

Studying the Impact of Anions Pre-generated Iron Corrosion Products on the Efficiency of Contaminant Removal in Fe⁰/H₂O Systems

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Abstract: The effects of Fe⁰ pre-corrosion by water, bicarbonate, chloride, phosphate and sulfate on the efficiency of Fe⁰ systems for water treatment were investigated. Batch experiments were conducted for a total duration of 72 days with MB (Methylene Blue) and MO (Methyl Orange). The efficiency of used Fe⁰ was assessed by characterizing the extent of MB and MO discoloration, pH variation and amount of iron released as a function of anion type. Before dye addition, used Fe⁰ in Fe⁰/sand and 100% Fe⁰ systems was allowed to equilibrate with H₂O or the anionic solution for 0 to 44 days. Pre-corrosion has low impact on MB discoloration but has negative impact on MO discoloration. Relative to the reference system (anion free system, H₂O), all the tested anions enhanced MB discoloration but decreased that of MO. HPO₄²⁻ and HCO₃⁻ severely affects MO discoloration. The pH of the medium governs the discoloration with MB performing better at higher pH and MO doing same at lower pH. For MB, Fe⁰/sand system shows higher efficiency than 100% Fe⁰ system. But the two systems show similar efficiency for MO. Results will help in the design and functioning of Fe⁰ based filtration systems and other water treatment designs using Fe⁰.

Key words: Corrosion products, dye discoloration, major anions, pre-corrosion, zero-valent iron.

1. Introduction

The contamination of the environment and particularly water sources is on the rise around the world. This is due principally to the continuous increase in world population with the corresponding increase in different activities that are aimed at sustaining life on earth. These activities which include principally industrial, agricultural and domestic pollute the already scarce water resources with different contaminants. This contamination modifies the properties of the water body, making it responsible for a number of environmentally related problems and particularly health related ones.

According to WHO (World Health Organization) estimates, up to 80% of all diseases and sicknesses in the world result from inadequate sanitation, polluted

water or unavailability of water [1]. It also estimated that approximately 1.6 million people are forced to use contaminated water globally and are at risk of exposure to diseases. This situation is even more alarming in developing countries where there is lack of appropriate water treatment technologies due to economic and technological constrains. In most rural areas of developing countries, water infrastructure is poorly developed or doesn't exist at all [2, 3]. Therefore, innovative, efficient but affordable technologies that are cheap and applicable without electricity are needed [2].

PRB (Permeable Reactive Barriers) based metallic iron (Fe⁰) has been demonstrated as a promising medium for environmental remediation and water treatment [2-4]. The use of PRB is advantageous over the other treatment methods due to its low energy input, continued productive use of installation, and cleans up on only the area of contamination [3]. The use of Fe⁰

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is particularly advantageous because it is easily available at low cost and can efficiently remove organic and inorganic chemicals and pathogens [5]. The main mechanisms of contaminant removal are degradation, precipitation and sorption of contaminants [3, 6]. Contaminant removal in Fe⁰ system occurs on the surface of different iron corrosion products produced in a cycle of aqueous iron corrosion processes [7]. But the major limitation of Fe⁰ system is that it undergoes volumetric expansion due to iron corrosion [8, 9], indicating the non-sustainable nature of pure Fe⁰ systems [8]. In Fe⁰ system there is the need for free space to quantitatively undergo corrosion. In the absence of free space, corrosion stops due to clogging [8]. This implies the filter based Fe⁰ system cannot more be used. Thus, for Fe⁰ filter to be more sustainable, the amount of Fe⁰ in the filtration system is reduced by mixing it with a non-expansive material. The most tested and used non-expansive material is sand [10], because it is cheap, non-reactive and porous [7].

Despite the fact that there are over 200 Fe⁰ reactive walls working satisfactorily throughout the world [11], the mechanism of operation of Fe⁰/H₂O system is far from been established [8]. There is still much controversy on almost all aspects of contaminant removal in these systems resulting from the fact that there are many factors determining the reactivity of Fe⁰ under realistic conditions [12]. One of the most widely recognized and thoroughly studied being solution chemistry, especially the coexisting anions as summarized in Table 1. These studies evaluate the influence of major anions on the corrosion behaviour

of metallic iron.

While the Cl⁻ and SO₄²⁻ enhance iron corrosion, bicarbonate ions passivate iron surface, but the role of phosphate ions is not very clear. Nonetheless, the contradictions may be due to experimental conditions.

