Evaluation of the effects of shaking intensity on the process of methylene blue discoloration by metallic iron

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Abstract

The term mixing (shaking, stirring, agitating) is confusing because it is used to describe mass transfer in systems involving species dissolution, species dispersion and particle suspension. Each of these mechanisms requires different flow characteristics in order to take place with maximum efficiency. This work was performed to characterize the effects of shaking intensity on the process of aqueous discoloration of methylene blue (MB) by metallic iron (Fe^0). The extent of MB discoloration by three different materials in five different systems and under shaking intensities varying from 0 to 300 min^{-1} was directly compared. Investigated materials were scrap iron (Fe^0), granular activated carbon (GAC), and deep sea manganese nodules (MnO_2). The experiments were performed in essay tubes containing 22 mL of the MB solution (12 mg/L or 0.037 mM). The essay tubes contained either: (i) no reactive material (blank), (ii) 0 to 9.0 g/L of each reactive material (systems I, II and III), or (iii) 5 g/L Fe^0 and 0 to 9.0 g/L GAC or MnO_2 (systems IV and V). The essay tubes were immobilized on a support frame and shaken for 0.8 to 5 days. Non-shaken experiments lasted for duration up to 50 days. Results show increased MB discoloration with increasing shaking intensities below 50 min^{-1}, a plateau between 50 and 150 min^{-1}, and a sharp increase of MB discoloration at shaking intensities ≥ 200 min^{-1}. At 300 min^{-1}, increased MB discoloration was visibly accompanied by suspension of dissolution products of Fe^0/MnO_2 and suspension of GAC fines. The results suggest that, shaking intensities aiming at facilitating contaminant mass transfer to the Fe^0 surface should not exceed 50 min^{-1}.

Keywords: Adsorption; Co-precipitation; Methylene Blue; Shaking Intensity; Zerovalent Iron.

Introduction

The processes occurring at the interface Fe^0/H_2O are of great interest for the use of metallic iron in environmental remediation (e.g. in Fe^0/H_2O systems). A great deal of work has been reported in this area during the past 20 years [1-10]. Since the seminal work of Matheson and Tratnyek [1], a substantial amount of literature concerning the removal mechanism of various contaminants in Fe^0/H_2O systems has been published. This is not surprising given that: (i) the concept of permeable reactive barrier (PRB) is regarded as a significant advance in remediation technology [11,12], and (ii) iron PRBs have been demonstrated very efficient to mitigate contaminants in surface and ground waters [3-5]. Moreover, Fe^0/H_2O systems have been shown to effectively removed aqueous species of various nature. These include viruses [13], bacteria [14], inorganics [15,16], redox-sensitive organics [1,17], and redox-insensitive organics [18]. The large diversity of contaminants successfully removed in Fe^0/H_2O systems has recently prompted the revision of the initial "reductive transformation" concept [1,19]. The "reductive transformation" concept is obviously inconsistent with quantitative removal of redox-insensitive species. A new concept of "adsorption/co-precipitation" was introduced [20,21] stipulating that adsorption and co-precipitation are the fundamental mechanisms of contaminant removal in Fe^0/H_2O systems. The adsorption/co-precipitation concept is free of contradictions inherent to reductive transformation concept and explains some controversial experimental facts [20]. After the new concept, a Fe^0/H_2O system should be regarded as a zone of precipitating iron oxides. Each species (including contaminants) entering this zone will be first adsorbed onto and/or co-precipitated with iron (hydr)oxides but could undergo further abiotic transformations [including reduction by electrons from Fe^0, Fe^{II}, H_2/H and oxidation by Fenton reagents (Fe^{II} and H_2O_2), , which react to highly oxidizing $^{\bullet}$OH-radicals].

Regarding Fe^0/H_2O systems as zones of precipitating iron oxides suggests a profound analysis of the process of iron precipitation to better characterize its impact on contaminant removal under given relevant conditions. The adsorption of a contaminant onto a solid/H_2O interface involves a cascade of complex events occurring almost simultaneously: (i) transport of contaminant molecules from the bulk solution to the interface by diffusion or diffusion/convection processes; (ii) adsorption of contaminant molecules at the solid/H_2O interface; (iii) structural modifications of the fixed molecules together for high surface coverages and interactions of the incoming molecules with previously accumulated contaminant molecules [22]. In real natural systems, adsorption competition between molecules of different nature and molecular weight should be additionally considered.

The particularity of Fe^0/H_2O systems is three fold: (i) Fe^0 dissolution and precipitation yields a complex hydroxide and oxide mixture of unknown composition, (ii) Fe^0 and Fe^{II} are potential reducing agents, and (iii) the weight fraction of iron hydroxide and oxide particles increases from zero at the beginning to more or less higher proportions depending on the reaction progress. The net result is a multi-solid reaction system involving many types of solids of widely differing sizes and density (Fe^0 and various iron hydroxides/oxides). The large changes in the solid composition during the reaction will certainly influence the mass transfer of species to the Fe^0/H_2O interface and thereby play a significant role in the determination of reaction rates [23]. Moreover, in situ formed iron oxides are not inert with regard to contaminant removal [20,21]. Therefore, the effective mass transfer to the Fe^0/H_2O interface depends also on the affinity of iron hydroxides/oxides to the contaminants.

