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Textile wastewater decolorization by zero valent iron activated peroxymonosulfate: Compared with zero valent copper

Farshid Ghanbari [a], Mahsa Moradi [b,*], Mohammad Manshouri [b]

[a] Department of Environmental Health Engineering, School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran
[b] Department of Environmental Health Engineering, School of Public Health, Shahid Beheshti University of Medical Sciences (SBMU), Tehran, Iran

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ABSTRACT

Textile wastewater must be decolorized before discharging into the environment. In this study, peroxymonosulfate (PMS) was activated by zero valent iron (ZVI) to produce sulfate radical for degradation of organic compounds. The optimum condition for activation of PMS was provided in pH of 4 and 3000 mg/L ZVI. ZVI compared to zero valent copper (ZVC) was more effective in terms of COD and color removals. PMS and H_2O_2 performances were compared and the results showed that PMS had more efficiency in similar conditions. Simultaneous use of PMS and H_2O_2 synergically increased decolorization rate. The TOC and COD removal efficiencies of various processes were in the following order: ZVI–PMS–H_2O_2 ≥ ZVI–PMS > ZVI–H_2O_2 > ZVC–PMS > ZVC–H_2O_2. The average oxidation state (AOS) was considerably increased after oxidation processes using PMS and H_2O_2. This result indirectly proves biodegradability improvement of real textile wastewater. Finally, the oxidative processes were economically compared based on cost of chemicals.

Introduction

Textile mill is one of the largest groups of industries inducing intense water contamination. The effluents originated from textile mills are severely colored and contaminated with organic pollutants [1,2]. Color removal from textile wastewater has attracted much attention among scientific researchers and environmentalists. Color of textile wastewater is dominantly due to the presence of unfixed dyes that has been formerly used during the dying process. These unfixed dyes may affect the aquatic environment in an adverse manner.

Moreover, the presence of color in receiving waters is esthetically objectionable for consumers [1,3,4]. Many methods have been proposed for the treatment of textile wastewater being categorized into biological and physico-chemical processes. The reduction of color is the main objective of these treatment technologies. Complete decolorization is not achieved by biological processes due to toxicity of some dyes and their intermediates for microorganisms [5]. Adsorption and coagulation processes have disadvantages which include the need for adsorbent regeneration and also the chemical sludge generation [6]. In fact, these processes transfer organic pollutants from liquid phase to solid phase and are not destructive technologies [4,6]. Recently, Advanced Oxidation Processes (AOPs) have been used for decolorization of wastewater. These processes are based on the production of highly reactive radicals; commonly hydroxyl radicals with oxidation potential of 2.7 V [7,8]. Within homogenous systems, radical species can be generated through several ways including electron transfer during activation of oxidants by transitional metals, thermolysis, photolysis and sonolysis [9]. The most conventional homogenous AOP is the Fenton process in which H_2O_2 is activated by ferrous ion to produce the $HO^{\bullet}$ [10]. However, Fenton based processes have several limitations such as narrow range of pH in acidic condition (pH 2.8–3) and slow kinetics of ferrous ion regeneration. Alternatively, peroxymonosulfate (PMS) is a new oxidant for the degradation of organic pollutants. Activation of PMS by the transitional metals results in formation of sulfate radical ($SO_4^{\bullet-}$) with oxidation potential of 2.5–3.1 V [8,11]. PMS has some advantages in comparison with H_2O_2 such as application in wide range of pH and ability of oxidation of some organic chemicals without catalytic activation [12,13]. Zero valent iron (ZVI) is commonly used as a source of Fe^{2+} for catalytic decomposition of the peroxides. The use of ZVI has been shown to be successful in Fenton-like reagent for the

* Corresponding author. Tel.: +98 9126907929; fax: +98 2122432037.
E-mail address: moradi.env@gmail.com (M. Moradi).

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degradation of pollutants. ZVI can be oxidized to Fe^{2+} according to Eqs. (1) and (2), consequently producing sulfate radicals in presence of PMS [14].

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (1)$$

$$Fe + HSO_5^- + 2H^+ \rightarrow Fe^{2+} + HSO_4^- + H_2O \quad (2)$$

$$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + HSO_4^{\bullet -} + OH^- \quad (3)$$

There are few investigations on organic pollutants degradation by iron powder and PMS or persulfate. Hussain et al. studied the degradation of *p*-chloroaniline by persulfate and ZVI. They have stated that ZVI is an alternative source of ferrous ion to activate the persulfate [15]. Decolorization of real textile wastewater based on sulfate radicals has not still been studied. Besides, zero valent metals (especially copper) have rarely been considered for the activation of peroxides. Herein, we study the decolorization of real textile wastewater by PMS in presence of iron and copper powders. In addition, performance of PMS was compared with that of the H_2O_2 in terms of color, COD and TOC removals.