Though the influence of these majors anions on iron corrosion has been widely studied as evident from Table 1, available literature on the role of iron corrosion products (FeCPs) pre-generated by these anions on the functioning of Fe⁰/H₂O systems is scarce. The present study deals with the impact of anions pre-generated iron corrosion products on the efficiency of Fe⁰/H₂O systems in removing MB (Methylene Blue) and MO (Methyl Orange) from aqueous solution for 28 days. Prior to the introduction of dyes (MB and MO), Fe⁰ is pre-corroded for 0 to 44 days in the presence of 0.0464 M of a major anion. Tested anions include: Cl⁻, HCO₃⁻, H₂PO₄⁻ and SO₄²⁻. The reference system used is deionised water (anion free). 100% pure Fe⁰ and Fe⁰/sand systems were investigated. Results of this study will help improve the understanding and functioning of Fe⁰/H₂O systems for contaminant removal.

2. Materials

Working solutions of anions were prepared with demineralized water. 0.0464 M of each anion (Cl⁻, SO₄²⁻, HPO₄²⁻ and HCO₃⁻) was prepared by dissolving the corresponding mass of salt in 1 L of demineralized water: 1.647 g NaCl, 4.45 g Na₂SO₄, 4.45 g NaHPO₄ and 2.27 g NaHCO₃. Used salts were of analytical grade.

Table 1 Influence of anions on the corrosive behaviour of zero valent iron.

Decreasing order of ZVI corrosion (or reactivity)	Reference
HSiO ₃ ⁻ > HCO ₃ ⁻ > H ₂ PO ₄ ⁻ > ClO ₄ ⁻ ≈ NO ₃ ⁻ > Cl ⁻ > SO ₄ ²⁻	[13]
PO ₄ ³⁻ > HSiO ₃ ⁻ > NO ₃ ⁻ > CO ₃ ²⁻ > SO ₄ ²⁻	[14]
HCO ₃ ⁻ > SO ₄ ²⁻ > Cl ⁻ > NO ₃ ⁻	[15]
Na ₂ SiO ₃ > H ₂ O > NaHCO ₃ > NaCl > Na ₂ SO ₄ > NaH ₂ PO ₄ > NH ₄ Cl	[16]
Chloride > nitrate > sulphate > phosphate	[17]
Nitrate > iodide > perchlorate > bromide > chloride > sulfate	[18]
CO ₃ ²⁻ > Cl ⁻	[19]
Pb(NO ₃) ₂ > NaHCO ₃ > KI > CaCO ₃ > KBr > NaNO ₃ > MnSO ₄ > MgSO ₄ > NaCl > KCl > Na ₂ SO ₄	[20]

MB and MO are widely used as model contaminants to characterize the suitability of various systems for water treatment [21, 22]. Both dyes were of analytical grade. They are selected due to (i) similitude in their molecular size (molar mass: 319.85 g·mol⁻¹ for MB and 327.33 g·mol⁻¹ for MO) and (ii) differences in their chemical character (MB cationic and MO anionic). Used initial dye concentration was 10 mg·L⁻¹ for each dye. The working solutions were prepared by diluting a 50 times more concentrated stock solution (1,000 mg·L⁻¹) of each dye using the demineralized water. The pH value of the initial solution was 7.6 ± 0.1. The used initial concentration (10 mg·L⁻¹) was selected to approach the concentration range of natural waters (MB and MO as model micro-pollutants) [23, 24].

A standard iron solution (1,000 mg·L⁻¹) from Aldrich Chemical Company, Inc., was used to calibrate the spectrophotometer used for analysis. All other chemicals used were of analytical grade. In preparation for spectrophotometric analysis, ascorbic acid was used to reduce Fe³⁺ in solution to Fe²⁺. 1.10 orthophenanthroline was used as reagent for Fe²⁺ complexation. Other chemicals used in this study included L(+)-ascorbic acid and L-ascorbic acid sodium salt. Ascorbic acid also degrades dyes (in particular MO) and eliminates interference during iron determination [24].

The used Fe⁰ material was purchased from iPutech (Rheinfelden, Germany). The material is available as fillings with a particle size < 630 µm. The fraction 0.3 to 0.5 mm was used in the experiments. The elemental composition of the material as analysed by X-ray fluorescence was: Mn: 0.62%; Si: 0.52%; Cu: 0.23%; Cr: 0.2%; Ni: 0.1%. The material was used without any pre-treatment.

The used sand was a natural material from the Maroua (Cameroon). Maroua sand was used as received without any further pre-treatment or characterization. The particle size between 0.3 to 0.5 mm was used. Sand was used because of its

worldwide availability and its use as admixing agent in Fe⁰/H₂O systems [7, 10].

