Materials and Design 119 (2017) 244–253

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Rapid malachite green degradation using $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ metallic glass for activation of persulfate under UV–Vis light

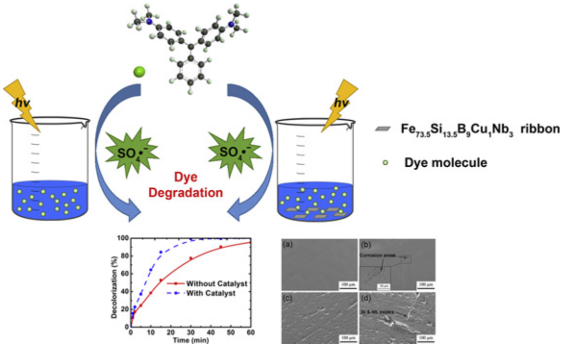
S.X. Liang [a], Z. Jia [a], W.C. Zhang [b], W.M. Wang [c], L.C. Zhang [a,]*

[a] School of Engineering, Edith Cowan University, 270 Joondalup Drive, Joondalup, Perth, WA 6027, Australia
[b] Environmental Protection Administration of Ji'an City, Ji'an, Jiangxi Province 343000, China
[c] School of Materials Science and Engineering, Shandong University, Jinan, Shandong 250061, China

HIGHLIGHTS

- Influence parameters of malachite green dye degradation using $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ metallic glass are investigated.
- First-order kinetic model fits well with malachite green degradation process.
- Inclusion of Nb and Si enhances the surface stability of $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$.
- High reusability with acceptable dye degradation efficiency is observed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 October 2016
Received in revised form 19 December 2016
Accepted 12 January 2017
Available online 13 January 2017

Keywords:
Metallic glass
Reusability
Surface stability
Persulfate
Malachite green
Degradation

ABSTRACT

In this work, it is the first time to report that $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ metallic glass having unique atomic structure was employed for activation of persulfate under UV–Vis light. The investigation evaluated the importance of influencing parameters, including dye concentration, persulfate concentration, ribbon dosage and light intensity, on malachite green (MG) dye degradation. The results reveal that 100% dye color removal with a reaction rate of $k = 0.0849\ \text{min}^{-1}$ could be achieved within 30 min under specific parameters control. In addition, surface decay behavior of the catalyst also plays a significant effect on the reusability and sustainability. The inclusion of Nb atom in $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ promotes enrichment of Si atom on the ribbon surface, causing the formation of Si and Nb oxides to further improve the surface stability on both of free and roller-contacted surfaces. The precipitations on reused ribbon surface are confirmed as α-Fe, iron oxide and Si, Nb oxides, revealing a high potential of catalytic reusability for wastewater treatment. The present work will open a new gate for further realizing the high performance of industrial water treatment using metallic glass.

1. Introduction

Amorphous alloys, also known as metallic glasses, with a short-range ordered and long-range disordered atomic structure have recently attracted increasing attention for researchers as advanced materials. For example, Al-based amorphous alloys with higher wear resistance

---

* Corresponding author.
E-mail addresses: l.zhang@ecu.edu.au, lczhangimr@gmail.com (L.C. Zhang).

http://dx.doi.org/10.1016/j.matdes.2017.01.039

and corrosion resistance are employed as coating by cold gas spray [1]. Fe-based amorphous alloys with high mechanical properties, soft ferromagnetic and high glass forming ability (GFA), exhibit super potential in industrial applications [2]. In addition to the easy alteration of chemical compositions, the amorphous alloys present a high surface stability and corrosion resistance in various applications [3], such as the high anticorrosion ability in strong acids or alkalis for Zr-based amorphous alloy [4]. Recently, due to the ultrafast water treatment efficiency and the superior chemical property [5], amorphous alloys are also treated as superior candidates for environmental wastewater remediation. It is found that the Fe—Si—B—Mo and Fe—Si—B metallic glasses present a very high potential for the acid orange II dye degradation [6,7]. Using Fe—B amorphous alloy as a catalyst exhibits 89 and 1.8 times faster than the commercial iron powder and Fe—B crystalline alloy, respectively, when treating the direct blue 6 dye [8]. The reusability of the amorphous alloys is also a very attractive catalytic performance in wastewater purification [5,9-11]. The reusability of the Fe—Si—B—Y powder in amorphous state is achieved to 13 cycles [11]. Fe—Si—B metallic glass exhibits 30 times of reusability while activating persulfate for methylene blue (MB) degradation [12]. The dye adsorption behavior of Fe—Si—B and Fe—Si—B—Cu—Nb amorphous alloys for brilliant red 3B-A has also been studied [13]. The Fe—B—Y metallic glass with weak atomic bonds of amorphous atoms presents a high reactivity in degrading Orange G dye [14]. Extensive endeavors due to different compositions of metallic glasses have been made for investigating the mechanism for water treatment, such as Mg-based [15–17], Co-based [18], and Fe-based alloys such as Fe—B [8], Fe—Si—B [19], Fe—Mo—S—B [6,20] and Fe—Si—B—Cu—Nb [21]. Therefore, the study of metallic glass as a catalyst for water remediation is an active and challenging topic.