The process of iron oxide precipitation results from the hydrolysis and precipitation of Fe^{II}/Fe^{III} hydroxides followed by dehydration. Thereby, amorphous iron hydroxides [$Fe(OH)_2/Fe(OH)_3$] of very large surface areas are transformed to more crystalline oxides (FeOOH, Fe_2O_3, Fe_3O_4). The most characteristic feature is that the system undergoes an irreversible process controlled by hydrodynamic and physicochemical conditions. The present

work mainly pay the attention to the hydrodynamic conditions. In accelerated batch experiments, the reaction progress is largely dependent on the particle size of used Fe^0 and mixing procedure (agitating, shaking, stirring) and mixing intensity/speed. For a system in which new solid phases of various size and density are present, used mixing designs and mixing intensities should be one of the major sources of reported discrepancies. In fact mixing may hold original and new formed particles in suspension [24, 25], thereby disturbing the natural layered disposition of Fe^0 and Fe-oxides.

The two objectives of this work were: (i) to characterise the effect of shaking intensity on the process of methylene blue (MB) discoloration from the aqueous solution by metallic iron (Fe^0), and (ii) to identify the critical shaking intensity above which the process of MB discoloration by Fe^0 is significantly disturbed to be representative for natural situations. The critical shaking intensity is defined as the shaking intensity above which mixing operations induce more that speeding up external mass-transfer of contaminants from the bulk solution to the vicinity of Fe^0 (see next section). For this purpose separate discoloration experiments were performed in five different systems (i) metallic iron (system I), (ii) granular activated carbon (system II), (iii) manganese nodules (system III), (iv) "Fe^0 + GAC" (system IV), and (v) "Fe^0 + MnO_2" (system V). The results were comparatively discussed.

Background of the experimental methodology

In laboratory batch experiments mixing operations are mainly used for two purposes [24, 25]: (i) accelerating solid phase dissolution (process I), and (ii) accelerating mass transfer of solute to a solid/liquid interface (process II). The latter aspect includes efforts to keep reactive surface in suspension (process III). Depending on the aqueous chemical reactivity of the solid phase and the mixing intensity, process I, II and III are more or less likely to occur. For an inert solid phase as granular activated carbon (GAC) process I may not occur. But for reactive solid phases (Fe^0, MnO_2) process I through III may simultaneously occur depending on the mixing intensity. With other words, in a Fe^0/H_2O system mixing operations may induce at

least two antagonistic effects: (i) mass transfer to the Fe^0/H_2O interface and (ii) accelerated Fe^0 dissolution. Mass transfer to the Fe^0/H_2O interface has been largely considered while accelerated Fe^0 dissolution and its consequences on the process of contaminant removal have been almost overseen [20,21]. Moreover, vigorous mixing can also induce two negative effects: (i) breaking the material grains subject to friability (attrition) [25], and (ii) eliminating the diffusion inhibition of surface processes [26]. Tomashov and Vershinina [26] have shown that a sufficiently vigorous stirring and continuous renewal of the Fe^0 surface (scouring) eliminates the inhibition of the electrode-process step associated with adsorption or the formation of surface layers.

The transport of solutes in a Fe^0/H_2O system proceeds in two ways: advection and diffusion. Advection is caused by water flow, while diffusion is caused by the concentration gradient [27,28]. Diffusion of solutes in water corresponds with the chemical reactions, if advection due to the water flow is slow enough. Advection does not induce any additive process in the system but speeds up processes observable when diffusion is the sole transport mechanism (**Assumption 1**). Assumption 1 is the main argument on which this study is built. Thereafter, results achieved in non-disturbed systems (diffusion-controlled), relevant for environmental situations, should be reproducible under shaken conditions. Accordingly, relevant shaking intensities for Fe^0/H_2O systems should not induce further processes causing suspension of in-situ generated corrosion products or abrasion of oxide films. Clearly, applied mixing intensities should solely speed up external mass-transfer of contaminants from the bulk solution to the vicinity of the solid.

