 40	0,9956 ± 0,0005
	XLE (Filmtec)	280 ± 30	0,9960 ± 0,0007
	BW-30 (Filmtec)	340 ± 70	0,9977 ± 0,0004
	SW-30 (Filmtec)	180 ± 50	0,9985 ± 0,0004
Dichelate complex	TW-30 (Filmtec)	18 ± 4	0.9995 ± 0.0003
	XLE (Filmtec)	17 ± 2	0.9992 ± 0.0002
	BW-30 (Filmtec)	20 ± 2	0.9995 ± 0.0004
	SW-30 (Filmtec)	14 ± 5	0.9997 ± 0.0002

Acknowledgements: This work was financially supported by Polish Ministry of Science and Higher Education grant No.N523 560 138 during 2010 – 2013 period.

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CONCENTRATION DISTRIBUTION ALONG THE ELECTRODIALYZER

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In order to assess the ion-exchange membranes scaling risk during electrodialytic desalination, the method linking crystallization kinetics and hydrodynamic conditions can be used (1). This method requires that a concentration distribution along the membrane is known. During the electrodialysis of aqueous solutions, water flux across the ion-exchange membranes, caused by osmosis, electroosmosis and hydraulic pumping, can be observed. In a single-pass electrodialysis this causes a distribution of linear flow velocities along the membrane, an phenomenon confirmed by residence time distribution experiments on a working electrodialyzer (2), which also have shown that linear flow velocity along the concentrate compartment does not increase linearly. Thus, a non-linear concentration distribution along the electrodialyzer might be expected.

The electrodialytic desalination of a model sodium chloride solution was performed using a plate-and-frame electrodialyzer of effective membrane length 42 cm, having an intermembrane distance of 0.26 mm and four membrane pairs. The electrodialyzer worked in a single-pass mode, with diluate and concentrate in a counter-current arrangement. The linear flow velocities were in the range of 0.38-0.70 cm/s (concentrate) and 2.11-3.37 cm/s (diluate), current density varied from 0 to 722 A/m^2. Segmented electrode allowed to observe a quadratic current density distribution, as presented in the literature (3). The observed changes in linear flow velocities and outlet concentrations allowed the establishment of an electrodialysis model, showing the flow velocity and concentration distribution along the membrane in the concentrate and diluate compartments.

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MOLECULARLY IMPRINTED POLYMERS FOR SELECTIVE RECOGNITION OF BISPHENOL A AND ALKYLPHENOLS

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Molecularly imprinted polymers (MIP) are a class of selective materials which show ability to recognize only particles of target compound or its closely related analogues. These polymers are obtain during copolymerization of precisely chosen functional monomers and cross-linking agents and process is carried out in the presence of template molecule. Artificially generated three-dimensional cavities which are complementary in size, shape and functionality to defined compound allow to bind solely target analytes.

MIPs demonstrate high thermal and chemical stability (resistance to acids, bases and organic solvents). Moreover, these selective materials have other various advantages, such as ease of preparation, low cost and possibility of long-term of storage without loss of their properties. All these attributes make that molecularly imprinted polymers are attractive and notable in many fields of application.

The aim of this research is the use of molecularly imprinted polymers for selective recognition of bisphenol A and selected alkylphenols (2-phenylphenol, 4-*tert*-octylphenol, *n*-nonylphenol). MIPs were prepared by non-covalent approach using bisphenol A as template, ethylene glycol dimethacrylate as cross-linking agent and 1,1’-azobis(cyclohexanecarbonitrile) as radical initiator. Various type of functional monomers (methacrylic acid, 4-vinylpirydine, acrylamide) and porogenic solvent (acetonitrile, chloroform, toluene, dichloromethane) were checked to obtain polymers, which showed high recovery values of analytes and good selectivity factor. The resulting molecularly imprinted materials were applied as sorbents in solid phase extraction for isolation and preconcentration of phenolic compounds from water samples.

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REMOVAL OF COBALT(II) BY MICELLAR–ENHANCED ULTRAFILTRATION

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Liquid radioactive waste containing ions of heavy metals have a huge attention because of the significant threat they pose to the environment and to human health. Heavy metals (such as cobalt) are not biodegradable. Accumulated in organisms can cause acute or chronic toxicity and therefore should be eliminated from the environment. Both low- and intermediate-level radioactive waste coming from nuclear power need to be processed. There are several methods for treating wastewater containing heavy metals and radionuclides, for example: chemical precipitation, adsorption, ion exchange, and distillation. However, they have several disadvantages, such as: the generation of secondary waste and high-energy requirements.

Micellar-enhanced ultrafiltration (MEUF) process is one of the promising methods of separating substances from the wastewaters. Advantages of MEUF are high removal efficiency, low energy consumption and good performance resulting from high fluxes (1). MEUF employs ultrafiltration membrane and anionic surfactant, e.g. sodium dodecyl sulfate (SDS), which act in synergy. The process exploits the ability to carry out hydrophobic substances, sparingly soluble or non-water-soluble solution by the introduction of a surfactant (at a concentration exceeding the Critical Micelle Concentration) or by electrostatic interactions between the charged micelle and a separated metal ion. CMC is explained as concentration of surfactants, which micelles starts to form spontaneous and it is one of the most important physical parameters of surfactants (2).

Efficiency of MEUF process applied for cobalt removal depends on various factors, such as concentration of surfactant, pH of solutions, membrane type and its characteristics. Efficient removal of Co^{2+} from wastewater was performed by MEUF using a regenerated cellulose ultrafiltration membrane, with sodium dodecyl sulfate (SDS) as the surfactant. The ability of surfactant micelles to bind Co^{2+} ions in MEUF was studied by changing the surfactant concentration in the feed.

Preliminary results indicate that with increasing concentration of the surfactant increases the membrane retention of cobalt. Rejection coefficients in the range of 65-80% were achieved when the concentration of surfactant was above 8 mM. The attempts of separating cobalt ions by MEUF in boric acid environment were done.

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SEPARATION AND RECOVERY OF RARE EARTH METALS BY USING SOLVENT IMPREGNATED RESIN COATED BY CROSSLINKED CHITOSAN

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Solvent impregnated resin (SIR) has been developed to apply extractant for solvent extraction to ion exchange process. One disadvantage of SIR is that the reuse of SIR is limited because of leakage of the extractant impregnated. In the present work, SIR of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) coated with chitosan crosslinked by glutaraldehyde (GA) was prepared for investigating separation and recovery of Eu/Y from phosphor material.

Figure 1 shows the effect of pH on the adsorption of Eu and the leakage of the extractant. The adsorption of Eu is dependent on pH value in all cases, indicating the adsorption mechanism is cation exchange. In the case of the uncoated SIR, since the leakage of the extractant during batchwise operation is ca. 3 %, the coated SIR can be suppressed by coating with chitosan. The leakage of the extractant is decreased by increasing chitosan concentration, while the kinetics of the adsorption is decreased. Coating with 3 wt.% chitosan is therefore suitable.

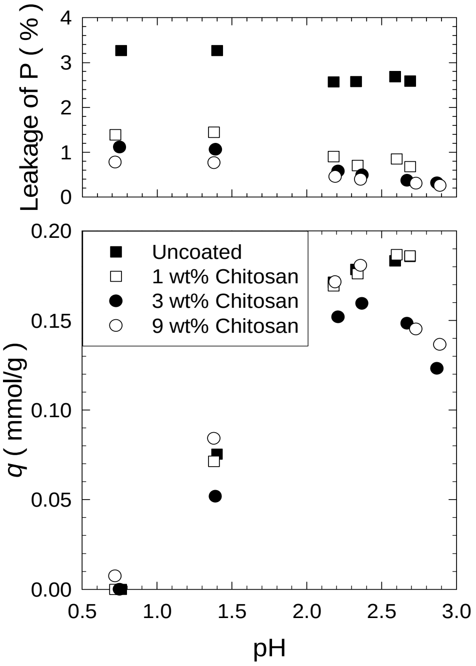

Fig. 1. Effect of pH on the adsorption of Eu(III) and the leakage of the extractant

The coated SIR is then applied for the separation of Eu/Y by chromatographic operation. Separation of the metals is difficult with the frontal separation mode. Developing column is therefore connected to the column adsorbed with the metals, and elution mode is applied for the separation of the metals. In addition, concentration of the eluent is gradually increased to improve the separation. Figure 2 shows elution curves of Eu and Y with gradient elution mode using SIR coated with 3 wt.% chitosan. The separation of the metals can be completely achieved, although elution curve of Y is split due to the disturbance of laminar flow at the connection of the columns.

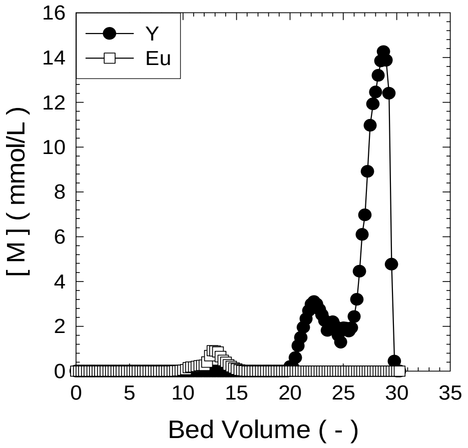

Fig. 2. Elution curves of Eu and Y from the coated SIR with gradient elution mode.

SELECTIVE TRANSPORT OF TOXIC METAL IONS ACROSS PLASTICIZER MEMBRANES WITH *p*-TOLYL-AZOCALIXPYRIDINE

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Azocalixpyridines are a class of pirydyne macrocycles with ability to recognize and discriminate among metal ions, what makes them suitable as specific receptors. The incorporation of azocalix[4]arene agents such as *p*-tolyl derivatives into PIM membranes have been used to test their transport ability towards transition metal cations.

The polymer inclusion membranes (PIMs) were prepared by physical immobilization the *p*-tolyl-azocalix[3]pyridine (**1**) and *p*-tolyl-azocalix[4]pyridine (**2**) into cellulose triacetate containing plasticizer (*o*-nitrophenyl octyl ether) as solvent. Transport experiments were carried out in permeation cell in which the membrane was tightly clamped between two compartments. The aqueous source phase containing 0.0005 mol/dm^3 $Pb(NO_3)$, $AgNO_3$ and $Cu(NO_3)_2$ as well as chloride complexes Cd(II) and Zn(II) in acidic aqueous solutions; the receiving phase were sodium tiosulphate, sodium acetate or ethylenediaminetetraacetic acid solutions.

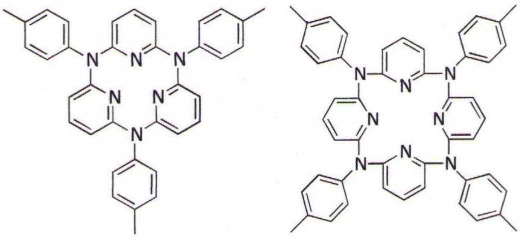

Fig. 1. Structures of (**1**) and (**2**)

Competitive transport of Zn(II) and Cd(II) from acidic aqueous chloride solutions (source phase), through PIMs, with **1** and **2** as ion carriers into 0.10 M aqueous $CH_3COONa(NH_4)$ or $Na_2S_2O_3$ (receiving phases) was studied. It was found that the Cd(II) fluxes are higher for PIM with **1** transport that for PIM with **2** transport. However, the separation coefficients are higher for PIM transport into CH_3COONa. The fluxes are higher for **1** than for **2** as the ion carrier and were equaled for Cd(II) and Zn(II) 4.1 µmol/m^{2}s and 0.9 µmol/m^{2}s, respectively. We found also that the transport of Ag(I), Pb(II) and Cu(II) across PIM with **2** via carrier mediated mechanism depends on size-**fit** concept in the complexation of metal ions with azocalixpyridine as driving force processes. The competitive transport of Ag(I), Pb(II) and Cu(II) from aqueous phases across PIM is an effective method for silver(I) separation. The affinities of the metal complexes investigated for **2** follows the selectivity order: Ag(I) > Cu(II)>> Pb(II).

