



Characterizing the ion-selective nature of Fe⁰/H₂O systems in batch experiments



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ABSTRACT

The effect of the ionic charge on the efficiency of Fe⁰/H₂O systems for dye discoloration was investigated in quiescent (0 rpm, 45 d) and shaken (75 rpm, 14 d) batch experiments. Tested systems for each dye were: (i) pure sand, (ii) pure Fe⁰, (iii) pure MnO₂, (iv) Fe⁰/sand, and (v) Fe⁰/MnO₂. Tested dyes were methylene blue (MB/cationic), orange II (O-II/anionic) and reactive red 120 (RR 120/anionic). Used initial dye molar concentration was 31 μM. Each system was characterized by the extent of dye discoloration (%) and the variation of the pH value. Results from pure material systems clearly demonstrated a discoloration selectivity that is to a large part due to electrostatic interactions between dye molecules and tested aggregates. The discoloration efficiency in Fe⁰-based systems confirmed the ion-selective nature of Fe⁰/H₂O systems. The extent of dye discoloration in individual systems depended on various concurrent factors of which the availability of 'free' corrosion products for dye (adsorption and) co-precipitation appeared to be the most relevant. Results questioned the use of MB as model contaminant to test metal oxide-based adsorbent for water treatment.

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1. Introduction

Water treatment with metallic iron (Fe⁰) is a technology reported to have started in 1972 and further developed around 1990 [1]. On the contrary, water treatment with iron oxides is univocally recognized as a very old remediation technology [2]. This general perception of the Fe⁰ technology is difficult to conciliate with the evidence that, at the pH value of natural waters, the Fe⁰ surface is constantly shielded by an oxide scale, making the Fe⁰/H₂O system necessarily ion-selective [3–5]. Research on dye discoloration using both types of materials documents clearly this apparent controversy.

Adsorption onto iron oxides (nm, μm and mm in size) is a well-documented physical method for dye removal from aqueous solutions [6,7]. Its applicability is justified by its simplicity and its efficiency. The adsorption capacity of iron oxides for dissolved species can be attributed to the ability of surface hydroxyl groups to form a bond with molecules of the adsorbed species. At pH values of natural waters, the surface hydroxyl group is positively charged [8]. Thus, selectivity is an important parameter for the

efficiency of adsorption onto iron oxides. This key issue has been mostly properly addressed while testing iron oxides for dye removal. For instance, Saha et al. [7] tested seven different dyes in adsorption experiments using iron oxide nano-particles and reported on an enhanced adsorption of the dyes containing hydroxyl groups (OH). Tested dyes containing OH groups were erichrome black-T, bromophenol blue, bromocresol green and fluorescein. The three other dyes were methyl red, methylene blue (MB) and methyl orange. It is important to point out that MB adsorption onto iron oxides is not favourable and this is known for several decades [9].

In the remediation industry, metallic iron (Fe⁰) is currently regarded as an 'environmentally friendly strong reducing agent' [1,10,11]. Fe⁰ has been accordingly widely studied for dye discoloration in the last 18 years [12–22]. In this context, chemical reduction by Fe⁰ (direct reduction) is mostly considered the most important path of degradation [12,13]. However, it is universally recognized that adsorption precedes chemical reduction [17]. Thus, dyes exhibiting high affinities to iron oxides (e.g. containing OH groups) should be better degraded (e.g. chemically reduced) in Fe⁰/H₂O systems. Actually, Fe⁰ materials are manufactured and tested using MB, a cationic dye with little affinity to iron oxides [19,21]. On the other hand, MB has been recommended as an indicator for characterizing processes yielding contaminant

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removal in $\text{Fe}^0/\text{H}_2\text{O}$ systems [23–25]. This recommendation is based on the evidence that because of its low adsorptive affinity to iron oxide, early MB breakthrough is expected (and was observed) in Fe^0 -based column studies [5]. Thus, while comparing two Fe^0 materials in parallel column experiments, the most reactive will exhibit the earlier MB breakthrough [25].

Though the Fe^0 technology has been reported efficient for environmental remediation and water treatment [10,11,26–28], the presentation above suggests that a pivotal scientific issue as system's selectivity is still to be solved before an optimal application is realized. In particular, clarifying why MB with little affinity to the $\text{Fe}^0/\text{H}_2\text{O}$ system is quantitatively removed might help design better filtration systems.