Materials and methods

Reagent and materials

Methylene blue (MB) is a traditionally favourite dye of choice for laboratory and technical purposes [29-31]. Its molecule has a minimum diameter of approximately 0.9 nm [31] and is used as redox indicator [32]. As positively charged ions, MB should readily adsorb onto

130 negatively charged surface. That is at pH > pH_{pzc}; pH_{pzc} being the pH at the point of zero
131 charge [33]. The used initial concentration was 12 mg L^{-1} (~0.037 mM) MB and it was
132 prepared by diluting a 1000 mg L^{-1} stock solution. All chemicals were analytical grade.
133 The used Fe^0 material is a readily available scrap iron. Its elemental composition was
134 determined by X-Ray Fluorescence Analysis and was found to be: C: 3.52%; Si: 2.12%; Mn:
135 0.93%; Cr: 0.66%. The material was fractionated by sieving. The fraction 1.6 - 2.5 mm was
136 used. The sieved Fe^0 was used without any further pre-treatment.
137 The used granular activated carbon (GAC) from LS Labor Service GmbH
138 (Griesheim/Germany) was crushed and sieved. The particle sized fraction ranging from 0.63
139 to 1.0 mm was used without further characterization.
140 Manganese nodules (MnO_2) collected from the deep sea was crushed and sieved. An average
141 particle size of 1.5 mm was used. Its elemental composition was determined by X-Ray
142 Fluorescence Analysis and was found to be: Mn: 41.8%; Fe: 2.40%; Si: 2.41%; Ni: 0.74%;
143 Zn: 0.22%; Ca: 1.39%; Cu: 0.36%. These manganese nodules originated from the pacific
144 ocean (Guatemala basin: 06°30 N, 92°54 W and 3670 m deep). The target chemically active
145 component is MnO_2, which occurs naturally mainly as birnessite and todorokite [34].
146 **Rationale for choice of test conditions**
147 Materials selected for study were known to be effective for adsorbing MB (GAC), discoloring
148 MB (Fe^0, MnO_2) or delaying the availability of iron corrosion products in Fe^0/H_2O systems
149 (MnO_2) [35]. MB co-precipitation with in situ formed iron corrosion products was
150 demonstrated to be the main mechanism of discoloration [36].
151 Table 1 summarises the function of the individual materials and gives the material surface
152 coverage in individual reaction vessels. The detailed method for the calculation of the surface
153 coverage (θ) is presented by Jia et al. [18]. The minima of reported specific surface area
154 (SSA) values of the adsorbents were used for the estimation of surface coverage. The Fe^0 SSA
155 was earlier measured by Mbudi et al. [37]. The value 120 $Å^2$ is considered for the molecular

cross-sectional area of MB [31]. From Tab. 1 it can be seen that, apart from Fe^0 ($\theta = 18.8$), all other materials were present in excess "stoichiometry" ($\theta \leq 0.13$). This means that the available surface of Fe^0 could be covered by up to 18 mono-layers of MB, whereas the other materials should be covered to less than one fifth with MB ($\theta = 1$ corresponds to a mono-layer coverage). Therefore, depending on the initial pH value and the affinity of MB for the individual materials (pH_{pzc}) and the kinetics of MB transport to the reactive sites (material porosity, shaking intensity), the MB discoloration should be quantitative for sufficient experimental duration. A survey of the pH_{pzc} values given in Tab. 1 suggests that MB adsorption onto all used adsorbents should be favourable because the initial pH was 7.8. At this pH value all surfaces are negatively charged; MB is positively charged. Because the available Fe^0 surface can be covered by up to 18 layers of MB, a progressive MB discoloration in presence of Fe^0 is expected.

Discoloration studies

Batch experiments with shaking intensities varying from 0 to 300 min^{-1} were conducted in essay tubes for experimental durations varying from 0.83 to 50 days. The essay tubes were immobilized on a support frame and shaken for 0.8 to 7 days. A rotary shaker HS 501 D from "Janke & Kunkel", DCM Laborservice, with a maximum shaking intensity of 300 min^{-1} was used. A non-disturbed experiment was conducted for 25 and 50 days. The batches consisted of 0 to 9.0 g L^{-1} of a material (GAC, Fe^0, MnO_2 systems I, II and III) or 5 g L^{-1} Fe^0 and 0 to 9.0 g L^{-1} GAC (system IV) and MnO_2 (system V) respectively. A reaction time of 25 d for the non-disturbed experiment was selected to allow a MB discoloration efficiency of about 80% in the system with Fe^0 alone. The experiment with 50 d reaction time targeted a better characterization of system V (Fe^0 + MnO_2). The extent of MB discoloration in the five systems was characterized under various shaking intensities. For this purpose 0.0 to 0.20 g of Fe^0 and the additives were allowed to react in sealed sample tubes containing 22.0 mL of a MB solution (12 mg L^{-1}) at laboratory temperature (about 20° C). Initial pH was ~7.8. After

equilibration, up to 3 mL of the supernatant solutions were carefully retrieved (no filtration) for MB measurements (no dilution). In the experiments at shaking intensities > 150 min^{-1} the samples were centrifuged at 5000 min^{-1} for 20 min prior to spectrophotometric analysis [38].

Analytical methods

MB concentrations were determined by a Cary 50 UV-Vis spectrophotometer (Varian) at a wavelength of 664.5 nm using cuvettes with 1 cm light path. The pH value was measured by combined glass electrodes (WTW Co., Germany). Electrodes were calibrated with five standards following a multi-point calibration protocol in agreement with the current IUPAC recommendation [39].

Each experiment was performed in triplicate and averaged results are presented.