AVAILABILITY OF MICROREACTOR EXTRACTION SYSTEM INCORPORATING CALIXARENE DERIVATIVES FOR RARE METAL SEPARATION

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Calix[4]arene derivatives provide rigid structure for unique and specific metal selectivity, whereas there are some drawbacks to use them as extraction reagents such as poor lipophilicity, slow extraction rate, and so on. Microreactor exhibits some advantages in using extraction system such as easy fluid operation, economically effective micro process, large interfacial area for rapid extraction. In the present work, silver and divalent palladium extraction with ketonic and 2-pyridyl derivatives of *p*-t-octylcalix[4]arene by using microreactor system is reported together with that in batchwise extraction system.

Both extraction reagents were prepared in similar manner as described in the previous papers (1,2). The microreactor was fabricated in Pyrex glass and silicon plates using micromachining process followed by bonding each other irreversibly. The silicon microchannel surface for organic phase was coated with Ti using vapor deposition, and then coated with Au. The Au surface was chemically modified using octadecanethiol in ethanol. The surfaces of glass and silicon sides for microchannel are hydrophilic and hydrophobic, respectively. Therefore, aqueous solution was flowed through the glass side of the microchannel, while organic solution was through the silicon one.

Effect of reaction time on silver extraction of with tetraketonic derivative by using microreactor system is shown in Fig. 1. In the microreactor system, the equilibrium was reached after 15 s and the %extraction of silver ion was about 80%, while it was reached after 72 h with 80% in batchwise system. The extraction rate was significantly improved by using this micro system due to the increased liquid-liquid interface area.

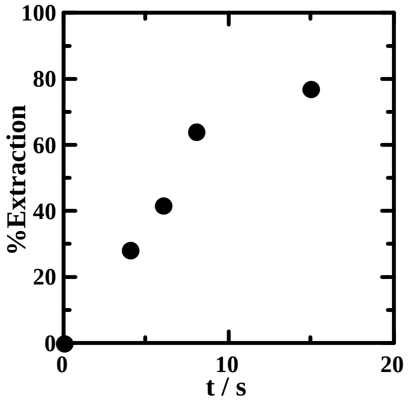

Fig. 1. Effect of reaction time on %extraction of silver with tetraketonic derivative by using microreactor system

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REMOVAL OF Hg(II) IONS FROM AQUEOUS SOLUTION BY QUATERNARY p(4VP)-g-CHITIN BEADS

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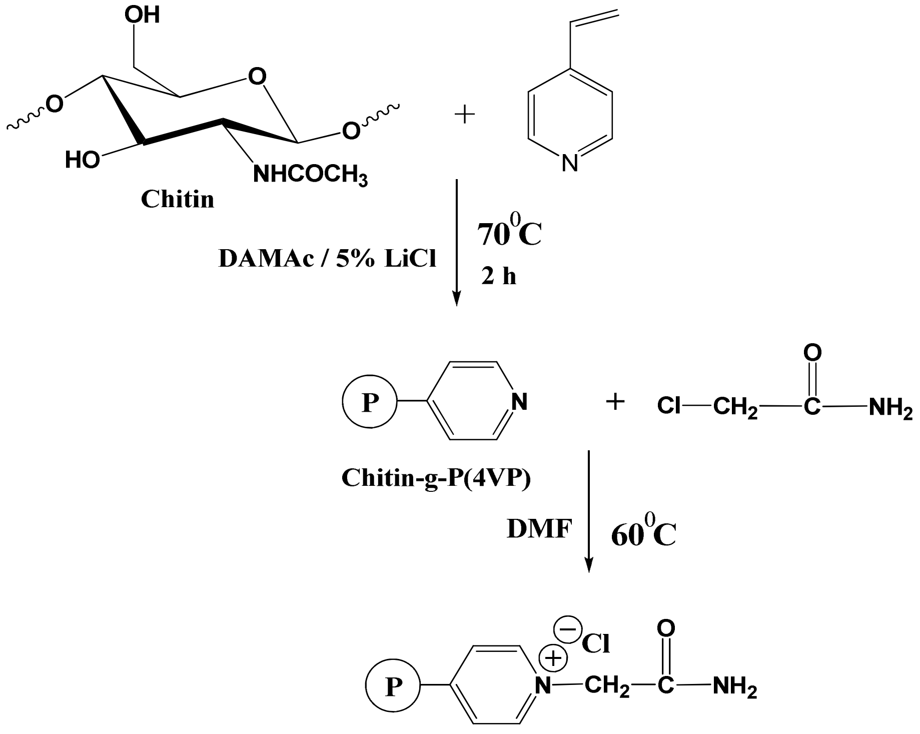
Among heavy metals such as cadmium, cobalt, chromium, copper, lead, mercury, nickel and zinc which are highly toxic and dangerous, mercury deserves special attention. Therefore, removal of mercury from aqueous solution especially drinking water but also in hydrometallurgical and waste water treatment (1) is very important. Chitin-DMAc 5% LiCl solution is well known as capable of forming uniform beads upon the addition of non-solvent ethanol. The grafting reaction was carried out in homogeneous conditions using potassium persulphate ($K_2S_2O_8$) as the initiator. The effect of monomer concentration on the extent of grafting (% G) was studied. Values of grafting percentages up to 226% were reached under homogenous condition. The grafting was confirmed by FTIR. The grafted chitin beads were quaternized in the presence of chloroacetamide in DMF. The quaternization reaction was characterized by FTIR. The mercury adsorption capacity of quaternized chitin-g-(poly(4-vinylpyridine)) was determined as 2.67 mmol g^{-1}.



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SOLVENT EXTRACTION OF COPPER(II) IONS FROM CHLORIDE SOLUTIONS BY PYRIDYLKETOXIMES WITH BRANCHED ALKYL CHAIN

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Hydrophobic pyridylketoximes have been proposed as extractants in liquid-liquid extraction of Cu(II), Cd(II), Fe(III) and Zn(II) ions from chloride, ammonium chloride and sulphate, sulphate/chloride solutions (1-3).

The aim of the work was to study the extraction of copper(II) ions from chloride solutions by the hydrophobic 2- and 3-pyridylketoximes containing 2-ethylhexyl chain. The extraction studies were carried out at constant pH of 3.8, water activity $a_w = 0.835$ and at ionic strength $I = 4$ M. Also, the influence of ligand, chloride and copper(II) ions concentrations on the metal extraction were studied.

The obtained results showed that the 3-ethyl-1-(2-pyridyl)heptan-1-one oxime removed all copper(II) ions from solution and the extraction did not depend on concentration of chloride ions. In case of the 3-ethyl-1-(3-pyridyl)heptan-1-one oxime the extraction increased with the increase of chloride ions concentration and the effect was mainly observed for the aqueous solutions containing below 2 M Cl^-. With the increase of metal ions concentration in the aqueous phase the copper extraction by 2-pyridylketoxime increased, however, the concentration of copper(II) ions above 0.08 M caused the precipitation of the complexes. After extraction with the 2-pyridylketoxime, copper can be stripped with 10% solution of ammonia or sodium oxalic solution with 0.2% addition of mineral acid. After extraction with the 3-pyridylketoxime copper(II) ions were effectively stripped from the loaded organic phase with by water or 0.2% aqueous solution of HCl.

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SEPARATION PROPERTIES OF SORBENTS BASED ON LIMESTONE

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Currently, limestone, mainly after the treatment, is widely used in several industry branches (e.g. constructions, lime, cement, chemical, sugar and power industry, as a sorbent in flue gas desulfurization process) (1). Limestone as the calcium carbonate is used in the iron and steel industry, as a fluxing agent for the manufacture of glass and in agriculture, as a fertilizer. Its main application is role of sorbent in flue gas desulfurization process (2).

High-temperature absorption of sulfur dioxide by limestone is one of the examples of a gas–solid reaction which is industrial relevant. In practice, the gas–solid reaction yield usually does not reach the maximum value. Possibility of increasing the sorption and separation capacity of the calcium based sorbents against sulfur oxides are the subject of many studies, especially in terms of minimizing the amount of limestone required to achieve a high degree of desulfurization of gases. Main goal would be to reduce the amount of waste during the fluidized bed combustion of coal. Sorption and separation properties of limestone can be changed using physical and chemical methods. The methods consist mainly in the physical sorbent precalcination to obtain the appropriate porosity and by chemical means to use additives, for example NaCl and/or catalysts for oxidation of SO_2 to SO_3 (3).

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NEW ION EXCHANGERS BASED ON MACROPOROUS COPOLYMERS: 2,3-(2-HYDROXY-3-METHACRYLOYLOXYPROPOXY)NAPHTHALENE/STYRENE

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The toxicity of heavy metal ions consists in an inhibiting effect on the enzymatic processes by binding to the thiol groups of proteins and enzymes. Their accumulation over time in the organism is very dangerous. For this reason, purification of the environment from toxic metals is an important topic (1-3). To this aim the chelating ion exchangers are often used. Among them those with thiols, dithiocarbamate, dithiozone or thiosemicarbazide are often applied. Thiols are able to react with some heavy metals such as mercury. The affinity of mercury for thiolate ions is so important that a preferential binding between different species in competition is possible.

In this paper crosslinked and macroporous 2,3-(2-hydroxy-3-methacryloyloxypropoxy)naphthalene / styrene (2,3-NAF.DM-ST) microspheres are presented. The copolymer was obtained by the emulsion-suspension polymerisation at constant mole ratio of tetrafunctional monomer : styrene (1:1 w/w) and constant volume ratio of pore-forming diluents (toluene : dekan-1-ol) (4). In order to introduce thiol (–SH), methylenethiol (-CH_2SH) and sulfonyl hydroxide (-SO_2OH) groups on the surface of the microspheres, the multistage modification was carried out. Different types of modifications will be applied.

The course of the modification was controlled by elemental analysis and the spectroscopic method. The sulfur group concentration, thermal properties (thermogravimetric analysis), FTIR as well as the swelling characteristics of the functional microspheres were examined. The porous structures of the obtained copolymers in dry (from the nitrogen adsorption-desorption measurements) state was investigated. Additionally, the surface texture was visualised by the AFM method.

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SORPTION OF PHENOLIC COMPOUNDS ON NEW DIMETHACRYLATE BASED COPOLYMERS

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Three new copolymers and products of their sulphonation were studied as adsorbents for off-line preconcentration of phenol and its chlorinated derivatives. The copolymers were synthesized using suspension-emulsion polymerization method. As comonomers: styrene (St), divinylbenzene (DVB), bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]sulphide (BES.DM) and 2,2-[4,4'-di(2-2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (Epidiane 5DM) were used. Detailed procedure of synthesis of the BES.DM and their copolymerization were described previously (1). Prepared materials possessed different parameters of porous structure. Their specific surface areas and total pore volume were in the range of 1 to 50 m^2/g and 0.004-0.320 mL/g, respectively.

Mixture of phenol, 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol was used to evaluate sorption ability of the polymeric materials as adsorbents in SPE method. The phenols showed differentiated affinity towards the studied polymers.

The most efficient adsorbent was Epidiane 5DM-DVB. This polymer, despite the lowest surface area (~1 m^2/g), reached the highest breakthrough volume (700 mL of the sample solution). Recoveries of 2,4,6-trichlorophenol were on high level (~100 %) even for large volumes of the sample solution (600 mL). It means, that interactions of 2,4,6-TCHP with the polymer surface were very strong. Interactions of the other phenols were weaker.

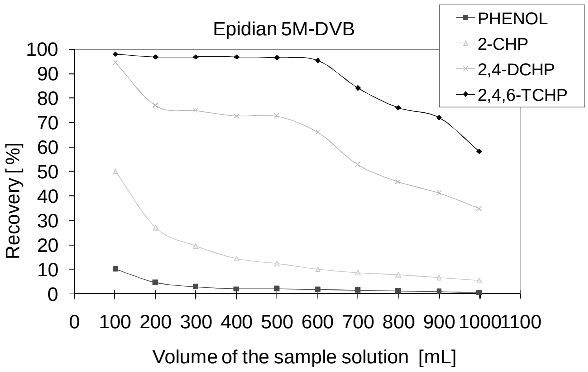

Fig. 1. Breakthrough curves of the phenols for Epidiane 5DM-DVB copolymer

Therefore, their molecules (especially phenol) were removed by 2,4,6-TCHP from the surface of the polymer and for this reason the values of recovery and breakthrough volumes for these compounds were on lower level.

