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# Impact of Fe<sup>0</sup> amendment on methylene blue discoloration by sand columns

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#### HIGHLIGHTS

▶ Reliable methods for designing Fe<sup>0</sup> filtration systems are still lacking.

- ▶ Inert admixtures are mostly to account for construction width requirements.
- $\blacktriangleright$  A recent concept for Fe<sup>0</sup> bed design is verified here for the first time.
- ▶ The suitability of sand to sustain Fe<sup>0</sup> reactivity in dynamic systems is corroborated.
- ▶ The Fe<sup>0</sup> volumetric proportion should be between 30% and 50%.

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### ABSTRACT

The influence of metallic iron (Fe<sup>0</sup>) amendment on the efficiency of sand to discolor a 2.0 mg L<sup>-1</sup> methylene blue (MB) solution was investigated in column studies. MB was used as an indicator to identify the optimum Fe<sup>0</sup>/sand ratio for efficient filtration systems. Columns contained 0, 100 or 200 g of a Fe<sup>0</sup> material. The volumetric proportion of Fe<sup>0</sup> in the reactive layer of the columns with 100 g of material varied from 10% to 100%. Results showed that, Fe<sup>0</sup> amendment significantly impaired MB discoloration by sand for experiments lasting for up to 132 days. Early MB breakthrough in Fe<sup>0</sup>/sand columns delineated the paramount importance of particle cementation, which has caused preferential flow with a negative impact on discoloration efficiency. The most efficient Fe<sup>0</sup>/sand mixtures were the ones with 30–50% Fe<sup>0</sup> (v/v). These volumetric ratios correspond 33–41% weight ratios showing that the commonly used 1:1 weight ratio (50%) may not be optimal. Further research with compounds exhibiting different affinities to both Fe<sup>0</sup> and sand is needed before this observation can be generalized.

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1. Introduction

Metallic iron (Fe<sup>0</sup>) has been demonstrated in numerous studies to represent one of the best available materials for subsurface permeable reactive barriers [1–6]. Fe<sup>0</sup> is also a very efficient material for above-ground wastewater treatment and safe drinking water provision [7–9]. New applications of Fe<sup>0</sup> for water treatment usually involve extensive pilot-scale studies although several models have been developed for predicting the performance of Fe<sup>0</sup> material [10–13]. Moreover, despite 20 years of intensive research, the question as to whether iron should be used alone or mixed to a cost efficient material is yet to be properly addressed [14–24]. The suitability of  $Fe^0$  for water treatment arises from its aqueous instability (Eqs. (1)–(4)). Immersed  $Fe^0$  is oxidized by water according to Eq. (1):

(1)	$+H_2\uparrow$	$^{+} \Rightarrow \mathrm{Fe}^{2+}$	$Fe^0 + 2I$
(1	$+H_2\uparrow$	$^{+} \Rightarrow \mathrm{Fe}^{2+}$	$Fe^0 + 2I$

$$Fe^{0} + 1/2O_{2} + H_{2}O \Rightarrow Fe^{2+} + 2HO^{-}$$
 (2)

$$2Fe^{2+} + 1/2O_2 + H_2O \Rightarrow 2Fe^{3+} + 2HO^{-}$$
(3)

$$Fe^{n+} + nHO^{-} \Rightarrow Fe(OH)_n \Rightarrow FeOOH/Fe_xO_y$$
 (4)

In the presence of dissolved  $O_2$  the more favorable redox reaction is given by Eq. (2), but reaction following Eq. (1) still significantly occurs due to the abundance of water [25]. Moreover, it has been traceably shown that even under external oxic conditions, Fe<sup>0</sup> is oxidized by water (Eq. (1)) and Fe<sup>II</sup> by  $O_2$  (Eq. (3)) [26]. In other words, accelerated Fe<sup>0</sup> oxidation under oxic conditions results from Fe<sup>II</sup> consumption by  $O_2$  (Le Chatelier's principle) and not from any direct interactions between Fe<sup>0</sup> and  $O_2$  [26,27].





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