Results and Discussion

After the determination of the residual MB concentration (C) the corresponding percent MB discoloration was calculated according to the following equation (Eq. 1):

$$P = [1 - (C/C_0)] * 100\% \quad (1)$$

where C_0 is the initial aqueous MB concentration (about 12 mg L^{-1}), while C gives the MB concentration after the experiment. The operational initial concentration (C_0) for each case was acquired from a triplicate control experiment without additive material (so-called blank). This procedure was to account for experimental errors during dilution of the stock solution, MB adsorption onto the walls of the reaction vessels and all other possible side reaction during the experiments.

Evidence for the effect of shaking on the process MB discoloration

Preliminary qualitative experiments at 300 min^{-1} showed that the MB solution in the essay tubes in all systems became very turbid due to particle attrition (breaking the grains of GAC, MnO_2) or suspension of in-situ generated iron oxides (Fig. SC1 – supplementary Content). In systems IV and V (see table 2), suspended iron oxides may compete with MB for adsorption site on GAC or MnO_2. Attrition of GAC and MnO_2 certainly increases the surface area of the

adsorbents, accelerating the MB adsorption kinetics. Keeping in mine that relevant mixing operations should solely provide a uniform distribution of the MB in the solution (Assumption 1), further experiments targeted at better characterizing the effects of shaking intensity on the process of MB discoloration.

Effects of the shaking intensity on the MB discoloration in investigated systems

Figure 1 compares the extent of MB discoloration in the five investigated systems as the shaking intensity varies from 0 to 300 min^{-1} for an experimental duration of 24 h (1 d).

The observed general trend can be summarized as follows: (i) shaking at 50 min^{-1} significantly increases the extent of MB discoloration in all systems comparatively to non-disturbed experiments; (ii) increasing the shaking intensity from 50 to 200 min^{-1} has no significant effect on MB discoloration (except for system II); (iii) increasing the shaking intensity from 200 to 300 min^{-1} resulted in total MB discoloration for all systems except system I.

Interestingly, the expected lower MB discoloration in system V relative to system I could not be observed at all tested shaking intensity for 1 d. In other words, the well-documented reductive dissolution of MnO_2 by Fe^{II} [40,41] could not be observed. Therefore, shaking operations definitively significantly influences the mechanism of contaminant removal in Fe^0/H_2O systems.

The increased discoloration efficiency of system II at 200 min^{-1} comparatively to system IV suggests that suspended corrosion products have impaired MB discoloration by competing for GAC adsorption sites. Accordingly, fines from GAC which are responsible for increased discoloration at a shaking intensity of 200 min^{-1} in system II are (at least partly) covered by suspended corrosion products in system IV yielding lower MB discoloration. At 300 min^{-1} enough fine are present for total MB discoloration despite the inhibitory effects of suspended corrosion products. The fact that MB discoloration was the lowest in system I (Fe^0 alone) is consistent with the hypothesis of discoloration inhibition by suspended corrosion products.

With regards on the mechanism of MB discoloration [36] it should be considered that suspended corrosion products are kept in the solution and their polymerisation is impaired yielding low precipitation and thus, low extent of MB co-precipitation.

The fact that the well documented impact of MnO_2 on the process of MB discoloration (MB co-precipitation) by Fe^0 could not be experimentally observed could suggest that, for a mass of 5 g/l, a reaction time of 1 day was too short (**Assumption 2**). Before testing the validity of assumption 2, the results of shaken experiments for 5 days should first be presented and compared to that of non-disturbed experiments for 25 days. Kurt [38] demonstrated increased MB discoloration with increased shaking time.

Effects of shaking intensity on the kinetics of MB discoloration

Figure 2 compares the extent of MB discoloration as function of material loading in systems I, II and III under non-disturbed conditions for 25 days (Fig. 2a) and at a shaking intensity of 150 min^{-1} for 5 days (Fig. 2b). The results showed that under non-disturbed conditions less than 60 % of the initial amount of MB could be discoloured in all systems and Fe^0 was the most efficient material (58 %). The order of increasing discoloration efficiency was MnO_2 < GAC < Fe^0. At mass loadings ≥ 8 g/L the discoloration efficiency of GAC and Fe^0 were very comparable. This observation can be explained by the porous nature of GAC: slow intra-particle diffusion [25].

Under shaken conditions, Fe^0 was clearly the less efficient material and its maximal discoloration efficiency was 50 %. This result confirms that shaking is someway inhibiting for the process of MB discoloration. The discoloration efficiency for MnO_2 and GAC was larger than 60 %. The order of increasing discoloration efficiency was Fe^0 < MnO_2 < GAC. It is important to note that: (i) MB discoloration was completed in the presence of GAC for mass loadings > 5 g L^{-1}, and (ii) in all the systems a plateau was observed for loadings > 4.5 g L^{-1}. This plateau corresponds to slow processes that can not be significantly accelerated under the experimental conditions (150 min^{-1}, 5 days). This conclusion is supported by the fact that an

higher discoloration efficiency could be observed under non-disturbed conditions with Fe^0 for 25 days. As all materials were at the bottom of the essay tubes a slow process common to all systems can be inter-particle MB diffusion to the material (re)active sites. For Fe^0 additional slow processes are the oxidative dissolution of Fe^0 (chemical reaction) and the MB diffusion across the oxide film on Fe^0 surface [23]. For MnO_2 the additional slow process can be the reductive dissolution (yielding Mn^{II} species) or MB intra-particle diffusion to the reactive site. For porous GAC possible slow processes are MB inter-particle and intra-particle diffusion.