After sulphonation chemical character of the polymers changed for more acidic. In all cases, sorption of the phenolic compounds decreased. That was caused by: 1 - repulsive interactions between sulphonic groups on the polymer surface and hydroxyl groups of the phenols; 2 - decreased porous structure parameters of the polymers after sulphonation process, 3 - changes in dissociation process of phenols.

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HETEROGENEITY OF CARBON NANOTUBES IN ADSORPTION OF MONOCYCLIC AND POLYCYCLIC AROMATIC COMPOUNDS FROM AQUEOUS SOLUTIONS

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The theoretical description of the phenol, 1-naphthol and 1-naphthylamine adsorption from aqueous solutions on original and oxidized multiwalled carbon nanotubes (MWCNTs) has been presented. The oxidation process most often applied to enhance the hydrophilicity introduces further oxygen-containing functional groups, particularly acidic in nature, such as carboxylic, lactones or phenols. Moreover, the accessible traces of the metal catalyst and the amorphous carbon are practically removed. All these reactions may lead to morphological changes of nanotubes. The MWCNTs form aggregated structures. Aggregation of MWCNTs creates additional energetically different adsorption sites. For MWCNTs adsorption can occur: 1) on the external surface of the nanotubes, 2) in the interstitial channels between nanotubes, 3) in the hollow space inside nanotubes, etc. The heterogeneity of MWCNTs is also associated with presence of different oxygen functional groups and impurities (traces of metal catalyst, amorphous carbon). The generalized form of the Dubinin-Astakhov and Langmuir-Freundlich isotherms have been applied to study the cooperative effect of the surface heterogeneity and the lateral interactions between the admolecules (1-4). Theoretical isosteric heats of adsorption connected with isotherm models have been calculated too. Knowledge of both adsorption equilibria and heats of adsorption is complementary for appropriate description of any adsorption process. Theoretical studies were completely reviewed using the literature experimental adsorption data (5).

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THE APPLICATION OF LAGERGREN PSEUDO-FIRST ORDER EQUATION TO STUDY THE BALANCE BETWEEN DIFFUSIONAL AND SURFACE REACTION KINETIC MODELS

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Over the last few decades, the wide application of adsorption phenomena in the chemical, environmental, and biotechnology industries can be observed. Purification and separation using adsorption processes is environmentally friendly and more economical than traditional methods. As the software - controlling apparatus should quickly respond to the changing process conditions, there is a need for analytical expressions describing equilibrium and rate of adsorption.

In the literature many theoretical models of adsorption kinetics can be found. They can be divided into two groups: one of them is based on the assumption that the rate of adsorption is controlled by the intraparticle diffusion and the other one describes the adsorption kinetics as the adsorption reactions occurring at the solid/liquid or solid/gas interface. But generally it is difficult to resolve the nature of kinetic process of a given adsorption system.

In the present work we showed that the well-known Lagergren pseudo-first order equation can still be helpful to answer whether surface reaction or diffusional mechanism is the rate-determining step. To estimate quantitative information of the time-dependence of the Lagergren parameter as a statistical tool the coefficient of variation can be used.

The balance between the surface reaction and the diffusional mechanisms is directly dependent on the surface energetic heterogeneity. The value of the dispersion of adsorption energy is the linear function of the Lagergren parameter. It can be stated that in the case of strongly energetically non-ideal adsorption systems, the rate of adsorption is controlled by the surface reaction mechanism. But it is true only when the transport of adsorbate molecules to the adsorption centers is fast enough. If such condition is not fulfilled, the rate of adsorption is determined by the slowest step of adsorption process.

STABILITY OF THREE-PHASE SOLID PARTICLE-WATER-OIL SYSTEM IN RELATION TO OIL AGGLOMERATION

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Oil agglomeration is a process usually used to recover or separate fine particles dispersed in water through the addition of a binder (oil), which form the bridges between particles (1). The process is dependent on many parameters, but the most important are surface properties of particles as well as physicochemical properties of immiscible liquid (2).

The particles to by agglomerated must be wet by oil, i.e. sufficiently hydrophobic. For hydrophilic particles it could be achieved through the use of surface-active agents. The ionic surfactant, which lowers the oil-water interfacial tension, facilitates emulsion preparation. The presence of surfactant can also affect the attachment of oil droplet to the particles and its spreading on the surface (3).

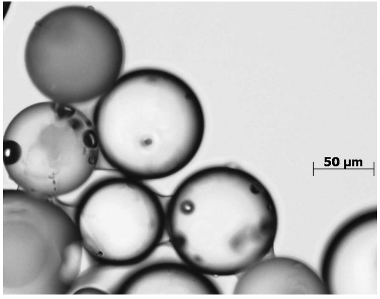

Fig. 4. Oil bridges between glass beads

The aim of this work was to investigate the stability of three-phase system where solid particles situated in the oil-in-water emulsion regarding the oil agglomeration process. The surface of model glass beads has been modified with ionic surfactant (cationic - dodecylammonium hydrochloride or cetyl-trimethylammonium bromide and anionic ones - sodium dodecylsulphate or sodium oleate). The ultrasound energy comparing mixing shear force where used to generate n-heptane-water emulsion. The stability of emulsions as well as the resulting mixtures was recorded using a Turbiscan La*b*Expert (Formulaction) apparatus, allowing detection of small changes in analysed probe by scanning a vial with the coherent beam. The transmission (T) and backscattering (BS) profiles were worked-up and the stability index (TSI) was calculated. Additionally, the zeta potential measurements of oil droplets as well as glass beads have been performed to indicate the role of modifying agents on the system stability and eventually the results of oil agglomeration process. The liquid bridges formed between particles (Fig. 1) were analysed by using a microscopic examination.

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SYNERGISTIC EXTRACTION AND TRANSPORT OF Cu(II) AND Zn(II) ACROSS POLYMER INCLUSION MEMBRANES USING CYANEX 921 AND ALIQUAT 336

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In this work separation of copper(II) and zinc(II) from aqueous chloride solutions by solvent extraction and transport across polymer inclusion membranes (PIMs) has been studied. Many industrial processes produce wastes containing heavy metals. Solvent extraction can be efficiently applied for recovery of non-ferrous metals from waste solutions and leach liquors using different extractants. Instead of using a single extractant, mixtures of extractants can give rise to synergistic effects and better selectivity of metal ions extraction from aqueous solutions. Synergism has been observed in the extraction of Cu(II) over Zn(II) using the mixtures of Alamine 336 and LIX 54 (1), Cyanex 301 and LIX 984N (2) and with the mixtures of solvating and chelating reagents (3). Recently, we observe growing interest in membrane processes for metal ions separation. Transport processes across PIMs are a good alternative to conventional solvent extraction due to their advantages such as high selectivity, operational simplicity, low solvent inventory, as well as combination of extraction and stripping into one single stage (4-6).

This paper will present the results for the synergistic extraction and transport of Zn(II) and Cu(II) from aqueous chloride solutions. Cyanex 921 (trioctylphosphine oxide) and mixture of Cyanex 921 and Aliquat 336 have been applied as the extractants/ion carriers in these separation processes. The extraction of Cu(II) and Zn(II) depends on the many different factors. The effects of pH, hydrochloric acid concentration and extractants concentration on the metal ions separation have been studied. Zn(II) ions was successfully separated from Cu(II) ions in solvent extraction process using 0.025 M TOPO with 3 vol.% Aliquat 336 at pH ~ 1. Cellulose triacetate (CTA) membranes containing the mixture of TOPO and Aliquat 336 as a carrier were prepared and their performance tested for the transport of Cu(II) and Zn(II) ions. The transport studies revealed that permeability of metal ions was dependent on membrane thickness, concentration of TOPO and Aliquat 336 and the presence of plasticizer, which plays significant role on the membrane physical properties.

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REMOVAL OF CHROMIUM(III) IONS FROM DILLUTED AQUEOUS SOLUTION BY ADSORPTION AND MEMBRANE PROCESSES

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In recent years, the advanced studies on the use of non-conventional separation techniques in the treatment of industrial effluents are carried out. There are works concerned with the process of adsorption on a natural sorbent and ultrafiltration enhanced by addition of micellar solutions (MEUF). These methods are promising for the purification of aqueous solutions of heavy metal ions of low concentration.

The paper presents results of our research on removal of chromium(III) ions from the model aqueous solutions using the MEUF technique and adsorption on a modified bark of willow *Salix americana*. Initial concentration of aqueous solution of Cr(III) was: 0.05 and 0.1 g/dm^3.

A laboratory-scale ultrafiltration system (SPIRLAB, Tami Industries) was used in the study. The ceramic membrane, which is a composite membrane consisting of a ceramic bracket α-Al_2O_3 (support layer) and a layer of active TiO_2 with the effective area equal to 0.64 dm^2 was used. Molecular resolution limit of the applied membranes (cut-off) was equal to 15 kDa. In the experiment two surfactants were considered: sodium dodecyl sulfate (SDS) and Rofam10 as a non-ionic surfactant which is a product of rape-seed oil fatty acids ethoxylation of the general formula $R\text{-}CO(OCH_2CH_2)_nOCH_3$ ($R = C_{12} – C_{24}$ is a fatty acid hydrocarbon chain and n =10 is a number of oxyethylene segments). Moreover, the mixtures of both surfactants in the different molar ratios were used.

The adsorption process was carried out on willow bark *Salix americana* coming from the Nowy Tomysl county. Bark was dried at 100ºC for 48 h. Then its portions were crushed into smaller fibers in a blender. Bark was used after sieving (fraction < 0.212 mm), which was stored in polyethylene containers in a desiccators. As modifier nitric acid(V), at a concentration equal to 5 or 15% was used.

Previous studies have shown that removal efficiency of chromium(III) ion in the MEUF as well as adsorption process is satisfactory, with retention equal to 90-95%. The degree of retention in the MEUF process depends on the type of surfactant used, while the process of adsorption on a modified willow bark *Salix americana* is affected by the modification time and concentration of the nitric acid(V).

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DETERMINATION OF THE PERCOLATION THRESHOLD FOR THE OXALIC, TARTARIC AND LACTIC ACIDS TRANSPORT THROUGH POLYMER INCLUSION MEMBRANES WITH 1-ALKYLIMIDAZOLES AS A CARRIER

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In recent years, there has been considerably increasing interest in biotechnological processes in which fermentation broths containing high-quality products can be obtained in a result. Main components of fermentation solutions are organic acids, such as an oxalic, tartaric and lactic acids. These acids are used extensively in food, pharmaceutical, cosmetic and textile industry (1-3). One of the possible ways of separating the desired products from fermentation solutions are membrane techniques exploiting the polymer inclusion membranes (PIM).

In the presented research the possibility of the transport of oxalic, tartaric and lactic acids by PIM containing 1-alkylimidazoles as a carrier was studied. The aim of the study was to determine the percolation threshold for the transport of analyzed organic acids by PIM.

In the Fig. 1 an example of the results obtained are shown. As it can be seen, below some limiting value the oxalic acid transport by the PIM does not occur. Further, at the value of 0.1 passing through a percolation threshold and the continuous increase of the flux can be observed. For each of the carried out process the percolation threshold and the maximum concentrations of the active compound in order to obtain optimal conditions for the transport of the organic acids were determined.

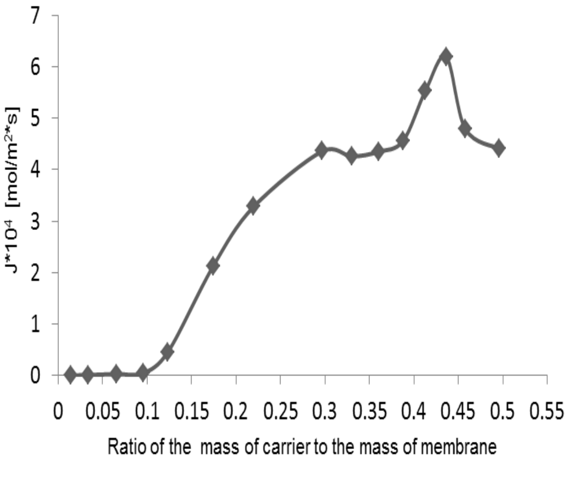

Fig. 1. Flux as a function of the mass of a carrier to the mass of membrane

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SEPARATION OF DICARBOXYLIC ACID USING NANOFILTRATION, BIPOLAR ELECTRODIALYSIS AND REACTIVE EXTRACTION OPERATIONS

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Organic acids are commonly used in food, pharmaceutical and chemical industries (1). Nowadays, they are mainly produced by microbial fermentation resulting in generation of fermentation broth containing organic salts and some impurities like sugars and mineral salts (2). In fact, many operations are necessary to separate and purify the final product (organic acid) from fermentation broth (3).

