



# Novel sequential process for enhanced dye synergistic degradation based on nano zero-valent iron and potassium permanganate



Xiangyu Wang<sup>a</sup>, Peng Liu<sup>a</sup>, Minglai Fu<sup>b</sup>, Jun Ma<sup>c</sup>, Ping Ning<sup>a,\*</sup>

<sup>a</sup> Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China

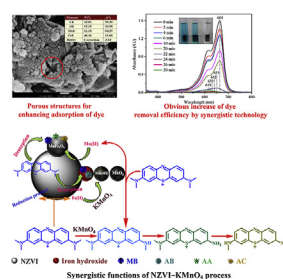
<sup>b</sup> Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

<sup>c</sup> School of Municipal and Environmental Engineering, State Key Laboratory of Urban Water Resources and Environment, Harbin Institute of Technology, Harbin 150090, China

## HIGHLIGHTS

- A novel sequential technology based on NZVI and  $\text{KMnO}_4$  was developed.
- Synergistic degradation of dye was 1.6–1.9 times more effective than sole methods.
- The *in situ* formed materials played a key role in the removal of dye.
- The adverse effect caused by dissolved Fe to ecosystem was avoided.
- Water chromaticity from excessive  $\text{KMnO}_4$  of the sole  $\text{KMnO}_4$  method was reduced.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel synergistic technology based on nano zero-valent iron (NZVI) and potassium permanganate ( $\text{KMnO}_4$ ) was developed for treatment of dye wastewater. The synergistic technology was significantly superior, where above 99% of methylene blue (MB) was removed, comparatively, removal efficiencies of MB with the sole technology of NZVI and  $\text{KMnO}_4$  at pH 6.39 being 52.9% and 63.1%, respectively. The advantages of this technology include (1) the *in situ* formed materials (manganese (hydr)oxides, iron hydroxides and Mn–Fe oxide), resulting in the stable and high removal efficiency of MB and (2) high removal capacity in a wide range of pH value. Compared with simultaneous addition system of NZVI and  $\text{KMnO}_4$ , MB removal was remarkably improved by sequential addition system, especially when  $\text{KMnO}_4$  addition time was optimized at 20 min. Analyses of crystal structure (XRD), morphological difference (FE-SEM), element valence and chemical groups (XPS) of NZVI before and after reaction had confirmed the formation of *in situ* materials, which obviously enhanced removal of MB by oxidation and adsorption. More importantly, the roles of *in situ* formed materials and degradation mechanism were innovatively investigated, and the results suggested that N– $\text{CH}_3$  bond of MB molecule was attacked by oxidants ( $\text{KMnO}_4$  and *in situ* manganese (hydr)oxides) at position C1 and C9, resulting in cleavage of chromophore. This study provides new insights about an applicable technology for treatment of dye wastewater.

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## 1. Introduction

Effluent from the textile, pharmaceutical, and printing industries often contain dyes, which represent an increasing environmental problem (Wang et al., 2015a, 2015b; Ai et al., 2010). Even

\* Corresponding author. Tel./fax: +86 871 65170906.  
E-mail address: [ningping58\\_2015@sina.com](mailto:ningping58_2015@sina.com) (P. Ning).

trace amounts of dyes can inhibit the sunlight and oxygen reaching the deep-water, hence resulting in the negative effect on growth of aquatic life critically (Wang et al., 2015b; Guo et al., 2014). Methylene blue (MB), one of the most widely applied dyes, is used as coloring paper and chemical analysis reagent (Qi et al., 2015; Kuan and Chan, 2012). The harmful effects of MB on human health and aquatic organisms have been well documented because it can arouse nausea, gastritis and potential carcinogenicity (Guo et al., 2014; Wang et al., 2014). The traditional technologies (including adsorption (Guo et al., 2014), electrochemistry (Ai et al., 2010), and biological degradation (Pazdzior et al., 2009)) applied for treatment of dye wastewater have been studied extensively. However, the defects of these methods (such as high operation costs and production of a concentrated sludge) make them not suitable for removal of MB (Qi et al., 2015). Consequently, developing an alternative technique with environmental friendliness, simple operation and high removal efficiency of dye is urgently required.

The application of nano zero-valent iron (NZVI) as adsorbent and reducing agent has been widely reported in environmental remediation. Compared with microsize ZVI, NZVI has received great concerns and has been successfully used in disposition of various pollutants such as heavy metals (Li et al., 2015), halogenated organic compounds (He et al., 2010), and antibiotics (Fang et al., 2011), due to its smaller particle size and larger specific surface area (Chen et al., 2015; Guan et al., 2015). Studies about removal of dyes using NZVI are already investigated by numerous researchers. Compared with other methods, NZVI can cleave chromophore ( $-N=N-$ ) and reduce dye molecules into intermediate products (Yun et al., 2013; Fujioka et al., 2016). Meanwhile, NZVI has a high adsorption capacity for dye and intermediates. Even though the reactivity of modified NZVI increases, aggregation of NZVI particles and unknown environmental effect of used reagents for modification of NZVI still exist. Furthermore, the removal efficiency of dye by NZVI would deteriorate with reaction time prolonged, which thus inhibits the large-scale application of NZVI.