Figure 2 clearly shows that shaking accelerates the kinetics of MB transport to the surface of GAC and MnO_2 yielding higher discoloration efficiency relative to non-disturbed systems. Thereby GAC is always more efficient than MnO_2. Therefore, assumption 1 is verified for GAC and MnO_2. As concerning the system with Fe^0, it is obvious that shaking the system for at 150 min^{-1} for 5 days was not sufficient to achieved more than 50 % MB discoloration . These results may suggest either that (i) iron corrosion was too slow to produce enough corrosion products for MB co-precipitation, (ii) the kinetics of corrosion products precipitation was too high to induce quantitative MB co-precipitation, or (iii) in-situ formed corrosion products are kept suspended in the solution (co-precipitation occurs to a lesser extent). To bring more clarity in this issue, the effect of MnO_2 on MB discoloration by Fe^0 (systems I and V) in non-disturbed experiments and experiments at 150 min^{-1} for 5 days were compared.

Effects of shaking intensity on MB discoloration in $Fe^0/MnO_2/H_2O$ systems

Figure 3 compares the extent of MB discoloration as function of material loading in systems I, III and V under non-disturbed conditions for 25 days (Fig. 3a) and at a shaking intensity of 150 min^{-1} for 5 days (Fig. 3b). The results of systems I and III have already been discussed (Fig. 2). This section will focus on system V to test the validity of assumption 2.

Figure 3a clearly shows that under non-disturbed conditions, MB discoloration is inhibited in the presence of MnO_2 as expected. However, this inhibition is limited to low MnO_2 mass

286 loadings (≤ 4.5 g/l). The initial discoloration efficient of 48 % at 0 g/l MnO_2 decreases to 13
287 % at 1.1 g/l MnO_2 and then increases with increasing MnO_2 mass loading. The fact that the
288 discoloration efficiency at MnO_2 mass loading > 4.5 g/l was higher than in both system I and
289 system III (Fig. 3a) suggests that MB serves as redox indicator [32] to evidence extensive
290 oxidation of Fe^{II} to Fe^{III} in the presence of large amounts of MnO_2. Because the experiments
291 were performed under oxic conditions, the observed reducing conditions should be regarded
292 as a transition state afterwards the colorless Leuco-Methylene Blue (LMB) is backwards
293 oxidized to MB by diffused molecular oxygen. Note that, in his experiments for 35 days using
294 20 mg/l MB and the same experimental conditions, Noubactep [36] could not observed the
295 redox indicator properties of MB but a slight further decrease of MB discoloration with
296 increasing MnO_2 mass loading. The redox indicator properties of MB was also not observed
297 in shaken experiments (Fig. 3b). Hence, the merit of non-disturbed experiments to evidence
298 theoretically foreseeable processes [42] is underlined here.
299 Figure 3b shows no significant effect of MnO_2 on the process of MB discoloration by Fe^0. It
300 can be seen that the extent of MB discoloration remains constant to approximatively 40 %
301 when the MnO_2 loading increases from 0 to 9 g/l. Therefore, assumption 2 is not verified,
302 showing that shaking disturbs the process of iron precipitation and thus the process of MB co-
303 precipitation with iron corrosion products. On the other side, the redox indicator properties of
304 MB are not also evidenced as discussed above.
305 Figure 4 compares the MB discoloration efficiency in system V after 25 and 50 days. It is
306 very interesting to see that for sufficient long experimental duration (50 d), MB discoloration
307 is quantitative for all MnO_2 loadings (≤ 9.1 g/l). This result corroborates the ability of non-
308 disturbed experiments to evidence theoretically foreseeable processes. Accordingly mixing
309 operation may accelerate investigated process in such a way that important aspects are
310 overseen. Two examples could be given in this study: (i) the well-documented redox indicator

properties of MB [32], and (ii) the reductive dissolution of MnO_2 inducing delay in the availability of free corrosion products for MB co-precipitation [36].