The aim of this study is the removal of a dicarboxylic acid from fermentation broth using procedure which consists of three operations: nanofiltration, bipolar electrodialysis and reactive extraction (Fig. 1). In the first step nanofiltration with tubular ceramic membranes to separate organic salts from by-product was investigated. Afterward, electrodialysis with bipolar membrane was used to concentrate and convert organic salts to their acidic forms. Moreover, reactive extraction with Cyanex 923 and Aliquat 336 as hydrophobic extractants was considered to recover fumaric acid remaining in nanofiltration permeate and in dializate from bipolar electrodialysis process. The presented studies have shown that application of the membrane techniques and reactive extraction enables effective separation of fumaric acid from fermentation broth.

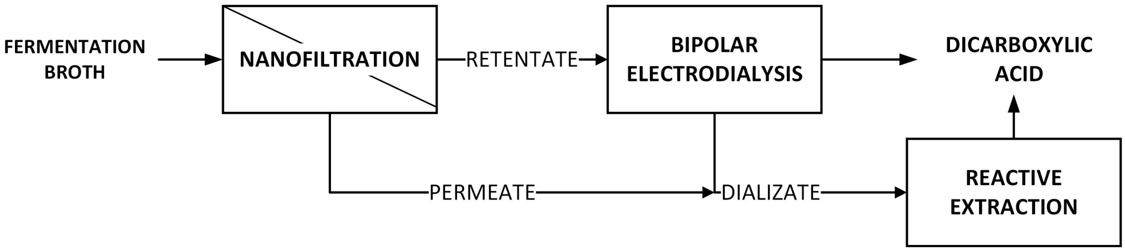

Fig. 5. Schematic diagram illustrating the principle of recovery of a dicarboxylic acid from fermentation broth

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EXTRACTION OF Ni(II), Co(II), Zn(II) AND Cu(II) FROM SULPHATE SOLUTIONS WITH BINARY MIXTURES OF CYANEX 272 AND TRIBUTYL PHOSPHATE OR LIX 860-I

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There are many papers about research on Cyanex 272 application and confirmation of the selectivity of cobalt extraction from solutions containing nickel sulphate (1,2). However, recently, literature has provided many data that acidic extractants such as Cyanex 272, Cyanex 301, Cyanex 302 or DEHPA, can be successfully replaced by their sodium salts for extraction of various metal ions from aqueous solutions (3). Good extraction efficiency of Na-Cyanex 272 towards Cu(II) is proven by Staszak et al. (4). Some mixtures of various types of extractants are able to enhance their extraction properties, and show synergy giving higher distribution ratios than organic phases including individual extractants. Mixture of D2EHPA and Cyanex 272 or Cyanex 302 can be given as an example of selective binary mixture for Ni(II) and Co(II) extraction (5).

Ni(II), Co(II), Cu(II) and Zn(II) enter into composition of crude nickel sulphate (CNS), a technical grade commercial product by KGHM, sold for its nickel value. CNS contains mainly Ni(II) (25-30%), Co(II) (near 0.5%) and trace amounts of Zn(II), Cu(II), Mg(II) and iron ions (6). Solvent extraction can be applied for separation of pure $NiSO_4$ from sulphate contaminants. However, the processing of solutions containing Zn(II), Fe(II), Cu(II) and Co(II) from sulphate solutions is difficult and makes necessary apply many steps of the treatment.

Thus, the aim of the work is to investigate extraction-stripping of Zn(II), Co(II), Cu(II) and Ni(II) with binary mixtures of Cyanex 272 (acidic form or its sodium salt) and tributyl phosphate or LIX 860-I (2-hydroxy-5-dodecyl salicylaldoxime) from sulphate solutions to obtain selective separation of the metal ions. The following issues are investigated: i) the effect of initial pH of feeds on the percentage extraction, ii) the composition and the molar ratio of organic components of binary mixtures on metal ion extraction, iii) structure of complexes formed by the metal ions with the extractants studied iv) flowsheet for selective extraction of metal ions studied from their sulphate mixture.

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APPLICATION OF POLYMER-DERIVED CARBON MATERIALS IN ADSORPTIVE DESULFURIZATION OF FUEL

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The hydrodesulfurization (HDS) process is efficient for the removal of thiols, sulfides and thiophenes, but less effective for removing refractory sulfur compounds such as benzothiophene, dibenzothiophene, and their alkyl derivatives (1,2). For these reasons, alternative desulfurization processes are absolutely necessary for producing clean fuels. Possible strategies to realize deep desulfurization include, among others, adsorptive processes.

This work presents the sorption experiments using newly obtained polymer-derived carbon materials obtained by carbonization of phosphorylated styrene-divinylbenzene copolymers having various ionic form. The dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) solutions have been prepared in isooctane (50 mg S/dm^3). In order to examine the competitive sorption of aromatic compounds that have aromatic skeleton structure similar to the coexisting sulfur compounds the mixture of DBT and naphthalene (1:1 w/w) was used. Static and dynamic sorption was investigated.

The investigations indicate that the transition metal-based carbon materials have favorable features for the removal of sulfur compounds from fuels. Example of results for the sorption material containing iron is presented in Figure 1.

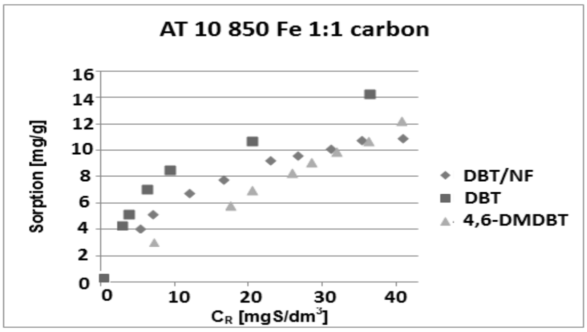

Fig. 1. Sorption of DBT and 4,6-DMDBT on AT10 850 Fe 1:1 carbon material

The structure of the carbon adsorbents has the effect upon their sorption ability towards DBT. The good selectivity results probably from the interaction between the heteroatom in the adsorbate and the metal introduced into the carbon surface.

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TRANSPORT THROUGH PDMS MEMBRANES IN PERVAPORATION AND THERMOPERVAPORATION

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Pervaporation (PV) is well known membrane separation technique. In PV liquid mixture is in a direct contact with one side of a nonporous membrane, whereas permeate vapours are removed from the other side of the membrane (1). Thermopervaporation (TPV) is the least studied mode of pervaporation, in which a temperature difference between feed and permeate sides creates a driving force. During TPV process permeate is condensed on a cold wall at atmospheric pressure (2).

The aim of this work is to compare the transport through the PDMS based membranes in pervaporation and thermopervaporation modes.

PV and TPV experiments were performed for pure water and water-ethanol mixtures. Feed temperature in PV was equal to 60ºC. Temperature difference between feed and permeate in TPV was also equal to 60ºC. Transport and selective properties of three commercial PDMS based membranes (Pervap, Pervatech, PolyAn) were investigated.

It was found that higher fluxes are produced in PV mode, comparing to TPV one. Among the membranes studied, the highest water flux was obtained for PolyAn membrane (3.1 kg m^{-2} h^{-1}). This membrane produced also the highest ethanol flux (0.7 kg m^{-2} h^{-1} in contact with feed containing 2 wt.% EtOH).

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MAGNETIC MIXED MATRIX MEMBRANES COMPOSED OF VARIOUS POLYMER MATRICES FOR THE GAS SEPARATION

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Over the past few decades, membrane separation process was found to be promising for various medical and industrial applications (air separation, hydrogen recovery and CO_2 removal) (1). Because of that the development of new polymers or the modification of existing polymers for gas separation is a very important factor (2). One of the strategies for improving the mass transport through polymer films is the incorporation of inorganic materials into a polymer matrix. They are called mixed matrix membranes (MMMs), a new class of membrane materials. These membranes combine the selectivity of zeolites and the simplicity of polymeric membrane processing (3). In this work, we have investigated magnetic mixed matrix membranes (4,5) with various polymer matrices (PPO, EC, LPI) and with different magnetic powder MQP-14-12 content, used for an air enrichment. All membranes were examined for N_2, O_2 and air permeability. Mass transport coefficients were obtained using Time Lag method and D1-D8 system. It was found that the incorporation of inorganic fillers into the polymer matrix can alter the gas transport properties through the magnetic membranes. In these hybrid membranes, inorganic particles of filler create preferential permeation pathways for selective permeability of paramagnetic oxygen and posing a barrier for undesired diamagnetic nitrogen in order to improve the separation performance. The increase of magnetic powder addition and of magnetic field has given rise in permeability and weak increase in selectivity (especially in the case of PPO and LPI matrix), too. The results also showed that the magnetic powder addition enhanced significantly gas diffusivity in EC, PPO and LPI membranes.

Acknowledgements: The authors would like to thank The Silesian University of Technology for providing financial support under the projects GG-113/CZP2/2012 and GG-104/CZP2/2012.

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EXTRACTION OF METAL ION WITH POLYMERIC PARTICLES WITH INTERCONNECTED SPHERICAL PORES CONTAINING EXTRACTANT

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The immobilization of the extractant in polymer particles using techniques of microencapsulation (1) and solvent impregnation (2) has been investigated to build effective separation process by fusion of advantages between solvent extraction and adsorption methods.

Porous microcapsules with large interconnected spherical pores have been prepared from a (W/O/W) emulsion by an *in situ* polymerization method (3). The interconnected spherical pores are open to the outside of the microcapsules and can be freely accessed by water from outside the microcapsules. The (W/O/W) type microcapsules are considered to be an effective material for the immobilization of extractants thus providing a large surface area through the many interconnected pores.

We prepared polymeric particles containing PC-88A for Zn(II), Co(II) and Ni(II) extraction by the *in situ* polymerization method (4) and impregnating LIX84-I for the extraction of Ni(II) by the solvent evaporation method (5), respectively. The SEM image of the cross sectioning of the porous polymeric particles impregnating LIX84-I is shown in Figure 1 as a typical example. The polymeric particles had a porous and rough surface and many large interconnecting spherical pores in their inner side. By the quantitative analysis of the extraction properties of the extractant, it is confirmed that two PC-88A molecules reacted with one metal ion and three molecules of LIX84-I reacted with one Ni(II) ion. The mechanism for PC-88A is same with the solvent extraction system, however, for LIX84-I is different. The extraction rate of metals was effectively accelerated by the presence of the interconnected-spherical pores in the inside of the polymeric particles.

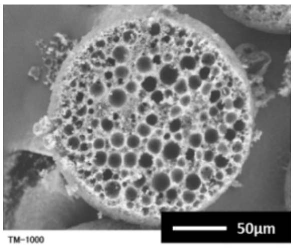

Fig. 1. The SEM images of the cross-section of the polymeric particles impregnated with LIX84-I ($W_{LIX84\text{-}I}$ = 10wt%)

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ADSORPTION OF Zn^{2+} IONS AT THE HYDROXYAPATITE/AQUEOUS ELECTROLYTE INTERFACE

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Hydroxyapatite (HAP) [$Ca_{10}(OH)_2(PO_4)_6$] plays important role in many environmental and medical processes. HAP is the structural prototype for the main inorganic constituent of bone and teeth (1-4).

Dislocation of cations in solutions is controlled mainly by adsorption at the solid/aqueous solution interface and depends on the presence of other compounds in the solution e.g. other cations as competitive adsorption can proceed between them. Ions adsorption at the solid/electrolyte solution interface is most frequently interpreted through the reactions of complex combination formation on the adsorbent surface. Mechanism of ions adsorption is defined as the ligand exchange one. As a result of this process, cations form intersphere or extra sphere complexes on the mineral surface, as mentioned earlier.