3. Methods

Fe⁰ pre-corrosion was realized in essay tubes containing 10 mL of demineralized water (H₂O) or individual anions (Cl⁻, HCO₃⁻, HPO₄²⁻ and SO₄²⁻). The anion initial concentration was 0.0464 M. The 10 mL solution was equilibrated with Fe⁰ alone and Fe⁰/sand mixtures for 0 to 44 days in order to in-situ generate iron corrosion products (FeCPs). Each essay tube contained 0.1 g of Fe⁰ (Fe⁰ alone or 100% Fe⁰) or 0.1 g of Fe⁰ and 0.2 g sand (Fe⁰/sand system). The ensemble was placed in a closed cupboard, protected from day light. During the pre-equilibration period, essay tubes already containing materials (Fe⁰ and/or sand) were gently turned end-over-end once per week. This operation intended to avoid compaction of the material by gelatinous FeCPs (cementation) [24]. At the end of the pre-corrosion period, prior to dye addition the pH value of all investigated systems was recorded.

Dye discoloration was initiated by adding 10 mL of the dye solution (20 mg·L⁻¹) to the 10 mL of pre-equilibrated systems (Cl⁻, SO₄²⁻, H₂O, HPO₄²⁻ and HCO₃⁻). The resulting working dye concentration was 10 mg·L⁻¹. Investigated systems were: (i) Fe⁰ alone and (ii) Fe⁰/sand. The reaction vessels were kept static (no agitation) in a laboratory cupboard to avoid any photo-catalytic interferences. The efficiency of individual systems for dye discoloration was characterized at laboratory temperature (about 25 ± 5 °C) for 28 days. The initial pH value was ≈ 7.6. After equilibration, up to 3.0 mL of the supernatant solutions were carefully retrieved (no filtration) for dye determinations (no dilution) and the pH value was recorded. The Fe⁰ system characterizes the extent of dye discoloration by Fe⁰. The Fe⁰/sand system characterizes the impact of sand on the availability of 'free' corrosion products and thus their impact on dye discoloration [23].

Aqueous dye and iron concentrations were determined by a Spectro 23RS UV-Vis spectrophotometer (Labomed. Inc.). The working wavelengths for the dyes are 664 nm for MB and 464 nm for MO. Fe was determined at 510 nm. Cuvettes with 1 cm light path were used. The iron determination followed the 1.10 orthophenanthroline method [25]. The spectrophotometer was calibrated for dye concentrations $\leq 10.0 \text{ mg}\cdot\text{L}^{-1}$ and iron concentrations $\leq 10.0 \text{ mg}\cdot\text{L}^{-1}$. The pH value was measured by a Mettler Toledo Education line pH meter.

After the determination of the residual dye concentration (C), the discoloration efficiency (E) was calculated (Eq. (1)) in order to characterize the magnitude of tested systems for dye discoloration:

$$E = \left(1 - \frac{C}{C_0}\right) * 100 \quad (1)$$

Where C_0 is the aqueous dye initial concentration ($10 \text{ mg}\cdot\text{L}^{-1}$), while C is the dye concentration at any date ($t > 0$).

4. Results

Fig. 1 shows the MB discoloration efficiency (E value) plotted as a function of the pre-corrosion time for the five investigated systems. The results of the Fe⁰/sand system are presented in Fig. 1a while those for the pure Fe⁰ system are summarized in Fig. 1b.

It is seen that larger discoloration efficiencies were

achieved in the Fe⁰/sand (70 to 95%) compared to the pure Fe⁰ system (25 to 80%). It is also seen that varying the pre-corrosion time from 0 to 44 days mostly has low impact on the MB discoloration efficiency for individual anions. This observation suggests that, under tested experimental conditions, similar amount of reactive site for MB discoloration by adsorption and co-precipitation were present in individual systems despite prolonged pre-corrosion time. This interpretation appears to be counter-intuitive given that increasing amounts of FeCPs were generated with increasing pre-corrosion time [24].

Fig. 1b shows that the MB discoloration efficiency decreased from 60% (H₂O-reference) to 30% in the HPO₄²⁻ system. For all other systems, a slight increase of the E value was observed (60 to 80%) in the order: HPO₄²⁻ < H₂O < SO₄²⁻ < Cl⁻ < HCO₃⁻. In other words, in the 100% Fe⁰ system, MB discoloration substantially increased when bicarbonate was present.