Conclusions

The effects of shaking intensity on the process of MB discoloration was characterized in a sequence of experiments. The working hypothesis was that any relevant mixing operation for real world situations should solely accelerate the diffusive transport of MB from the aqueous solution to the interface solid/H_2O. The results indicated that shaking intensities ≥ 50 min^{-1} lead to a suspension of in-situ generated iron corrosion products and to a delay of the process of MB co-precipitation. More importantly, apart from non-disturbed systems, none of the tested experimental conditions could reproduce the well-documented reductive dissolution of MnO_2 by Fe^{II} species [40,41] which would have been reflected by a delay in MB co-precipitation by Fe^0 in the presence of MnO_2. Finally, non-disturbed experiments could evidence the well-documented redox indicator properties of MB. Mixing intensity < 50 min^{-1} were not tested, but the complexity of mixing operations on processes in Fe^0/H_2O systems could be unambiguously evidenced. Generally, the mixing intensity is considered of utmost importance when it leads to attrition of the reactive media [25]. However, even this aspect is not usually taken into account in most studies, and mixing intensities higher than 300^{-1} min have been used in characterising redox processes in Fe^0/H_2O systems [43,44].

Implication for future works

As part of any proposed process, the fundamentals of the reaction need to be investigated to aid in the optimisation of the process [1,45]. The present work has unambiguously shown the influence of shaking intensity on the process of contaminant removal in Fe^0/H_2O systems on the example of methylene blue discoloration by metallic iron (Fe^0). It can be expected that other mixing procedures (stirring, agitating, vortex) have similar disturbing impacts. These disturbing impacts are yet to characterise and consider for further technology development.

The results of the present work have shown that, while using mixing operations as a tool to accelerate the reaction kinetics and achieve elevated removal efficiencies within relative short times, a severe bias was introduced. The net effect of elevated mixing intensities is two fold: (i) to inhibit the precipitation of iron oxides in the vicinity of Fe^0 by favouring the transport of Fe^{II} and Fe^{III} species away from the Fe^0 surface, and (ii) to sustain suspension of initial corrosion products and delay quantitative precipitation.

Given the large diversity of mixing devices used in experiments for contaminant removal in Fe^0/H_2O, the critical value of 50 min^{-1} given in this work has only an indicative value. For any mixing device preliminary investigations should help to identify the domain of mixing intensities for which mixing can be considered to facilitate contaminant transport to the interface Fe^0/H_2O without substantially disturbing the process of iron oxide precipitation. In general, experiments pertinent to subsurface Fe^0/H_2O systems should not be performed under shaking conditions higher than the groundwater flowing velocities.

Repeating reported experiments with several organic and inorganic compounds exhibiting various (i) redox reactivity, (ii) molecular sizes and (iii) affinity for iron oxides will enable a better comprehension of the influence of shaking on the process of contaminant removal for environmental remediation.

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Supplementary Content: Photographic documentation of turbid systems as results of shaking at 300 min^{-1} for 1 and 3 d.

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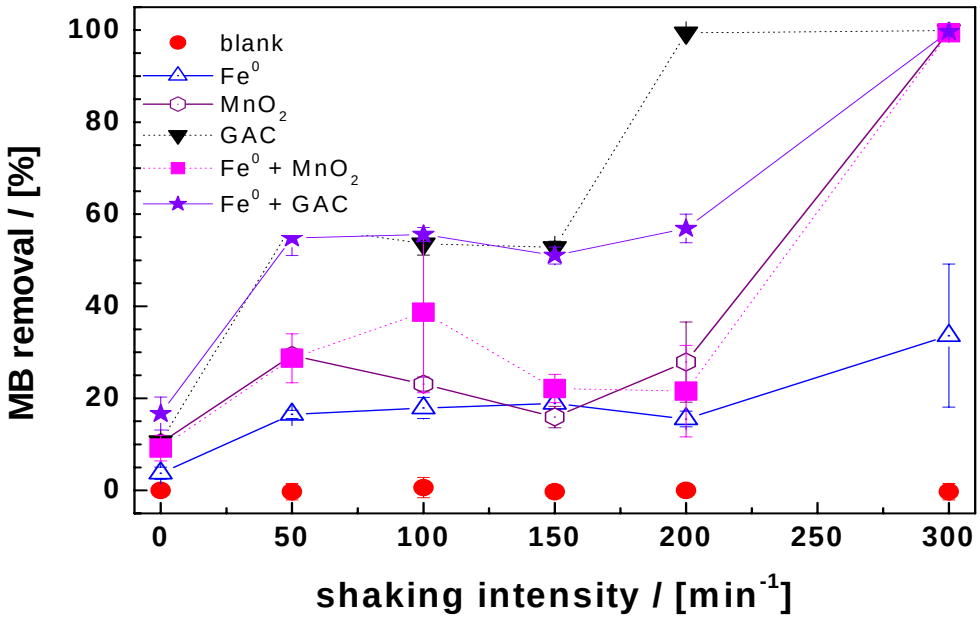
Table 1: Characteristics, surface coverage and function of the individual reactive materials of this study. Apart from Fe^0 the given value of specific surface area (SSA) for are the minima of reported data. The point of zero charge (pH_{pzc}) for all materials is lower than the initial pH value. Therefore, MB adsorption onto the negatively charged surfaces is favorable. The surface coverage is estimated using the method presented by Jia et al. [18]. The total surface that can be covered by the amount of MB present in 22 mL of a 0.037 mM is S_{MB} = 0.997 m^2. Modified after Noubactep [36].