The sample of hydroxyapatite has been synthesized on the base of the procedure described in literature (2). The investigation proposed in this paper will include measurements of adsorption of Zn cations at the hydroxyapatite/electrolyte solution interface by means the of radioisotope indicator method. The prepared hydroxyapatite sample has been characterized using X-ray diffraction (XRD), adsorption-desorption of nitrogen (ASAP), photon correlation spectroscopy (PCS), Raman spectra, microscopy. Zeta potential and surface charge density were measured in NaCl as a background electrolyte as a function of pH and concentration of Zn^{2+} ions. Investigations in the hydroxyapatite/electrolyte solution system are limited by dissolution of mineral and are limited to the pH range 7 - 11. The points pH_{pzc} and pH_{IEP} for the sample are $pH_{pzc} = 6.2$ and $pH_{IEP} = 5.5$. Adsorption of Zn ions does not change with the increase of pH in the range of 7 - 11. In the case of adsorption from solution with the initial concentration 0.000001 M adsorption kinetics of Zn ions is described by numerous models. However, the good model describing adsorption kinetics in the case of solutions at the initial concentration 0.001 mol/dm^3 is only the mulitiexpotential one. It shows that the process of Zn ions adsorption at the hydroxyapatite/solution interface has two phases, fast and slow. The second stage is related to the presence of natural microchannels network and in this way adsorbing ions may be exchanged with those in the hydroxyapatite crystal structure.

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ADSORPTION OF SILVER IONS ON SYNTHETIC HYDROXYAPATITE FROM SOLUTION

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Hydroxyapatite [$Ca_{10}(OH)_2(PO_4)_6$] is very interested adsorbent, can be classified as a bioactive material, most commonly found in nature in phosphate rock as a member of the apatite mineral group (1). The investigation proposed in this paper will include measurements of adsorption of silver ions at the hydroxyapatite/electrolyte solution interface by means of radioisotope indicator method.

The studied adsorbent was synthesized according to procedure given by Liu et al. (2). Surface properties of hydroxyapatite where studied by X-ray diffraction (XRD), adsorption-desorption of nitrogen (ASAP), photon correlation spectroscopy (PCS) and SEM microscopy. Physicochemical properties of hydroxyapatite [$Ca_{10}(OH)_2(PO_4)_6$] surface were studied by means of potentiometric titration and electrophoretic measurements. The surface charge density and zeta potential was measured for the basic electrolyte concentrations (0.001 mol/dm^3) as a function of pH and concentration of the silver ions ranged from 0.001 to 0.000001 mol/dm^3. Adsorption of silver ions was calculated from the uptake of ions from solutions, determined by radioisotopic method using labeled ^{110m}Ag.

Using the obtained data the structure of electrical double layer of the hydroxyapatite/NaCl solution system was described. The points pH_{pzc} and pH_{IEP} for the sample are $pH_{pzc} = 6.5$ and $pH_{IEP} < 3$. Adsorption of silver ions change with the increase of pH in the range of 6 - 10. The ζ potential for hydroxyapatite/NaCl system in presence of silver ions has negative values in the entire measured pH range. The ζ potential increases along with the increase of the silver ions concentration.

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pH-SENSITIVE PET MEMBRANS AS LITHIUM SEPARATORS

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In the European Union there is a few companies manufacturing alkali metals, thus the number of applied technologies is limited. Lithium is obtained by extraction method of mining or evaporation of brine. Development of the electronic industry (mainly mobiles and portable electronic equipments), as well as the expected development of the electric vehicles, will lead to an increasing demand for lithium. It is estimated that in 2015 the demand for lithium in automotive industry will reach the level of 10 000 tons while in 2020 it might get 80 000 tons. Large lithium requirements promote the development of new techniques aimed at increase of plant productivity and reduction of the labour cost (1).

Membrane surfaces can be easily modified by plasma treatment - fast, effective and ecological method that has attracted the growing interest of many research groups. Plasma dielectric-barrier discharge is a specific class of high-voltage discharge that can be used at atmospheric pressure. The treatment changes the surface properties of membrane and allows to anchor some functional groups. For some extent plasma is used to induce grafting of polymers (2-6).

The aim of this study was to graft poly(acrylic acid) and its copolymers with di(ethylene glycol) methyl ether methacrylate to the surface of porous poly(ethylene terephthalate) membranes. Poly(acrylic acid) chains change their morphology with pH of solution. Below pH = 4.4 chains are collapsed while above this value chains expand (5). In such way, a new kind of pH-sensitive membranes that are able to form lithium ion-permeable ducts were obtain.

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POLYPROPYLENE MEMBRANES WITH THE DOUBLE SENSITIVITY EFFECT

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Now stimuli responsive polymers have become interesting class of polymers and number of works related to this subject have been increasing significantly. This kind of polymers can change their properties in response to external impulses such as temperature, pH, ionic strength, electrical field etc. Solutions of these polymers have been applied for example in affinity precipitation (1) or in aqueous two-phase system (2). Polymer gels are used in construction of drug delivery system (3) or sensors (4). Polymers grafted to solid surfaces are used in chromatography or other separation processes (5). In certain conditions, it is possible to prepare nanovalves that control convective flow through the membrane in relation to the external stimulus.

Poly(N-isopropylacrylamide), PNIPAM, belongs to a group of termo-sensitive polymers. At temperatures below 32ºC (lower critical solution temperature, LCST) in aqueous solutions, PNIPAM chains are swollen. After crossing the LCST the chains collapse. This phenomenon is associated with hydrophobic interactions among some parts of polymer chain (6). Poly(acrylic acid), PAA, changes its properties also with pH and temperature value. Below pH = 4.5 and 20ºC chains shrink while above these values polymer expands. This is attributed to dissociation of -COOH groups and ionic interactions (7,8).

The aim of this presentation was to use dielectric barrier discharge plasma to graft acrylic acid, N-isopropylacrylamide and their copolymer on the surface of porous polypropylene membranes. In this way special kinds of membranes were obtained that could alter permeability in relation to both stimuli: changes of the solution pH value and temperature.

Acknowledgements: The research was supported by Wrocław Research Centre EIT+ under the project "The Application of Nanotechnology in Advanced Materials" - NanoMat (POIG.01.01.02-02-002/08) financed by the European Regional Development Fund (Innovative Economy Operational Programme, 1.1.2).

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FRACTAL ANALYSIS OF MAGNETIC MEMBRANES FOR MIXTURES SEPARATION

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The anomalous diffusion on fractal structure of polymer membrane with dispersed magnetic powder is discussed. Magnetic membrane is a medium with penetrant-scale gaps with size and position changing randomly, and it exhibits distinctive fractal characteristics and can be described by using the fractal geometry. We used a "box counting method" (BCM) for calculating fractal dimension d_f. For the self-similar sets the number of nonempty coverings $N(\epsilon)$ scales with the current size of covering ϵ in the following way:

$$N(\epsilon) \propto \epsilon^{-d_f}$$

where d_f is a fractal (or box) dimension.

Taking the logarithm at the limit $\epsilon \to 0$ we get

$$d_f = \lim_{\epsilon \to 0} \frac{\ln N(\epsilon)}{\ln \frac{1}{\epsilon}}$$

The above formulae are used to the image analysis of a sufficiently large section of the membrane. Images were acquired using the optical microscopy (Fig. 1). The fractal analyses were performed using digitized image of a membrane (Fig. 2)

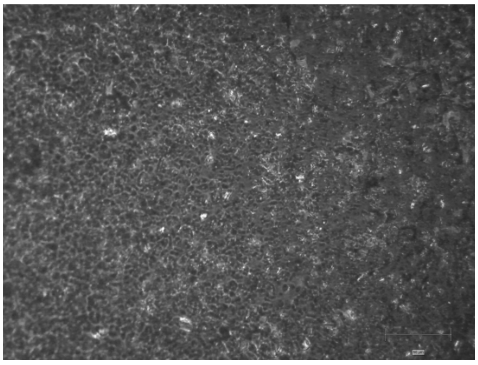

Fig. 1. Typical structure for ethylcellulose membrane with magnetic powder MQP-16 (5 μm) of amount of 1.5 g from optical microscopy (1350x magnification)

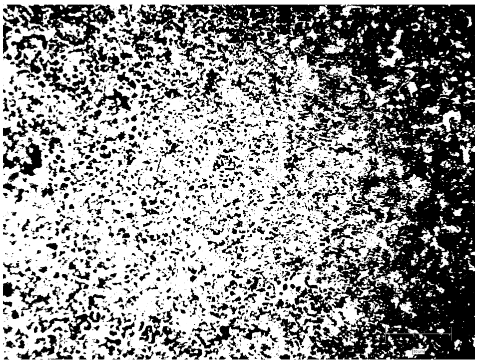

Fig. 2. Typical structure for ethylcellulose membrane with magnetic powder MQP-16 (5 μm), digitized image, as required for the fractal analyses

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THE STUDY OF ETHANOL-WATER VAPOUR PERMEATION THROUGH MAGNETIC CHITOSAN MEMBRANES

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Membranes are powerful tools for separation of liquid or gaseous mixtures and offer in many cases a cheaper, less energy consuming, eco-friendly alternative to classical processes. At the moment, the most widely used membrane materials for gas and vapour separation are polymers. New developments and innovations in material science give a better chance to find materials of good mechanical strength and chemical resistance, good stability, high permeability and selectivity. The type of membrane that should be used for the separation is determined also by the components that should be separated from the mixture.

Recently (1,2), we have discussed separation of vapours and gases through poly(2,6-dimethyl-1,4-phenylene oxide) composite membranes with ferroferic oxide magnetic nanoparticles. Now, we propose new chitosan membranes filled with different amount of magnetite, used for ethanol-water separation. The idea of implementing some external fields (in our case - magnetic) as a principal reason for mixtures separation is promising (3). We discuss the influence of the magnetite particles in chitosan membranes on the transport and separation properties in permeation process.

Acknowledgements: The authors would like to thank The Silesian University of Technology for providing financial support under the project GG 113/CZP2/2012.

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CHARACTERIZATION OF THE MORPHOLOGY AND CHEMICAL STRUCTURE OF THE SURFACE OF POLY(MAA-CO-EGDMA) SORBENTS

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One of the most broadly studied sorbents in molecular imprinting technology are the copolymers of methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA). Chemical structure of the poly(MAA-co-EGDMA) surface significantly depends on condition of copolymerization process including the type and amount of used porogenic solvent – especially in bulk polymerization technique.

Several kinds of poly(MAA-co-EGDMA) systems were synthesized by bulk polymerization technique in the presence of selected porogenic solvent. The obtained copolymers were crushed, grounded and sieved. Morphology of the sorbents were characterized by microscopic measurements as well as laser diffraction method.

The acid-base titration and pH measurements have demonstrated that chemical nature of the used porogen determines the acidic properties of the sorbent surface. The amount of carboxylic groups on the surface of copolymers obtained in the presence of methanol (ME4M4) and acetonitrile (ME4N4) is evidently higher in comparison with copolymers synthesized in the presence of toluene (ME4T4) and chloroform (ME4R4) – Fig. 1.