Meanwhile, Fig. 1a shows that the MB discoloration efficiency increased from 70% in the reference system (H₂O) to up to 95% in all other systems. In other words, in the Fe⁰/sand system, the presence of tested anions enhanced MB discoloration. Overall, the impact of tested anions on MB discoloration by the Fe⁰/sand system followed the order: H₂O < SO₄²⁻ < Cl⁻ < HPO₄²⁻ < HCO₃⁻. The main

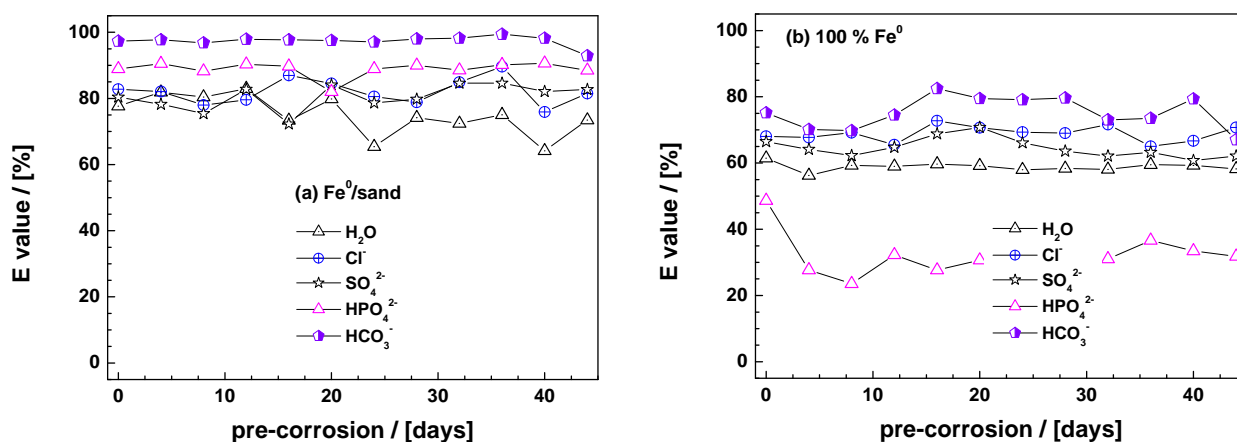


Fig. 1 Discoloration of MB using (a) Fe⁰/sand system and (b) 100 % Fe⁰ system.

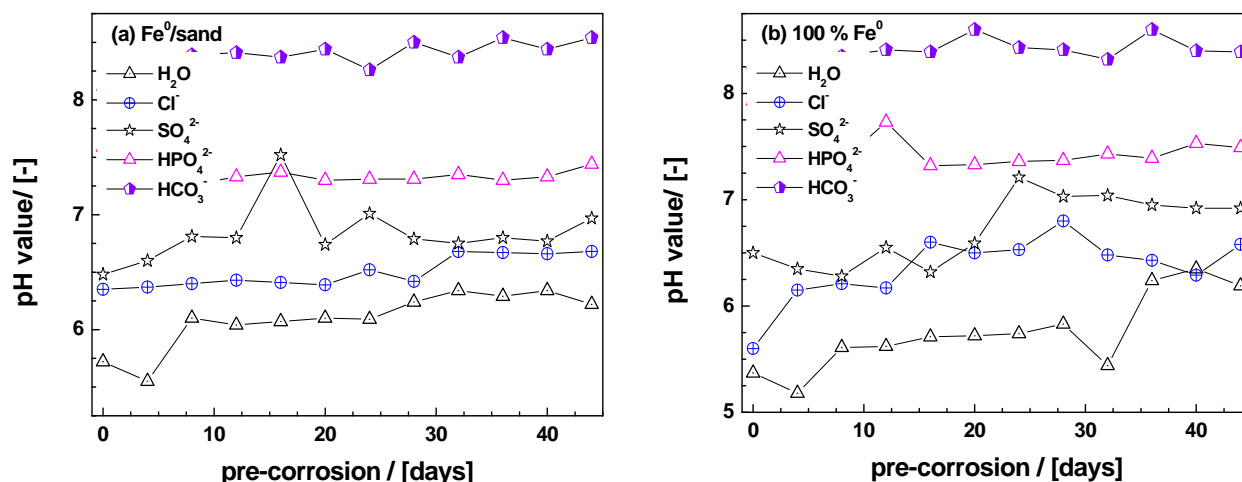


Fig. 2 Variation in pH for MB discoloration (a) Fe⁰/sand system and (b) 100% Fe⁰ system.

difference to the 100% Fe⁰ system is that HPO₄²⁻ enhances MB discoloration.

Results of the variation of pH for the two systems are presented in Figs. 2a and b.