In this study, three goals are considered: (1) decolorization of real textile wastewater with PMS–ZVI at various conditions, (2) performance comparison of iron and copper metals as the activators, (3) comparison of PMS and H_2O_2 for the treatment of real textile wastewater.

Materials and methods

Wastewater sampling

The studied textile wastewater was collected from Kukma factory located in Abhar city, Iran and was stored in 4 °C. The characteristics of the studied textile wastewater are presented in Table 1.

Chemicals and reagents

All chemicals in this study were of analytical grade and used without any further purification. All solutions were prepared with deionized water. Sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2, 30%) and sulfuric acid (H_2SO_4, 98%) were obtained from Merck & Co. Oxone ($2KHSO_5.KHSO_4.K_2SO_4$) was purchased from Sigma Inc. as the source of PMS. Zero valent iron powder used in this study was with purity of 97% and 325 mesh that was purchased from Aldrich Company. Zero valent copper (ZVC) was purchased from Aldrich Inc. with purity of 99% and particle size of 14–25 μm.

Experimental procedures

The experiments were conducted at room temperature (at 23–26 °C) in 500 mL batch reactors. All the experiments were carried out on 300 mL textile wastewater sample. In each experimental run, specific dosages of ZVI or ZVC were added to the reactor. Afterwards, various amounts of PMS in form of the oxone were added to the systems; then the solution pH was quickly adjusted to desired level by adding either sulfuric acid or sodium hydroxide of 1 N. Then the reactors were placed on the shaker with 200 rpm. At selected time intervals, an appropriate amount of aliquot was taken from the reactor for analysis. The experiments of H_2O_2 were similar with those of the PMS. For color measurement, samples were immediately analyzed by spectrophotometer. For the measurement of organic matters, samples quenching was carried out using sodium nitrite and then they were analyzed by the TOC analyzer. All the experiments were repeated twice and the results of color value are the averages of at least three measurements with an accuracy of ±5% while the results of COD and TOC values are the averages of two measurements.

Table 1
Characteristics of real textile wastewater.

Parameters	Unit	Value
COD	mg/L	1550
TOC	mg/L	496
BOD_5	mg/L	280
Color	ADMI	3080
EC	mS/cm	3.81
TSS	mg/L	<50
Cl^-	mg/L	228
pH	–	5.65

Chemical analysis

The color of real textile wastewater was measured by American Dye Manufacturers Institute (ADMI) method using spectrophotometer (DR 5000-Hach). This method is preference for real wastewater which is independent of hue. Total organic carbon (TOC) was measured using a Shimadzu TOC analyzer (model TOC-V_{CHS}, Japan). COD values were determined by the colorimetric method in wavelength of 600 nm. BOD_5 and chloride values were measured based on Standard Methods [16]. Electrical conductivity and pH were measured by EC meter (Hach-MM374) and pH meter (Corning-model 345) respectively. The oxidant concentration (PMS and H_2O_2) was determined by iodometric method [17].

Results and discussion

Effect of pH on decolorization

The solution pH is a critical parameter in all chemical processes of wastewater treatment. Fig. 1 shows the effect of pH on decolorization of real textile wastewater in constant PMS concentration of 10 mM and 2000 mg/L ZVI. Zero valent iron is oxidized to ferrous ion at acidic conditions. Thus, ferrous ion is significantly introduced to solution at pH of 2, 3 and 4. As shown in Fig. 1, pH 4 provides the highest decolorization efficiency (57.7% in 150 min reaction time). At pH above 4, ferrous deactivation arises with formation of ferric hydroxide complexes that are highly stable and have a lower catalytic activity which leads to reduction of sulfate radical [18]. At pH above 7, oxidation process reached to minimum efficiency that was attributed to self-decomposition of peroxymonosulfate at alkaline pH and the decolorization was only 18.7% at pH 9 [19,20]. These results indicate that pH of 4 is the

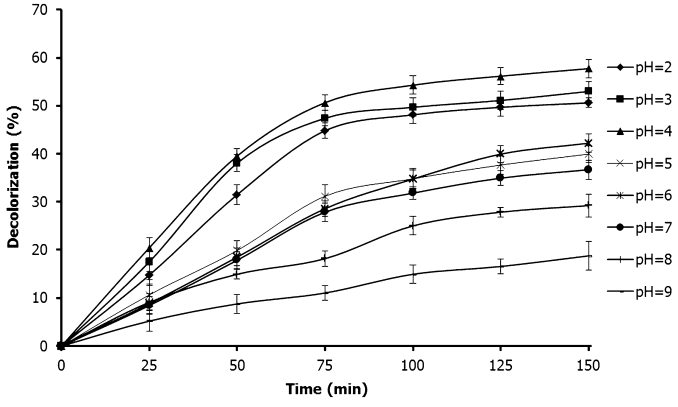

Fig. 1. The effect of pH on decolorization in 10 mM PMS and 2000 mg/L ZVI.