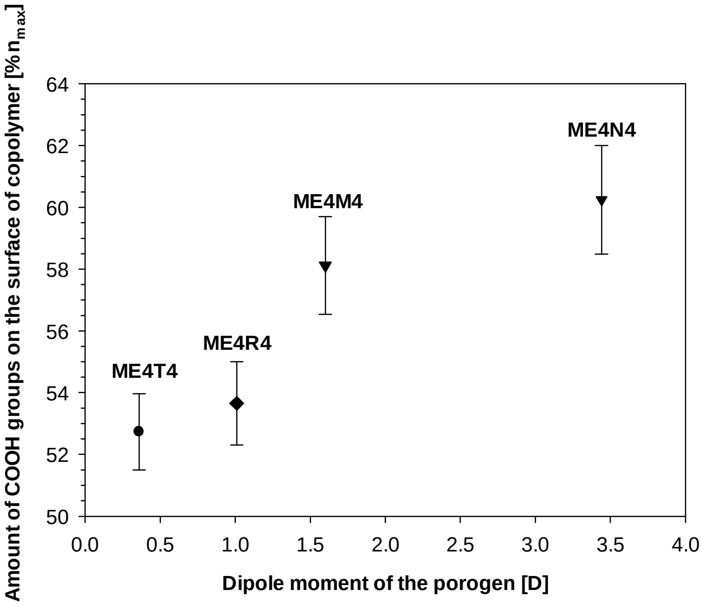

Fig. 1. Correlation of the amount of carboxylic groups on the surface of poly(MAA-co-EGDMA) with the dipole moment of porogenic solvent (mean ± SD, n = 3)

TRANSPORT AND SEPARATION OF ZN(II)/Mn(II) IN A MULTIMEMBRANE HYBRID SYSTEM

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A mutlimembrane hybrid system was used for the cations transport and separation. The system was composed of the feed phase solution (f), two cation-exchange membranes (CEM) a liquid membrane (LM) and the stripping solution (s) arranged in the following order:

f|CEM|LM|CEM|s.

Separation of Zn^{2+} from Mn^{2+} is one of the fundamental problems in the disposal of zinc-carbon spent batteries. Therefore, the pertraction experiments were performed in order to check the MHS applicability for selective recovery of Zn^{2+}. As a liquid membrane a solution of D2EHPA (di(2-ethylhexyl)phosphoric acid, c_{D2EHPA} = 0.001 – 0.1 M) in kerosene was applied. The experiments were carried out in the system with the Nafion-117 cation-exchange polymer membrane (17 cm^2). The aqueous feed solution composed of $ZnSO_4$ and $MnSO_4$ (1000 cm^3) with concentration ranging from 0.0001 – 0.01 M and aqueous stripping solution of 1M H_2SO_4 (100 cm^3) were used. Additionally, a real spent battery solution after leaching in concentrated H_2SO_4 and dilution, was also applied as the feed solution.

The results indicated that MHS is effective in transport and separation of Zn^{2+} from Mn^{2+} and can be applied for recovery of Zn^{2+}. For example the flux of Zn^{2+} and Mn^{2+} for the system with real spent battery leaching solution solution was 2.3×10^{-10} and 8.1×10^{-12} mol/cm^2s, respectively. It was also found, that the selectivity of Zn^{2+} pertraction increases by decreasing the carrier concentration in the liquid membrane. The effect of water transported osmotically to the organic phase was reduced by liquid membrane dehydration with using pervaporation technique (1). Compared to other liquid membrane systems (bulk, supported or emulsion), MHS exhibits some advantages i.e. high stability in a long time operation and high selectivity (2).

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BOND-GRAPH DESCRIPTION OF THE PERTRACTION EFFICIENCY DEPENDENCE ON LIQUID MEMBRANE VOLUME

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The study concerns the simplest case of pertraction process occurring according to a solution-diffusion mechanism (1). The pertraction efficiency in such a system depends on many factors e.g. the properties of the liquid membrane components, configuration of the membrane, (BLM, ELM, SLM) and operational parameters. Therefore, their influence on the liquid membrane transport efficiency is rather difficult to exact evaluation. For example, different volumes of agitated bulk liquid membranes (ABLM), results in incomparability of output fluxes (stripping rates) reported in literature.

In order to solve this problem by modelling using network analysis (2) and numerical simulations [] we formulate: (*i*) the phenomenological model, (*ii*) compartmental model, (*iii*) network model, and (*iv*) mathematical description (set of ordinary coupled differential equations).

To formulate the exact empirical relationship between the flux (stationary, pseudo-stationary, time dependent) and the liquid membrane volume, the following “experimental” conditions were, taking into account:

● steady state pertraction with assumed the feed and stripping solutions of infinite volumes.

● quasi-steady state pertraction with constant concentration of the feed and the receiving solution accumulation transported substance (time dependent concentration),

● non-stationary pertraction simulating typical experimental conditions with feed and striping solution of time dependent concentrations.

The results of calculations were compared with the experimental study of the pertraction of benzoic acid or bromothymol blue in the system with ABLM.

The numerical and experimental results indicated that indeed the fluxes in the system depend on the membrane volume. It was demonstrated by numerical calculations that the fluxes are going to their steady state value for the liquid membrane volume going to its infinitely small value. The maximum fluxes observed under non-stationary or pseudo-stationary conditions are not of general meaning and are far from these characteristic for the stationary-state system and can be described by the following empirical equation:

$$\log J = a_0 + a_1 \log V_m + a_2 \left(\log V_m\right)^2 + a_3 \left(\log V_m\right)^3 \cdots\cdots \quad (1)$$

To standardize the experimental results (maximum flux, time of its attaining, time lag, etc.) it seems be reasonable to extrapolate their values to the characteristic ABLM volume equal to the volume of unstirred diffusion layers as the closest to the steady state values.

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REACTIVE EXTRACTION AS AN EFFICIENT TECHNIQUE FOR REMOVAL OF SUCCINIC ACID FROM MODEL SOLUTIONS

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Reactive extraction is an effective technique for the recovery of low molecular weight dicarboxylic acids (e.g. fumaric or succinic) from fermentation broth because it is easy to control the pH in the fermentor by continuous removal of the acid. Moreover, the organic solvent can be recycled, thus reducing the amount of waste and reducing the production costs, and selective separation from other broth by-products can be achieved (1-3).

This work aims at investigation of reactive extraction of succinic acid from model solutions with solvating (eg. tributyl phosphate - TBP) or basic (e.g. trioctylamine - TOA) extractants and their mixtures. Effect of initial acid concentration and pH, presence of sodium chloride, extractant and solvent type and concentration on a dicarboxylic acid extraction is reported.

The results of the research indicate that efficiency of succinic acid extraction increases in the following order of the extractants used: TBP < TOA < TOA/TBP mixture. A synergic effect is reported for the mixture of TOA and TBP. Presence of sodium chloride in the aqueous phase does not affect the extraction efficiency, however it improves phase separation.

Acknowledgements: This research was supported by the project „Biotechnological conversion of glycerol to polyols and dicarboxylic acids," implemented within the Operational Programme- Innovative Economy, 2007- 2013, co-financed by the European Union. POIG 01.01.02-00-074/09.).

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SEPARATION AND RECOVERY OF LITHIUM WITH Λ-MNO$_2$-SUPPORTED POLYMERIC MONOLITH ADSORBENT

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Lithium (Li) is widely used as a material for Li-ion secondary battery, and demand for Li is therefore increasing. Adsorption technique is suitable for the recovery for Li from the waste materials, and λ-type manganese dioxide (λ-MnO$_2$) is well known to have high selectivity for Li (1). When λ-MnO$_2$ adsorbent is applied to column operation, granulation of the adsorbent is required to prevent the pressure loss, which leads decrease in adsorption rate and capacity. In the present work, therefore, polymeric monolith is used as a support for λ-MnO$_2$, and adsorption of Li with monolith adsorbent is investigated.

Figure 1 shows adsorption isotherms of Li with the monolith and the powdery adsorbents. Adsorption mechanism of both adsorbents was Langmuir type. The maximum adsorption amounts were determined as 1.68 mmol/(λ-MnO$_2$)g for the monolith adsorbent and 1.70 mmol/(λ-MnO$_2$)g for the powdery adsorbent, respectively. The monolith adsorbent has almost the same adsorption capacity as the powdery adsorbent.

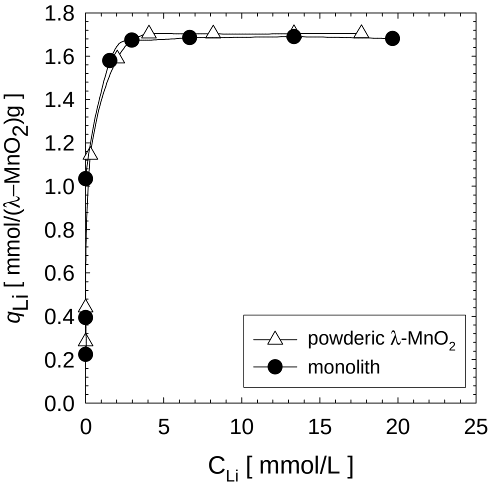

Fig. 1. Adsorption isotherms of Li with monolith and powdery λ-MnO$_2$

The monolith adsorbent was then applied for the column operation. Figure 2 shows the breakthrough curves of Li with the monolith adsorbent and granulated adsorbent at S.V. = 16 h^{-1}. In the case of monolith adsorbent, effective adsorption of Li can be achieved until B.V. = 200, while Li is immediately broken through in the case of the granulated adsorbent. Adsorption rate of Li is improved by using the polymeric monolith as the support.

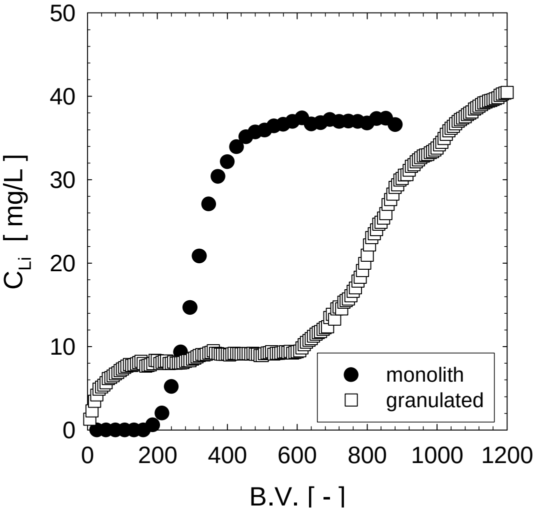

Fig. 2. Breakthrough curve of Li with monolith and granulated adsorbent

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NOVEL HIGHLY POLAR ADSORBENTS BASED ON VINYL IMIDAZOLE DERIVATIVES

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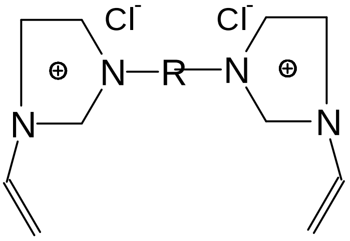
Polymeric adsorbents are widely used in the separations, both analytical (such as preconcentration of samples) as well as technological. This class of materials usually is prepared by a suspension polymerization of suitable monomers. Majority of polymeric adsorbents is based on styrene and divinylbenzene and consequently posses highly hydrophobic surface, which is dealing very well with adsorption of relatively hydrophobic compounds from aqueous solutions. Problems with the effectiveness of adsorption is observed when adsorbate is hydrophilic, able to form hydrogen bonds with water molecules. In such case it is necessary to use more polar and hydrophilic adsorbents. These materials are based on ethylene glycol dimethacrylate or contain mers having polar groups such as for example nitrile, carboxyl, aromatic amine etc. In the latter case adsorption can be realized due to various kinds of adsorbent-adsorbate interactions, including ion-exchange.

In our work we would like to present some properties of novel adsorbents obtained by polymerization of the monomers depicted in Fig. 1.



where R = -$(CH_2)_n$

n = 1 to 10

or R = Ph

Fig. 1. Monomeric vinyl imidazole derivatives

New adsorbents are synthesized by the polymerization of neat monomers or their mixtures with ethylene glycol dimethacrylate in the presence of various inert diluents. Characterization of these materials include SEM, FTIR, surface analysis by nitrogen adsorption/desorption and elemental analysis. The correlations between polymerization conditions and the properties of novel adsorbents will be presented.

APPLICATION OF POLYMER AND SUPPORTED MEMBRANES WITH 1-DECYL-4-METHYLIMIDAZOLE FOR PERTRACTION OF TRANSITION METAL IONS

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Various membrane processes are currently applied in the chemical, pharmaceutical, food industries and in the purification of wastewater. Water contamination with heavy metals has become a grave environmental issue. Heavy metals are discharged from a variety of sources in daily life and can be readily oxidized into ions when dissolved in water. Among the heavy metals, cadmium, lead, nickel, copper, and zinc are the most hazardous. These metals can be removed from wastewater using a variety of methods such as chemical precipitation, ion exchangers, solvent extraction and emulsion liquid membrane. Among them, extraction processes using liquid membranes have received significant attention for their potential as a technique for treatment of industrial liquid wastes due to the high interfacial area for mass transfer, the ability to remove and to concentrate selectively or collectively, and the requirement of only small quantities of organic solvent. The wider use of liquid membranes in practice is considerably limited by their low durability and instability of operation, resulting mainly from their structure and composition.