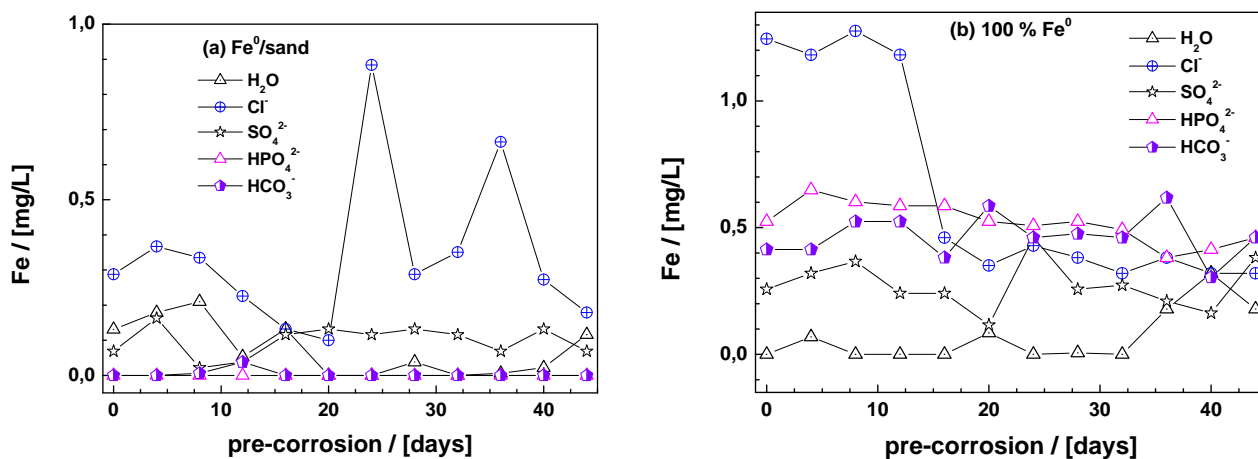
For the Fe⁰/sand system (Fig. 2a), the order of pH was: H₂O < Cl⁻ < SO₄²⁻ < HPO₄²⁻ < HCO₃⁻ (MB discoloration order: H₂O < SO₄²⁻ < Cl⁻ < HPO₄²⁻ < HCO₃⁻). The same order is observed for pH in the 100% Fe⁰ system (Fig. 2b) but the order of MB discoloration is different (MB discoloration order: HPO₄²⁻ < H₂O < SO₄²⁻ < Cl⁻ < HCO₃⁻). This analysis demonstrates that the pH (determined by products of corrosion) controlled the discoloration of MB. Thus, the discoloration was principally controlled by the electrostatic attractions between the cationic MB and charged anions iron solutions. This is why HCO₃⁻ (pH almost 9) significantly enhanced discoloration in the two systems. In the case of the 100% Fe⁰ system Fig. 2b, the same trend is observed but only for HPO₄²⁻ containing solution with very low MB discoloration despite its negative solution pH. During the pre-corrosion period (0-44 days) no change in colour or production of corrosion products (indicated by brown colouration) was observed in HPO₄²⁻ containing solutions for both systems. However, a white precipitate was deposited on the walls of the reaction tube (due to the reaction: Fe³⁺ + HPO₄²⁻ → FePO₄↓ + H⁺). This precipitate which is easily formed

(high enthalpy of formation) with Fe, is insoluble in water (Table 2). It then deposit and block the surface of iron thus giving low discoloration of MB in 100% Fe⁰ system. The higher MB discoloration in Fe⁰/sand system compared 100% Fe⁰ system is therefore probably due to the presence of sand which acted as a dispersant and limited clogging of iron corrosion products; creating more space for MB to react and also forming weak hydrogen bond with MB improving its discoloration [26]. Particularly, for solution containing HPO₄²⁻ in Fe⁰/sand system, discoloration was enhanced by sand through formation of weak hydrogen bonds between MB and OH- groups on sand surface. The similarity in behaviour of SO₄²⁻ and Cl⁻ can also be seen from Table 2 where they easily react with iron but their complexes are easily soluble in water (Cl⁻ more soluble), liberating the iron surface for further reaction.

The enthalpy of formation values, Table 2 shows that the formation of complexes with iron is of the order: phosphate > sulfate > carbonate > chloride. However, the order of solubility in aqueous media is chloride > sulfate > carbonate > phosphate. This indicates that soluble iron chloride dissolves on formation thus liberating the surface of the iron for more reaction and this tendency is followed by sulphate, carbonate and lastly phosphate where the formed precipitates block the iron surface.