The water treatment technology is a significant issue in industrial settings. In recent years, various water treatment processes have been established, such as biological methods (microorganisms, biosorption, *etc.*) [22,23], physical methods (adsorption on solid phases, ion exchange, *etc.*) [24,25] and chemical methods (ozonation, chemical precipitation, *etc.*) [26,27]. Among these methods, advanced oxidation processes (AOPs) have been extensively studied as a promising technique due to their superior degradation and mineralization efficiency on pollutants in wastewater [12,13,28–31]. Compared to other methods, most of the non-biodegradable compounds are easy to be mineralized to CO_2, small molecules or other harmless products [32,33]. For example, Jiang et al. [34] reported that bisphenol A removal rate in aqueous solution increased up to 97% by Fe^{2+}/persulfate and 100% by Fe^0/persulfate system; Jia et al. [29] employed nano-sized ZnO as a photocatalyst to degrade cibacron brilliant yellow 3G-P dye; Idel-aouad et al. [35] reported that 99.3 ± 0.2% decolorization and 84 ± 5% mineralization were achieved by using heterogeneous Fenton reaction for C.I. acid red 14 under rational conditions. It is recently reported that sulfate radicals ($SO_4{\bullet}^-$) with a high redox potential of 2.60 V are easy to be produced by UV [36], ultrasound [37], transition metal ions (such as Fe^{2+}) [38], or thermal activation [39] by persulfate. The produced sulfate radicals are relatively stable in water at neutral pH and can be homogeneously distributed in the aqueous solution [40]. On the other hand, the persulfate ($E^0 = 2.01$ V) with the benefits of convenient storage, pH-independence and low cost also can be solely used for degrading various organic pollutants [41]. Due to the superior properties of non-toxicity, effectiveness and low price [38,42], zero valent iron (ZVI) has been promising attracted by many researchers as a persulfate activation catalyst [34]. The ZVI can convert to Fe^{2+} through corrosion in persulfate or aqueous solutions under both aerobic (Eq. (2)) and anaerobic (Eq. (3)) conditions by the reactions Eqs. (1)–(4) [43]:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{1}$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{2}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{3}$$

$$Fe^0 + S_2O_8{}^{2-} \rightarrow Fe^{2+} + 2SO_4{}^{2-} \tag{4}$$

$$Fe^0 + 2S_2O_8{}^{2-} \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2SO_4{\bullet}^- \tag{5}$$

Thus, the ZVI can act as a slow releasing source of Fe^{2+} and also provide a novel way to generate sulfate radicals without involving iron ions (Eq. (5)) [44]. However, the high ferrous ions leaching rate will cause secondary pollution, which requires additional pressure to eliminate redundant ferrous ions [44]. Therefore, an appropriate Fe-based catalyst that features sustainable development is highly in demand for wastewater remediation.

Malachite green (MG), *i.e.* basic green 4 ($C_{23}H_{25}ClN_2$, 4-[(4-dimethylaminophenyl)-phenyl-methyl]-*N*,*N*-dimethyl-aniline), a cationic triphenylmethane dye, is one of the largest group of hazardous dyes. It is commonly utilized in the aquaculture industry as an effective fungicide [45], textile industry as a coloring agent [46] and industries of leather, paper and pharmaceutical owing to its low price, readily availability and high efficiency [47]. However, due to its genotoxic and carcinogenic nature, extensive studies report that MG has serious drawbacks when existing in the water, such as the potential influences on human reproductive and immune systems [48]. Therefore, it is significant to explore an effective technique of dye removal for remediating toxic components in MG solution.

In this work, the MG dye degradation and mineralization were investigated by using $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ metallic glass ribbons as a catalyst, an alternative Fe^{2+} releasing source, for activating persulfate under UV–Vis light. The influenced parameters on MG degradation and pseudo-first-order kinetic model were studied in detail. Moreover, recycling experiments were carried out to fully discuss the stability and feasibility of the $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ ribbons.

2. Experimental methods

2.1. Materials and chemicals

Malachite green dye was supplied by Ji'an Haomai Fine Chemical Industry Co., Ltd., China (Product Number: 150120). Fig. 1 shows the MG dye nature ability of self-conversion between MG molecules and MG leucocarbinol. The physical characteristics of MG are summarized in Table 1. The sodium persulfate ($Na_2S_2O_8$) was supplied by BDH Chemicals Ltd., Poole, England. Amorphous alloy $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ was manufactured by vacuum melt-spinning [49–51]. All the alloy ribbons having the thickness of 30–40 μm were cut into approximately 5 × 20 mm (brittleness). The 18.2 MΩ·cm Milli-Q water was employed throughout experiments for all aqueous solutions. All chemicals used in the experiments are in analytical grade and there is no need to further purification.

2.2. Catalyst characterizations

X-ray diffraction (XRD) was employed to analyze the structure and phase contents of the ribbons by using a PANalytical Empyrean diffractometer with Co-Kα radiation at ambient temperature. The scanning electron microscope (SEM) equipped with EDS detector (JEOL 6000, Japan) was used to investigate the surface topography and atomic composition. The surface characterization was also recorded by ultraviolet-visible diffuse reflectance spectrum (UV–Vis DRS) by a Lambda 35 UV–Vis Spectrometer using $BaSO_4$ as the reference (Shelton, CT, USA).

2.3. Analytical methods

All the initial dye solutions were freshly prepared before each experiment in order to minimize variance in concentration due to hydrolysis