System	**pH_{pzc}**	**SSA** ($m^2\ g^{-1}$)	**$S_{available}$** (m^2)	**Coverage** (-)	**Function**
Fe^0	7.6	0.29	0.032	18.8	MB co-precipitant
$Fe^0 + MnO_2$	-	-	4.432	0.13	-
MnO_2	2.0 - 6.0	40	4.4	0.14	delays CP availability
GAC	7.0 - 8.0	200	22	0.03	MB adsorbent
Fe^0 + GAC	-	(-)	22.032	0.03	-

Table 2: Overview on the investigated systems with the predicted and observed effects of mixing on their behaviour.

System	Composition	Expected effect of the material(s)	Predicted mixing effects	Observed mixing effects
I	Fe^0	MB co-precipitation	scouring	suspension of Fe-oxides
II	GAC	MB adsorption	attrition	increased adsorption
III	MnO_2	MB adsorption	attrition	increased adsorption
IV	Fe^0, GAC	increased MB discoloration	unknown	adsorption and co-precipitation
V	Fe^0, MnO_2	decreased MB discoloration	unknown	adsorption and co-precipitation

482 **Figure 1**



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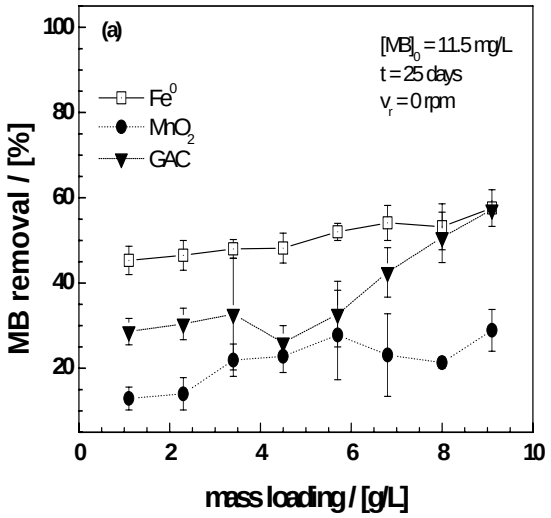
484 Figure 2



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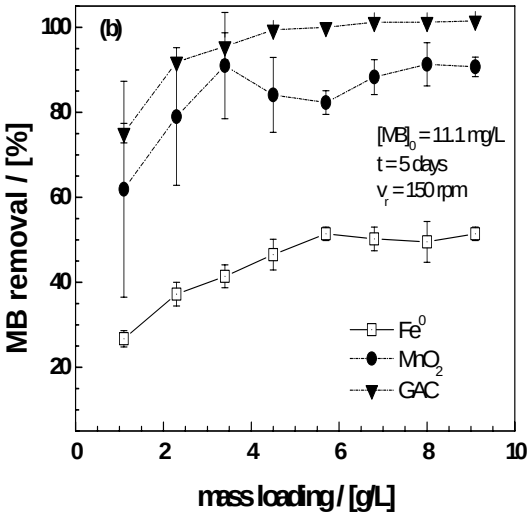

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489 **Figure 3**

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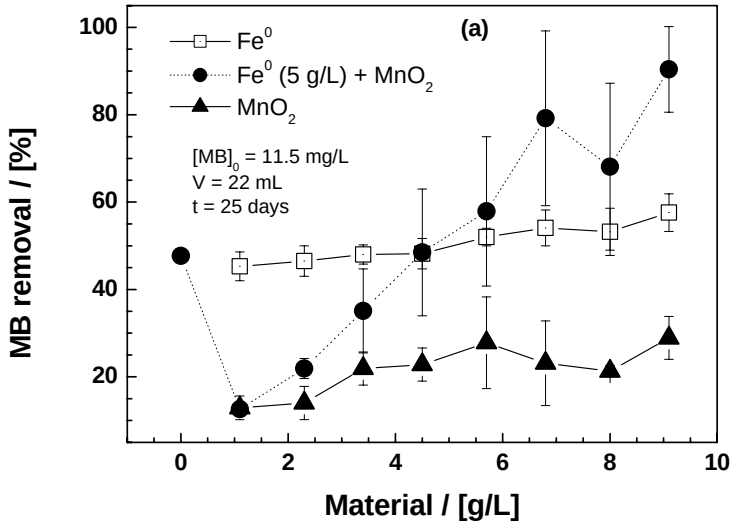