Table 2 Thermodynamic properties of some Fe-anions compounds [27].

Compound	Solubility in water at 298 K	$\Delta_f G_m^{\ominus} / \text{kJ/mol}$	$\Delta_f H^{\ominus} / \text{kJ/mol}$
FeCl ₃	912 g/L	-415.7	-399.4
Fe-sulfate	29.51 g/100 mL	-848.651	-991.235
Fe-carbonate	0.0067 g/L	-648.68	-750.6
Fe-phosphate	anhydrous: insoluble dihydrate: 0.642 g/100 mL (373 K)		-1,888

**Fig. 3** Quantity of Fe released during MB discoloration in (a) Fe⁰/sand system and (b) 100% Fe⁰ system.

The influence of the anions pre-generated iron corrosion products on the ability of the Fe⁰/sand and 100% Fe⁰ systems to release iron in to solution during discoloration of MB is shown in Figs. 3a and b.

For the Fe⁰/sand system, Fig. 3a, the order of release is: Cl⁻ > H₂O = SO₄²⁻ > HCO₃⁻ (0.00 mg/L) = HPO₄²⁻ and for 100% Fe⁰ system, the order is: Cl⁻ > HPO₄²⁻ > HCO₃⁻ > SO₄²⁻ > H₂O.

The high iron released in the presence of the chloride for the two systems is due to its ability to easily corrode iron. Also, the FeCl₃ precipitate formed between chloride and Fe surface is very soluble in water, thus releasing charged iron species in to solution continuously. The high release of iron in 100% Fe⁰ system by HPO₄²⁻ and HCO₃⁻ (with low iron corroding potentials) is due to the solubility of the precipitates formed with iron surface in the reagents used for iron determination (evidenced by the disappearance of white precipitate initially present). The amount of iron released in the two systems is basically identical especially for chloride and the values are moderate despite the pre-generation of iron

corrosion products.

Fig. 4 shows the MO discoloration efficiency (E value) plotted as a function of the pre-corrosion time for the five investigated systems. The results of the Fe⁰/sand system are presented in Fig. 4a while those for the pure Fe⁰ system are summarized in Fig. 4b.

It is seen that larger discoloration efficiencies were achieved in the two systems (0.00 to 96%). Contrary to MB, varying the pre-corrosion time from 0 to 44 days mostly has an impact on the MO discoloration efficiency for individual anions. Figs. 4a and b show that the MO discoloration efficiency decreased from 96% (H₂O-reference) to 0.00% in the HPO₄²⁻ systems, 4% for HCO₃⁻ in pure Fe⁰ system and 32% in Fe⁰/sand system. Fig. 4a, for all other systems, a decrease of the E value was observed. The decrease is in the order: HPO₄²⁻ > HCO₃⁻ > SO₄²⁻ > Cl⁻ = H₂O. In other words, in the Fe⁰/sand system, MO discoloration substantially increased when water and Cl⁻ were present or the HPO₄²⁻, HCO₃⁻ and SO₄²⁻ presence reduce MO discoloration, with HPO₄²⁻ and HCO₃⁻ attaining 0.00%

and 32% respectively. From Fig. 4b, the same trend is observed for the 100% Fe⁰ system (HPO₄²⁻ > HCO₃⁻ > SO₄²⁻ > Cl⁻ = H₂O) with reduction in MO discoloration attaining 0.00% and 4% respectively for HPO₄²⁻ and HCO₃⁻.

The variation of pH for the two systems are presented in Figs. 5a and b.

For the Fe⁰/sand system (Fig. 5a), the order of final solution pH was: HCO₃⁻ > HPO₄²⁻ > SO₄²⁻ > Cl⁻ > H₂O (MO discoloration order: HPO₄²⁻ < HCO₃⁻ < SO₄²⁻ < Cl⁻ = H₂O). The same order is observed for pH variation in the 100% Fe⁰ system (Fig. 5b) with same order of MO discoloration. Like for MB, the discoloration of MO was controlled by electrostatic attractions between the negatively charged anionic dye, methyl orange and the charged anions-iron solutions. HPO₄²⁻ and HCO₃⁻ significantly reduced MO

discoloration with increase pre-corrosion time due to increase in pH; for Fe⁰/sand system, pH decreased from 9.06 to 8.24 for HPO₄²⁻ and increased from 9.06 to 9.44 for HCO₃⁻ from 0-44 days of pre-corrosion while for 100% Fe⁰ system, pH decreased from 8.58 to 8.23 for HPO₄²⁻ and increased from 9.20 to 9.45 for HCO₃⁻ from 0-44 days of pre-corrosion. Thus, there was strong repulsion between negative charges of MO and those from solution containing these anions resulting in zero discoloration with solutions pre-corroded from the 12th day for HPO₄²⁻.