Previously the authors shown, that 1-alkylimidazoles and 1-decyl-2-methylimidazole can be used for separation of the Cu(II) or Zn(II) ions from an equimolar mixture of the Cu(II), Zn(II), Co(II) and Ni(II) ions in the transportation process across supported and polymer inclusion membrane. In this work, the authors present results of their investigation of the competitive transportation of Zn^{2+} from different mixture of transition metal ions as Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} ions across supported and polymer inclusion membranes containing 1-decyl-4-methylimidazole from dilute chloride solutions. The membrane is characterized by atomic force microscopy (AFM) and thermal analysis (DTA and TG) techniques. The studied PIM and SLM membrane exhibit good stability described using the Danesi's thermodynamic model. The transport selectivity coefficient and orders for metal ions transport across PIM and SLM doped with 1-decyl-4-methylimidazole was obtained. More details will be presented on poster. The stability of PIM with imidazole derivatives was confirmed in replicate experiments.

Acknowledgements: The author thank The Company Celgard® LLC, USA for the membrane Celgard® 2500.

APPLICATION OF SORBENT DOWEX PRS-3 FOR VARIOUS SORBATE REMOVAL

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With the rapid increase in global industrial activities, heavy metal and dyes pollution has become serious. Release of heavy metals and dyes from various industrial activities such as mining, ore processing, smelting, metal plating and textile dyeing creates pollutions and causes hazardous effects on humans and animals. The toxic effects of heavy metals and dyes on living tissues and environment directed the research to develop alternative technologies for wastewater purification systems. Conventional separation techniques used for the treatment of industrial effluents include adsorption, ion exchange, reverse osmosis, chemical precipitation or membrane filtration (1). Sorption with application of new types of ion exchangers such as weakly and strongly basic as well as the chelating once plays an important role in elimination of pollutants (metals and dyes) from aqueous solutions. Various sorbents have been used to remove heavy metal ions and dyes from aqueous solution e.g. (2-11).

The main goal of this paper was application of sorbent Dowex PSR-3, the macroporous strongly basic anion exchange (SBA) resin for various sorbate removal such as heavy and precious metal ions: Pd(II), Zn(II), Cd(II), Ni(II), Cu(II) as well as Acid Orange 7 dye. This work was mainly focused on the equilibrium and kinetic studies. Other aspects of the experiments such as the influence of auxiliaries on the sorption as well as desorption were taken into account, too.

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ION EXCHANGE RESIN AS EFFECTIVE SORBENT FOR BASIC DYE REMOVAL FROM AQUEOUS SOLUTIONS AND WASTEWATERS

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In acrylic, nylon and silk dyeing processes a large volume of effluent is discharged. It was estimated that 1000 mg/L of dye was used in a typical dye bath and 100 mg/L of dye was left in the spent dye bath (1). According to EPA (US Environmental Protection Agency) the amount of non-fixed basic dyes that may be discharged in the effluent were 1% (2). Basic dyes are considered one of the most toxic substances (3). They can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. One of the effective means of wastewaters purification after the dyeing processes is application of sorption methods.

The adsorption behavior of the cationic dye C.I. Basic Blue 3 (BB3) from aqueous solution on the cation exchanger Lewatit MonoPlus SP 112 (SP 112) and non-functionalized polymeric sorbent Amberlite XAD 1180 (XAD 1180) was investigated in order to identify the ability of these materials to remove textile dye from wastewaters. For this purpose a series of batch tests were carried out as a function of contact time (1 min - 96 h), dye concentration (100, 500, 1000 mg/L), auxiliaries presence (NaCl, Na_2SO_4, surfactants) and adsorption temperature (20-50ºC). The adsorption capacity (Q_0) determined from the Langmuir isotherm model at 20ºC was found to be 560.7 mg/g for SP 112 and 35.7 mg/g for XAD 1180. Q_0 increased with the temperature rise. Kinetic studies of the dye followed the pseudo-second order model rather than the pseudo-first order or intrapartical diffusion model. Total decolorization of basic dyes wastewater by means of SP 112 occurred after 1 h. Dye desorption from the cation exchanger reached 100% in four cycles of sorption-desorption using 1 M HCl in 90% CH_3OH. The working ion exchange capacities calculated from the breakthrough curves were equal to 205 mg/mL for SP 112 and 6.5 mg/mL for XAD 1180. These sorption properties of the polystyrene cation exchange resin Lewatit MonoPlus SP 112 recommend it as effective sorbent in the removal of organic ionic species like BB3 dye from aqueous solutions and industrial wastewaters.

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APPLICATION OF IONIC LIQUIDS FOR THE PRECIPITATION OF ORGANIC ACIDS DISSOLVED IN AQUEOUS SOLUTION

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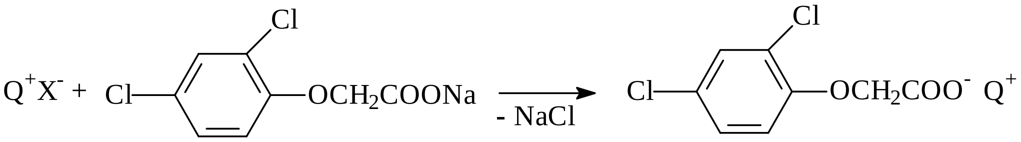
The poster deals with the application of the commercially available ionic liquids for the removal of organic acids from the wastewater streams. The poster presentation will be focused on the isolation of new low melting ionic salts obtained by precipitation of dissolved carboxylic (2,4-D-aminoisophtalic acid) or sulfonic (Acid Yellow 17) acids salts from aqueous solutions using cationic surfactants. This method enables recovery of by-product or a simple and rapid method for decentralized pretreatment for aqueous mother liquors contamined with organic acids.

To the best of our knowledge ILs were tested as volatile solvents replacements in extraction processes used earlier for isolation or purification of bellow mentioned industrially attractive acidic products:

1) aminoacids (1,2)
2) several aromatic sulfonic acids (3-5)
3) CO_2 and SO_2 removal from gaseous effluents (6)

Our work is focused on application of preferentially low cost cationic surfactants, Q^+X^-, like Aliquat 336, CYPHOS phosphonium salts, etc. as precipitants for the simple isolation (or removal) of anions of sulfonic and carboxylic acids, A^-, from their aqueous solutions under subsequent formation of organic low melting Q^+A^- salts (see Scheme 1).



Scheme 1. Precipitation of herbicide 2,4-D from aqueous solution using cationic surfactant

The removal efficiency of this method will be discussed.

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EXTRACTION OF COBALT(II) IONS FROM CHLORIDE/SULPHATE SOLUTIONS BY HYDROPHOBIC PYRIDYL KETOXIMES

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Liquid-liquid extraction is one of the most important technique for recovery of valuable metals from spent liquid solutions. Recovery of cobalt(II) ions from sulphate waste solutions by solvent extraction using Cyanex 272, Cyanex 301, D2EHPA, PC88A has been reported in many papers (1-3).

Hydrophobic pyridyl ketoximes have been proposed as extractants of copper(II), iron(III), zinc(II) and cadmium(II) ions from chloride (4-6) or as extractants of copper(II) ions from sulphate and sulphate/chloride solutions (7). The studies showed the influence of the extractant structure, the type of diluents and the concentration of chloride and/or sulphate ions in the aqueous feed on the metal extraction.

The aim of this work is to investigate the extraction properties of hydrophobic 2-, 3- and 4-pyridyl ketoximes dissolved in toluene with 10% (v/v) addition of decan-1-ol towards cobalt(II) ions. In this study various parameters such as pH, concentration of metal, sulphate and chloride ions, and type of structure of extractants on cobalt(II) extraction were investigated.

The obtained results showed that only hydrophobic 2-pyridyl ketoximes were the effective extractants of cobalt(II) ions from sulphate/chloride media. Moreover, the results indicated that the extraction efficiency slightly depended on pH and chloride ions concentrations.

Acknowledgements: The work was supported by Grant 32-045/13 DS-PB.

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INVESTIGATION OF FLOCCULATION POSSIBILITIES OF COLLOIDAL ALUMINA IN THE PRESENCE OF ANIONIONIC POLYACRYLAMIDE

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The processes of industrial wastewater and drinking water purification use the effect of significant reduction of the suspension stability in the presence of a polymer, resulting from the flocculation. The presented research concerns the determination of the adsorption mechanism of macromolecular polyacrylamide (PAM) on the alumina surface and flocculation possibilities of water Al_2O_3 suspension in the polymer presence (leading to removal of the solid from PAM solution). Two anionic polyacrylamides (with molecular weight 14 000 000) were applied in the studies – the content of carboxyl groups in their macromolecules were different, i.e. 20 and 30%. The adsorbed amount of PAM (Γ) were determined by the use of spectrophotometric method (1) and its adsorption layer thickness was calculated from viscosity data (2). Changes in the stability of the investigated systems as a function of time were monitored applying the turbidimetric method. The values of stability coefficients (TSI) were calculated with the special computer program. TSI changes in the range 0 to 100 and the lower the TSI is the more stable system is.

Table 1. PAM adsorbed amount (Γ), thickness of its adsorption layer (δ) and stability coefficient TSI of alumina suspension in the polymer presence at different solution pH, C_{PAM}=100ppm

PAM 14 000 000	Γ [mg/m^2]			δ[nm]			TSI		
	pH 3	pH 6	pH 9	pH 3	pH 6	pH 9	pH 3	pH 6	pH 9
20%	0.07	0.04	0.01	6.14	9.12	12.67	18.34	67.26	79.46
30%	0.14	0.05	0.02	8.46	10.1	15.31	18.17	71.61	86.11

As follows from the analysis of TSI values, the alumina suspension in the PAM presence is the most stable at pH 3. Its stability decreases drastically with the increasing solution pH. It may be caused by the fact, that polymer adsorption decreases with the pH rise, with a simultaneous increase of the thickness of its adsorption layer (carboxyl groups dissociation in polymer chains and changes in the solid surface charge density – $pH_{pzc} \approx 7.6$). Such structure of adsorption layer facilitates flocculation of solid particles through polymer bridges formation between them and ensures efficient removal of alumina from its water suspension. The most effective flocculant of Al_2O_3 particles is PAM containing 30% of carboxyl groups at pH 9 (the greatest development of polymer chains).

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EFFECT OF BOVINE SERUM ALBUMIN AND POLYASPARTIC ACID ADSORPTION ON CHROMIUM(III) OXIDE SUSPENSION STABILITY

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Natural and synthetic polymers adsorption on the solid surface influences the mineral oxide suspensions stability. The stability decrease is equivalent to the formation of larger solid particles aggregates which settle faster. Depending on the pH of the solution, the stabilization/destabilization mechanism of metal oxide suspension is changed. Addition of ionic macromolecular compound influences the interaction between solid particles, which can be helpful in removal of metal oxide particles from solution. Therefore, presented research could have the practical aspects, i.e. in environmental sciences during the treatment of drinking water and industrial wastewaters (1).

We used a natural polymer from the albumin group (bovine serum albumin, BSA) and a synthetic compound (polyaspartic acid, pASP) which can be classified as polyaminoacids. These macromolecular compounds were chosen based on their total biodegradability and similar structure. Both polymers are made up of aminoacids connected by peptide bond. Polyaspartic acid is composed of one kind of aminoacid and bovine serum albumin has a specific sequence of different aminoacids (2,3). Thus, it can be concluded that pASP is a primitive protein equivalent. In the experiments chromium(III) oxide (Cr_2O_3) was used as adsorbent due to its wide application in industry and the presence in wastewaters (4).