The present study is a continuation of previous works to understand the operating mode of $\text{Fe}^0/\text{H}_2\text{O}$ systems. Previous works have mostly demonstrated that admixing Fe^0 to non expansive aggregate (e.g. MnO_2 , pumice, sand) is a pre-requisite for sustainable filtration systems [24,29]. Herein, orange II (O-II) and reactive red 120 (RR 120), two anionic azo dyes, are tested in parallel batch experiments with the cationic dye MB. Investigated operational parameters include (i) Fe^0 mass loading, (ii) MnO_2 addition and (iii) sand addition. The aim is to confirm the ion-selective nature of the $\text{Fe}^0/\text{H}_2\text{O}$ system as already demonstrated in column experiments [5] (Fig. 1). Quiescent and shaken batch experiments are performed.

2. Materials and methods

2.1. Solutions

2.1.1. Dyes

Methylene blue (MB), Orange II (O-II) and Reactive Red 120 (RR 120) are widely used as model contaminant to characterize the suitability of various systems for wastewater treatment [9,30–33]. Used dyes were of analytical grade. They are selected due to differences in (i) their molecular size and (ii) their affinity to iron oxides (Table 1). While MB and O-II are of comparable size, RR 120 is a significantly larger molecule. Ojstršek et al. [31] reported that RR 120 has approximately twice the molecule size of a simple dichloro-s-triazine dye Reactive Orange 4. The molecular weight of

Table 1

Some relevant physico-chemical characteristics of tested dyes. The dye molar concentration was $31.5 \mu\text{M}$. The corresponding weight concentrations (mg L^{-1}) of individual dyes are specified. "d" is the diagonal length of each dye. The value for RR 120 is explicitly given by Gally et al. [33]. While MB and O-II molecular sizes are smaller than the micropore size (1.5 nm) of activated carbons [30].

Dye	Symbol	Nature (pH 8.2)	M (g mol^{-1})	d (Å)	λ_{max} (nm)	[Dye] (mg L^{-1})
Methylene blue	MB	Cationic	319.85	≤ 15	664.5	10.1
Orange II	O-II	Anionic	350.32	≤ 15	485.0	11.0
Reactive Red 120	RR 120	Anionic	1469.98	26	515.0	46.3

Reactive Orange 4 is $781.47 \text{ g mol}^{-1}$, which is two times larger than that of O-II ($350.32 \text{ g mol}^{-1}$). To account for significant differences in molecular weights, it was essential to initiate the experiments with working solutions having the same molar concentration. The working solutions have a molar concentration of $31.5 \mu\text{M}$ and were weekly prepared by diluting a $3150 \mu\text{M}$ stock solution (e.g. 1000 mg L^{-1} MB) using the tap water of the city of Göttingen. Its average composition (in mg L^{-1}) was: Cl^- : 12.9; NO_3^- : 7.5; SO_4^{2-} : 35.5; Na^+ : 9.7; K^+ : 0.9; Mg^{2+} : 8.2; Ca^{2+} : 37.3. The pH value of the initial solution was 8.2. The used concentration $31.5 \mu\text{M}$ (e.g. 10 mg L^{-1} MB) was selected to approach the concentration range of natural waters (MB as model micro-pollutant).

2.1.2. Iron

A standard iron solution (1000 mg L^{-1}) from Baker JT[®] 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 Fe^{III} in solution to Fe^{II} . 1,10 orthophenanthroline was used as reagent for Fe^{II} complexation. Other chemicals used in this study included $\iota(+)$ -ascorbic acid and L-ascorbic acid sodium salt. Ascorbic acid also degrades dyes (in particular O-II) and eliminates interference during iron determination.

2.2. Solid materials

2.2.1. Metallic iron (Fe^0)

The used Fe^0 material was purchased from iPutech (Rheinfelden, Germany). The material is available as fillings with a particle



Fig. 1. Photographs of sand from column experiments fed by the three dyes (at $31.5 \mu\text{M}$) for three months: (left) orange II, (middle) methylene blue (MB) and (right) reactive red 120. It is noticeable that sand affinity for MB is high.

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