Potassium permanganate ( $KMnO_4$ ) is already used in wastewater treatment for removal of dye (Xu et al., 2005), cyanotoxins (Li et al., 2014), and endocrine disrupting chemicals (Zhang et al., 2014), due to its relatively low cost and ease of handling. In addition,  $KMnO_4$  is attractive because its reduction product, manganese (Mn) dioxide, can serve as an oxidant, adsorbent and catalyst to enhance the removal of pollutants (Liu et al., 2010; Jiang et al., 2009). However, considering the unpleasant color of  $KMnO_4$ , only very low inlet concentration is allowed to avoid the appearance of chromaticity in the treated water (Zhang et al., 2014). It is therefore imperative to seek for one method with low dosage of  $KMnO_4$  to achieve the efficient removal of dye.

The advanced oxidation processes (AOPs) based on NZVI (e.g. NZVI/ $H_2O_2$ , NZVI/ $O_2$  and NZVI/ $O_3$ ) are regarded as the promising techniques for removal of pollutants (Xu and Wang, 2011; Xi et al., 2014; Thomas et al., 2008). However, a further optimization is necessary for these technologies due to the low selectivity of OH $\cdot$  and formation of toxic by-products (Han et al., 2013). The combination of NZVI and  $KMnO_4$  can be an alternative way to address above problems. Theoretically, the combined process of reduction and oxidation by NZVI and  $KMnO_4$  can efficiently improve removal efficiency of dye. Furthermore, the *in situ* formed materials by the reaction between released Fe(II) and  $KMnO_4$  may enhance removal of dye. Guo et al. (2015) found that  $KMnO_4$  could activate the reactivity of ZVI and hence remarkably enhance nitrate reduction. Btatkeu-K et al. (2014) evaluated the impact of  $MnO_2$  on the removal efficiency of MB by  $Fe^0$ , and found that  $MnO_2$  could enhance MB removal by  $Fe^0$ , due to (1) adsorption of MB by newly formed  $MnOOH$  and  $FeOOH$  and (2)  $Fe^0$  passivation being prevented via capturing soluble Fe(II) by  $MnO_2$ .

However, to the best of our knowledge, little information is accessible to the degradation of dye by NZVI– $KMnO_4$  process, which might not only avoid the deterioration of dye removal efficiency, but also address the adverse effect of NZVI and dissolved Fe to ecosystem. In addition, water chromaticity originating from  $KMnO_4$  would not be a concern. Accordingly, a detailed investigation of this technology is becoming a necessity for dye removal with lower dosage of NZVI and  $KMnO_4$ . The objectives of the current study are to (1) provide a novel and practical technology with high efficiency for treatment of dye wastewater, (2) explore the synergistic functions of NZVI– $KMnO_4$  process, (3) determine the *in situ* formed materials and propose their roles in enhancing MB removal, and (4) illustrate the reasonable degradation mechanism and pathways of dye with synergistic technology.

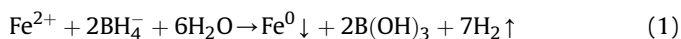
## 2. Materials and methods

### 2.1. Materials

All reagents were of analytical reagent grade or above unless otherwise stated and used as received without further purification. Ferrous sulphate heptahydrate ( $FeSO_4 \cdot 7H_2O$ ) and  $KMnO_4$  were supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Dyes, potassium borohydride ( $KBH_4$ ) and hydroxylamine hydrochloride ( $NH_2OH \cdot HCl$ ) were obtained from Kelong Chemical Reagent Co. Ltd (Chengdu, China). All solutions were prepared using Milli-Q water from a Millipore system.

### 2.2. Synthesis of NZVI

Nano iron was prepared as described in our previous study (Wang et al., 2013). In brief, NZVI was prepared by adding 100 mL 2.5 M  $KBH_4$  solution dropwise into 200 mL 0.5 M  $FeSO_4$  solution with vigorous magnetic stirring. And the solution was stirred for additional 10 min after  $KBH_4$  was added into  $FeSO_4$  solution completely. NZVI could be synthesized according to the following equation:



The obtained NZVI particles were rinsed 3 times with Milli-Q water and absolute ethanol, and dried in a vacuum drying oven under room temperature. Then, the prepared NZVI was restored in vials for further characterization and degradation experiments.

### 2.3. Batch experiments

Degradation experiments were conducted in 250 mL of reaction flasks which were filled with 100 mL MB solution. Reactions were initiated by quickly spiking fresh NZVI into pH-adjusted 100 mg  $L^{-1}$  MB solution (solution pH was not controlled during the experiments). After 20 min reaction between NZVI and MB, oxidation reaction proceeded with addition of  $KMnO_4$  powder into the mixed solution. The flasks were sealed with Teflon-lined rubber septum cap immediately once reactants were added into MB solution, and then placed on a rotary shaker at a speed of 150 rpm. At specific sampling time, 2.0 mL aqueous sample was withdrawn and filtered through a 0.45  $\mu m$  filter membrane, then terminated with 100  $\mu L$   $NH_2OH \cdot HCl$  (1.0 M) before analysis of the filtrates. Detailed procedures are presented in the Supplementary material. Series groups of batch experiments were performed to examine the effect of controlling factors including solution pH, addition time of  $KMnO_4$ , reactants dosage, initial MB concentration, and temperature on the effectiveness of MB removed by NZVI– $KMnO_4$  process.

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