Adsorption of applied polymeric compounds on the Cr_2O_3 surface was determined by spectrophotometric method. The charge density of the solid surface was measured using a potentiometric titration. All measurements were performed as a function of solution pH. Sodium chloride with concentration of 0.01 M was used as a supporting electrolyte. Measurements of the metal oxide suspension stability in the absence and presence of the polymer were carried out with turbidimeter. The stability results were presented as transmission and backscatter curves which allow the calculation of TSI parameter (Turbiscan Stability Index).

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REMOVAL OF BISPHENOL A BY MEANS OF HYBRID MEMBRANE-SORPTION PROCESS

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Bisphenol A (4,4'-isopropylidenediphenol), BPA, is a typical product of the chemical industry. It is synthesized in large quantities worldwide as more than 90% of it is being used as a monomer for the production of polycarbonate, epoxy resins, and unsaturated polyester resins (1). BPA is also widely used in preparation of household items. It is the reason of its presence in solid waste and wastewater. Due to structural similarity to estrogens and phytoestrogens, BPA is counted to an endocrine disruptor that causes the intersex effect (2).

Bisphenol A and other endocrine disruptors are active at concentrations of order of ng/L (3) and the search for effective methods of their depletion is still the hot topic for environment engineers. Many methods such as biological processes, advanced oxidation, membrane retention and adsorption have been evaluated (4,5). Adsorption is usually considered as one of the best choices, because it is suitable for the removal of hydrophobic compounds at trace concentrations (4).

Taking into account economic considerations it is still postulated to find more efficient and cheaper method. One of them is a hybrid system compromising sorption on fine adsorbent particles with membrane microfiltration (6,7). The objective of this paper is to evaluate the possibility for removal of bisphenol A from water by means of molecularly imprinted polymers and microfiltration membranes. The system was evaluated with four resins with and without BPA imprints and with various process parameters. The goal was to check the process efficiency and select these factors that offered the higher removal ratio. It was concluded that adsorption membrane filtration hybrid process is good alternative to the column removal of trace amounts of BPA.

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APPLICATION OF MOLECULARLY IMPRINTED POLYMERIC MICROSPHERES FOR REMOVAL OF ENDOCRINE DISRUPTORS

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During the last years, there has been growing concern about chemicals that can disrupt normal endocrine functions of living organisms, including humans. These compounds are defined as “Endocrine disrupting substances – EDs”. They include naturally occurring plant products, and natural or pharmaceutical hormones (1). Numerous substances, associated with production of toxic effects, such as dioxins, polychlorodiphenols, phthalate esters (PEs), nonylphenol, bisphenol A (BPA) have been suspected to show endocrine-disruptive mechanisms (2,3). Among them, a specific interest is directed to BPA and PEs.

Because of limited solubility BPA and PEs cannot be removed well by natural process such as hydrolysis or photodegradation. Usually these compounds are extracted from water and enriched through evaporation of solvent. It is necessary to find more effective methods to decrease the application of organic solvents (4,5). Due to refractory content of EDs in water bodies it is hardly to control a content of such pollutants as well as to develop the efficient methods for their removal. The presented studies are focused on preparation of molecularly imprinted polymers (MIPs) for selective removal of DEP and BPA. Uniformly sized MIPs microspheres have been synthesized by two-stage process: the membrane emulsification (ME) and suspension polymerization (6) in presence of DEP or BPA as a template. As the references, the samples obtained without templates were synthesized. The imprinted materials showed higher sorption capacity towards template than their off-template analogues. The uptake of DEP or BPA is depended on the composition of the reaction mixture. The imprinted sorbents have no specific affinity to other phenols in the case of materials prepared to remove BPA, and to other PEs in the case of synthesis with DEP as template.

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SEPARATION OF FERMENTATION COMPONENTS BY NANOFILTRATION WITH CERAMIC AND POLYMERIC MEMBRANES

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Glycerol is a major co-product of the biodiesel production. One of the promising utilization methods of this waste material is microbial fermentation, where glycerol can be used as a carbon source (1). Nowadays, many organic compounds, such as organic acid and polyols can be produced by biotechnological conversion of glycerol (2-3). However, the success of this process is also affected by purification step, because of some co-products like sugars, proteins and mineral salts are generated during fermentation processes.

The main goal of this study was testing the possibility of selective separation of low-molecular organic compounds from fermentation broth using two types of devices: pilot scale membrane module equipped with tubular ceramic membranes (TAMI Industries, France) with cut-off 450 Da and laboratory set-up equipped with polymeric flat sheet membranes MPF-43 from Membranes SEPA Osmonics (USA). All processes of nanofiltration were performed at room temperature and transmembrane pressure in the range 1.0÷1.6 MPa.

In preliminary experiments several model solutions containing final product-organic acids, polyols and some impurities, such as unreacted glycerol or mineral salts were tested. In this report the effects of concentration, pH and composition of the feed solutions for the retention of fermentation components were analysed. The influence of fouling phenomena was considered.

It was found that nanofiltration with tubular ceramic membrane and flat polymeric membrane as well can be used as the process of selective separation of organic compounds from fermentation broth.

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RECOVERY OF GOLD(III) IONS FROM METALLIC SECONDARY SOURCES ON THE SOLVENT IMPREGNATED RESIN DOWEX OPTIPORE L493

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Gold has been known for ages with regard to its specific chemical and physical properties, which can be exploited in many fields. Growing demand for gold makes it necessary to recover it from secondary sources such as electronic wastes (1).

As follows from the research the sorption without impregnation is not selective enough to remove gold(III) ions from large amounts of accompanying metals. This kind of resins exhibits selective for metal properties functional groups which are immobilized on the resin matrix by chemical bonds or physical adsorption (2). This solvent impregnated resin (SIR) approach avoids emulsification and simplifies the phase separation after extraction (3). Impregnation of an organic extractant into a polymeric support offers ease of solvent impregnated resin preparation and wide choice of reagents of desired selectivity (4).

Laboratory studies of selective removal of gold(III) from real solution on the solvent impregnated highly crosslinked styrenic polymer, Dowex Optipore L493 using Cyanex 272 were carried out. The solution was prepared by leaching of pins in the hydrochloric acid-hydrogen peroxide system. The pins were recycled from the 8P8C modular plug (an eight-wire connector used commonly to connect computers onto local-area networks (LAN), especially Ethernets). Gold concentration was determined by the AAS method. The gold(III) ions concentration was 16.53 ppm. The real solution contained also Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Co^{2+} ions.

In these experiments % R of gold(III) was obtained. The results demonstrated that % R was better for Dowex Optipore L493 impregnated with Cyanex 272 (94.19 %) than that of Dowex Optipore L493 before impregnation (89.23 %). Batch desorption experiments were carried out using 5% thiourea in the 0.1 M HCl solutions.

The described method using Dowex Optipore L493 impregnated with Cyanex 272 for selective separation of ions gold(III) proved to be effective for recovery of gold from secondary metallic sources.

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REMOVAL OF CHROMIUM(VI) BY ANION EXCHANGER BEARING PYRIDINIUM AND NITRILE GROUPS

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Chromate pollutants are introduced into the environment from a variety of processes such as mining, mineral weathering, industrial applications including leather tanning, textile dying, electroplating, metal finishing, inorganic chemicals production. These waste streams contain toxic heavy metals such as chromium, cadmium, lead, mercury, nickel, and copper. They are not readily removed without specialized or advanced treatment. Chromium is a common pollutant occurring in the surface or groundwater due to the discharge of a variety of industrial wastewaters. On the other hand, chromium based catalysts are also employed in various chemical processes, including selective oxidation of hydrocarbons. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0.05 $mg \cdot L^{-1}$.

A new anion exchanger with the nitrile group attached to the quaternary pyridinium functional groups has been prepared by the nucleophilic substitution reaction of a gel type 4-VP:DVB copolymer with 2-chloroacetonitrile as a halogenated reactive compound. The new compound exhibits better strong base exchange capacity than the commercial strong base anion exchangers. The obtained anion exchanger was used to remove Cr(VI) from the aqueous solution. Batch adsorption studies have been carried out to determine the effect of contact time, concentration of hexavalent chromium in the solution and pH on the sorption capacity. The kinetic parameters were determined on the basis of the static results. The thermodynamic parameters of Cr(VI) sorption process on the anion exchanger were calculated based on the Langmuir and Freundlich isotherms. Sorption was studied in the pH range from 1.5 to 7 and it was found that it depends on the solution acidity. At the pH values 1.5 and 7 the anion exchanger exhibited large values of chromium sorption capacity. The speciation of chromium was investigated in the studied pH range by the Diffuse Reflectance Spectroscopy (DRS) method. Reduction of chromium(VI) to chromium(III) under acidic conditions was observed. Nitrile groups have a strong polarity, so their existence in the chains could enhance the dipol-dipol interactions among the molecular chains. The prepared pyridine anion exchanger with the nitrile groups attached to the quaternary ammonium groups exhibited high sorption capacity for hexavalent chromium compared to the data presented in the literature.

ELECTRODIALYSIS AND REVERSE OSMOSIS AS AN ELECTRODEIONIZATION PRETREATMENT

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Electrodeionization (EDI) has become a laboratory and industrial standard in the ultra-pure water production. The drawback of this method is that it requires highly treated feedwater, typically having total dissolved salts content (TDS) lower than 25 mg/L. Typically, reverse osmosis (RO) is used as a pre-treatment before the EDI, however previous research has shown that if the electrodialyzer is equipped with thin, inter-membrane spacers, it is possible to reach very low diluate salinity, down to TDS of 1 mg/L (1). This creates the possibility of the application of ED as a pre-treatment before the EDI. Additionally, ED diluate should have lower ratio of chloride to sulphate concentration than RO permeate. The diminished chloride content should decrease the production of chlorine in the anodic compartment of EDI module and thus increase the lifespan of the ion-exchange membranes applied in the EDI.

To compare ED and RO as the EDI pre-treatment, a bench-scale ED of a tap water of TDS 1000 mg/L was performed using electrodialyzer equipped with four pairs of CMX/AMX membranes and 0.26 mm inter-membrane spacers. The ED was performed in a batch mode until the diluate TDS reached 10 mg/L. Next, the samples of RO permeate were collected from the RO installed in commercial RO-EDI system. Composition of both ED diluate and RO permeate was analysed and the concentration of halides, alkali metals, sulphates and silica was determined.

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THE RESORCINARENE CARBOXYLATE DERIVATIVE IMPREGNATED AMBERLITE XAD-4 RESIN FOR THE REMOVAL OF Pb(II) AND Cu(II) IONS FROM INDUSTRIAL EFFLUENTS

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The adsorption/solid phase extraction (SPE) processes are the most attractive methods for effective removal of heavy metals from different aqueous solutions due to their high efficiency in a wide range of metal ion concentration, and easy handling under relatively flexible working conditions; one should also point out the selectivity and rapidity of these methods (1,2). In SPE procedure, the choice of appropriate adsorbent is a critical factor to obtain full recovery and high enrichment factor (3).

For this reason, modification and impregnation techniques of solid phase have been employed to increase the surface adsorption capacity, and to enhance the removal efficiency and selectivity of the solid phase (4). Novel types of resins incorporating macrocyclic ligands may be the best choice for the removal of a variety of metal ions. The modification of Amberlite XAD-4 with resorcinarenes results in the high capacity and selectivity of the impregnated resins. The extractant is retained in the micropores of an inert polymer without any chemical bonds onto the polymer matrix and the properties of the impregnated extractant are responsible for the adsorption of novel resin (5).

In this study the efficiency of supported the octasubstituted-dodecyl-calix[4]resorcinarene with its carboxylate arms (**1**) as solid extractant using solid–liquid extraction and sorption characteristics of impregnated resin for the Pb(II) and Cu(II) ions were evaluated. For this purpose resorcin[4]arene **1** was chosen; the impregnated resin was prepared by combination of Amberlite XAD-4 with **1**. Results of the batch and fixed bed column systems showed that impregnated resin has high extraction ability towards Pb(II) ions and low one for Cu(II) ions. It was found that the removal of Pb(II) using impregnated resin depends particularly on pH and initial concentration of metal ions; the highest removal metal efficiency (99%) was achieved at pH 6.0 and initial concentration of 1×10^{-4} M. Moreover, the resorcinarene carboxylate derivative impregnated resin has been found efficient and easily regenerable and can be used several times.

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