According to Sejie, F. P., [28], for MO as pH is increased to more basic conditions, the double bond conjugation is lost and a proton is lost, and the molecule rearranges to form a negatively charged. Due to excess anions in the solution, there will be repulsion of the dye by the negatively charged

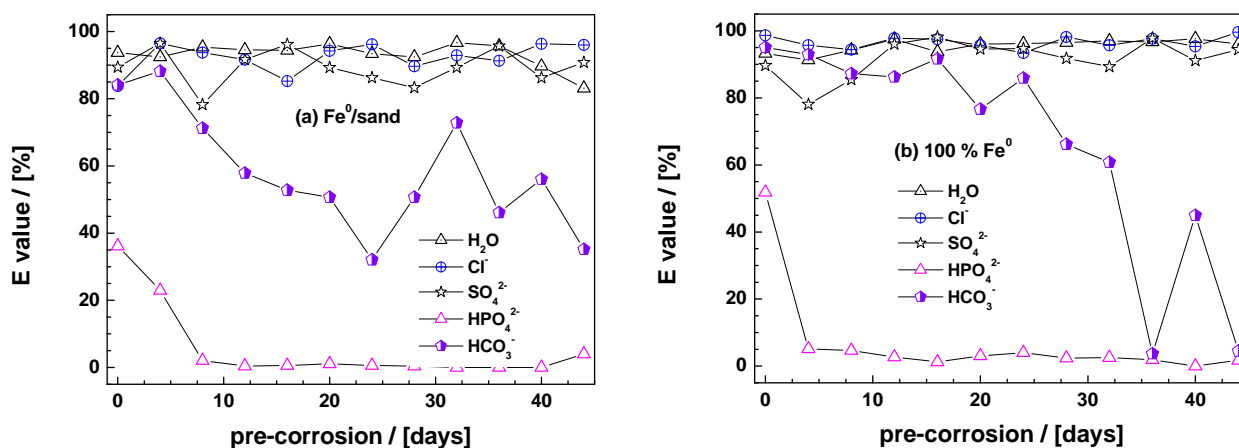


Fig. 4 Discoloration of MO using (a) Fe⁰/sand system and (b) 100% Fe⁰ system.

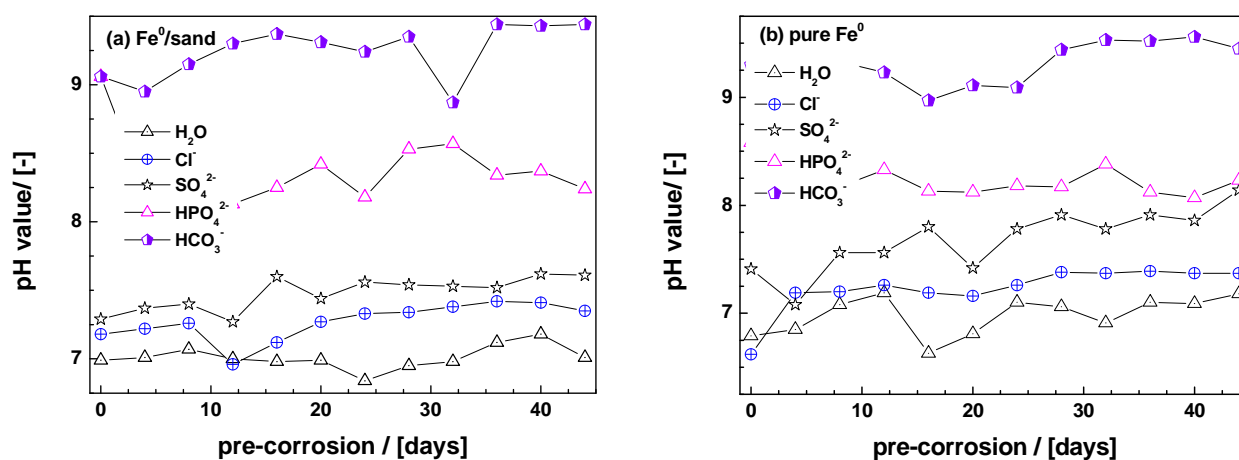


Fig. 5 Variation in pH for MO discoloration (a) Fe⁰/sand system and (b) 100% Fe⁰ system.