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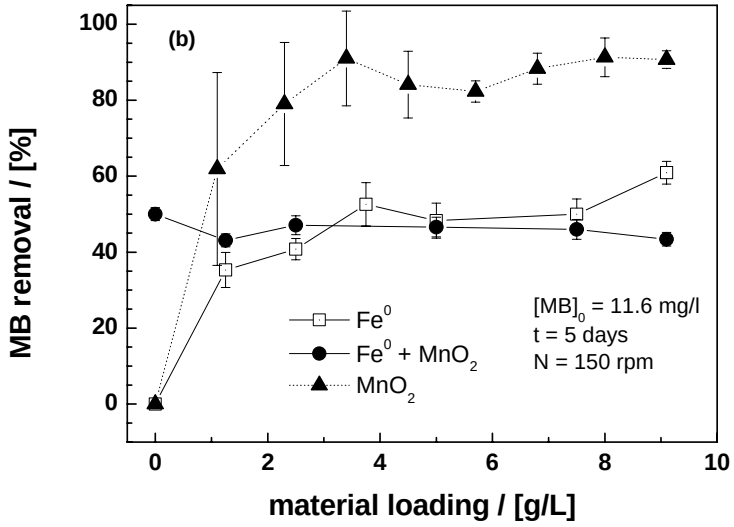

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495 **Figure 4**

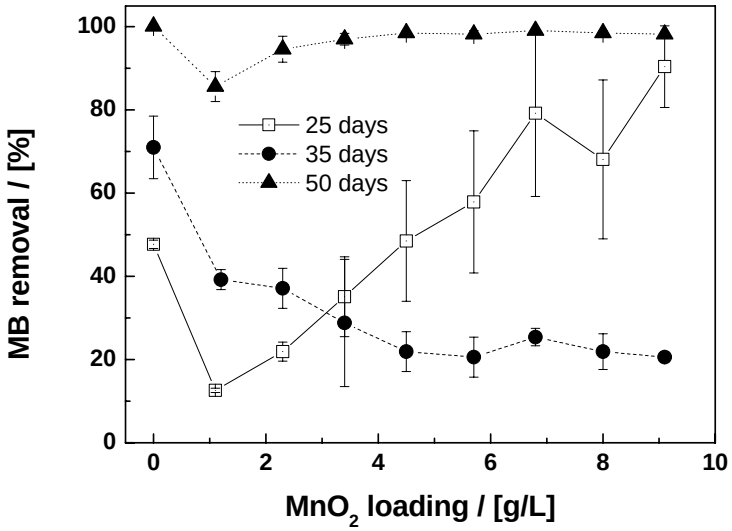

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Figure Captions

Figure 1: Methylene blue discoloration in all five systems for 24 hours as a function of the shaking intensity. The lines are not fitting functions, they simply connect points to facilitate visualization.

Figure 2: Methylene blue discoloration by the individual materials under non-disturbed conditions (a) and at a shaking intensity of 150 min^{-1} (b). The lines are not fitting functions, they simply connect points to facilitate visualization.

Figure 3: Methylene blue discoloration by Fe^0 as influenced by the presence of MnO_2 in non-disturbed experiments for 25 days (a) and experiments shaken at 150 min^{-1} for 5 days. the individual materials und non-disturbed conditions for 25 days. The lines are not fitting functions, they simply connect points to facilitate visualization.

Figure 4: Comparison of the extent of MB discoloration by Fe^0 (5 g/l) as influenced by the MnO_2 mass loading in non-disturbed experiments for 25, 35 and 50 days. It can be seen than if the experiments were performed only for 50 days, neither the redox indicator properties of MB (25 days) nor the delay in MB discoloration in the presence of MnO_2 (25 and 35 days) could be evidence (see text). It can be emphasized that, when using various Fe^0 mass loadings, mixing devices and reaction times, investigators have studies different processes and compared them to each other. The experiment for 35 days were performed with 20 mg/l MB [36]. The lines are not fitting functions, they simply connect points to facilitate visualization.

Supplementary Content

Evidence for the effect of shaking on the process MB discoloration

Figure SC1 shows the photographs of essay tubes containing all investigated systems in two experiments performed at a shaking intensity of 300 min^{-1}. The duration of the experiments were one and three days. The photographs show clearly that shaking at 300 min^{-1} induces suspension of Fe^0 and MnO_2 dissolution products. The photographs presented in Fig. 1 were made one week after the end of the experiments. Immediately at the end of the experiment, suspended fines could be observed in the essay tubes containing GAC alone, showing that the vibration induced by this shaking intensity was sufficient to produce fines from a chemically inert material (GAC). At this shaking intensity, the expected lower MB discoloration in system V (Fe^0 + MnO_2) relative to system I (Fe^0 alone) could not be observed. Therefore, assumption 1 (*Assumption 1: any shaking intensity relevant for natural situations should solely speed up processes observed under non-disturbed conditions*) is not verified suggesting that a shaken intensity of 300 min^{-1} is too high to be relevant for natural situations. Natural situations are mostly characterized be diffusion-controlled processed.

Figure SC1

Figure SC1: Photographs of shaken essay tubes containing from the left to the right: no additive (blank), Fe^0 alone, MnO_2 alone, GAC alone, Fe^0 + MnO_2 and Fe^0 + GAC. The essay tubes were shaken for 3 days (up) and 1 day (bottom). The photographs were made one week after the end of shaking operations.