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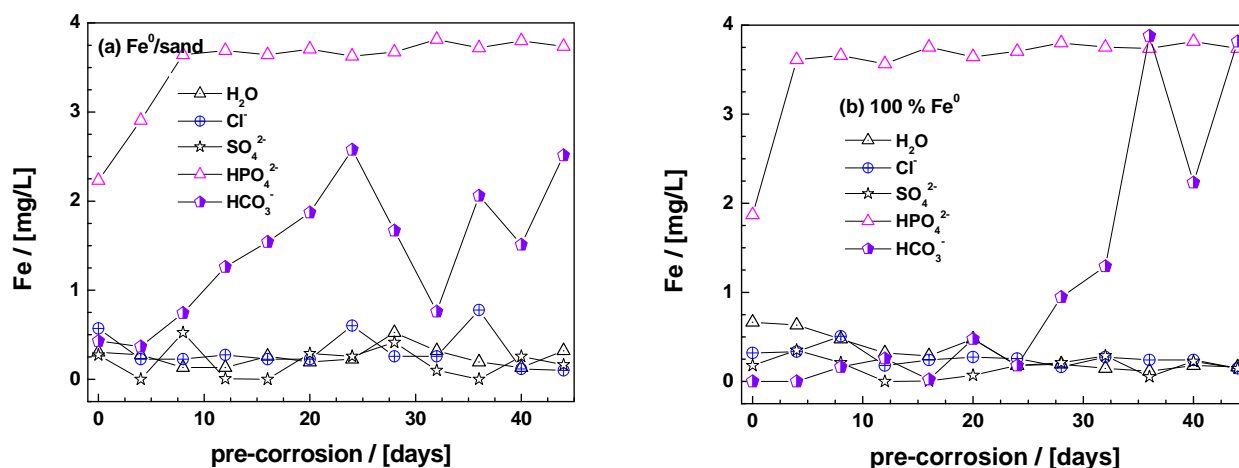


Fig. 6 Quantity of Fe released during MO discoloration in (a) Fe⁰/sand system and (b) 100% Fe⁰ system.

surfaces of the adsorbents, also an increase in pH leads to the modification of the pi (II) system delocalization pattern. They concluded that, the uptake of methyl orange on several adsorbents was similarly found to be favoured at lower pH. This confirms why MO discoloration was best in water and chloride medium with pH turning towards neutral region.

The concentration of iron released in to solution in the Fe⁰/sand and 100% Fe⁰ during discoloration of MO over the pre-corrosion period is shown in Figs. 6a and b.

For the two systems, the trend in iron release is the same with HPO₄²⁻ and HCO₃⁻ containing solutions highest amounts of iron. While this amount is constant from the second day of pre-corrosion for HPO₄²⁻, it increases steadily with time of pre-corrosion for HCO₃⁻. The amounts released are much higher than in the case of MB. This is probably due to the fact under strong basic conditions created by MO, HPO₄²⁻ and HCO₃⁻ easily form precipitates with Fe surface (they do not corrode the iron as their solutions were very clear during experiments) which are easily dissolved by reagents used in iron determination. Conversely, the iron released in the other anion containing solutions was negligible for the two systems as most of the iron charged species (corrosion products) produced were consumed by MO.

5. Conclusions

The impact of HPO₄²⁻, HCO₃⁻, SO₄²⁻, Cl⁻ and H₂O pre-generated iron corrosion products on the functioning of Fe⁰/H₂O systems for contaminant removal was investigated. The tested contaminants were methylene blue and methyl orange using Fe⁰/sand mixture and 100% Fe⁰ systems. The discolorations of the dyes, the variation of pH of the different systems as well as iron released in to solution were used to characterize each system. Water was used as the reference system. Results show that larger discoloration efficiencies were achieved in the Fe⁰/sand compared to the pure Fe⁰ system for MB. It is also seen that varying the pre-corrosion time from 0 to 44 days mostly has low impact on the MB discoloration efficiency for individual anions. MO also showed that larger discoloration efficiencies in the two systems. Contrary to MB, varying the pre-corrosion time from 0 to 44 days has an impact on the MO discoloration efficiency for individual anions. MO discoloration efficiency with all tested anions was all lower than that of the H₂O-reference but higher for MB. The pH of each system was the controlling factor in discoloration. MB discoloration was favoured at higher pH while MO discoloration was favoured at low pH (almost neutral). The presence of HPO₄²⁻ and HCO₃⁻ showed a significant negative impact on the discoloration of MO than MB

by Fe⁰/H₂O systems releasing much iron in to solution.

This work is very useful for design of Fe⁰ based Permeable Reactive Barriers, particularly filters for small homes and communities.

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