Rapid reductive degradation of azo dyes by a unique structure of amorphous alloys

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An Fe-based amorphous alloy was found to significantly enhance the reductive degradation of an azo dye in aqueous solution. The surface-area normalized rate constant was up to $2.0 \text{ L m}^{-2} \text{ min}^{-1}$ at room temperature, an order of magnitude larger than any previously reported value. The activation energy of the degradation process was calculated according to the Arrhenius equation, and a much lower value than those previously reported was obtained. Valence band measurement indicated that a depressed valence band maximum and a widened empty band were established in the amorphous ribbon. The unique structure of the amorphous alloy is important – it may reduce the activation energy of the degradation process and enhance the activity of the electrons, thus accelerating the degradation process.

amorphous alloys, azo dyes, UV-visible spectrophotometer, degradation, activation energy

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Amorphous alloys have attracted increasing attention both for their fundamental scientific importance and the potential engineering applications for short-range ordered and long-range disordered atomic structure. This special structure gives amorphous alloys some advantages such as high strength, good corrosion resistance and certain unique functional properties, which are superior to those of their crystalline counterparts [1–5].

Degradation of azo dye effluents has also received increasing attention because the dyes are used extensively in the textile, leather and dyestuff industries [6]. Most azo dyes have complex aromatic structures that are highly resistant to microorganisms and recalcitrant to conventional biological wastewater treatment processes, and their degradation products are always highly carcinogenic [7–9]. Thus various physical and/or chemical methods, such as biological treatment, flocculation, adsorption and advanced oxidation processes (AOPs) have been tried to treat azo dye wastewater [10–13]. However, these methods have limita-

tions. It is difficult to control the conditions for biological processes and microorganism treatment to reach a satisfactory level of degradation; flocculation and adsorption merely transfer the pollutants to another phase rather than destroying them; and AOPs are usually not a convenient remediation technique because of their tight working conditions.

The zero-valent iron (ZVI) method and variations of this method using nanoscale ZVI (NZVI) particles have recently been intensively studied because ZVI is able to reduce azo bonds [14–20]. Using this method, dye molecules can be cleaved into products that are more amenable to mineralization in biological treatment processes. When the other advantages of ZVI degradation such as easy retrieval of the spent iron powder by magnets, low residual iron concentration and no necessity for further treatment of the effluents, are considered, ZVI should be an ideal candidate for azo dye degradation [17]. However, traditional ZVI methods almost always used commercial grade ZVI which has relatively low reactivity, and needs prolonged reaction time and low pH conditions for adequate treatment [20]. Although

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these disadvantages can be overcome by decreasing the particle size to the nanoscale, this strategy is still not possible because of the high manufacturing cost and heavy surface oxidation that occurs during the processing of NZVI.

The unique structure of amorphous alloys can sometimes produce high reaction activity instead of low corrosion rate [21–24], and suggested that if the reductive ability of ZVI was well preserved in Fe-based amorphous alloys, they could be very effective in the degradation of azo dyes. In this work, by virtue of a melt-spinning technique, ZVI was successfully quenched into an amorphous state as $\text{Fe}_{78}(\text{Si}, \text{B})_{22}$ amorphous ribbons (defined as amorphous ZVI for comparison with crystalline ZVI). Structure changes always bring some special properties to materials, and thus the amorphous ZVI was expected to have its own characteristic properties, including different performance from its crystalline counterpart in the degradation of azo dyes.

1 Experimental

Amorphous ribbons with the nominal composition $\text{Fe}_{78}(\text{Si}, \text{B})_{22}$ in atomic percentage were obtained by melt-spinning the alloy melts, and the glassy nature of the ribbons was ascertained by X-ray diffraction (XRD). Orange II powder was dissolved in distilled water to give 100 mg/L aqueous solution. Beakers containing 150 mL or 180 mL of dye solution were prepared for reaction with the glassy ribbons. The beakers were placed in a controllable constant temperature water-bath trough at a particular temperature, and then the amorphous ribbons (cut into small pieces) were placed into the breaker, resulting in a certain iron surface area concentration (ρ_a), defined as the surface area of iron per liter of dye solution. Mechanical agitation at 200 r/min was used during reaction process. Aliquots of solution (5 mL) were taken from the beaker at intervals, filtered through a 0.45 μm membrane filter, and then the UV-vis spectra of the solutions were recorded from 200 to 700 nm using a UV-visible spectrophotometer (JASCO V-550). Valence band spectra of the amorphous ribbon and crystalline ZVI were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, monochromatic Al K_{α} X-ray source). All binding energies were referenced to the C 1s peak (284.7 eV) arising from adventitious carbon.

2 Results and discussion

The amorphous nature of the ribbon can be verified by the broad peak that appears in its XRD pattern as presented in Figure 1. This result demonstrates that the ribbon has a short-range ordered and long-range disordered structure, with iron atoms forming clusters several angstroms to several nanometers in size.

The changes in UV-vis spectra as a function of reaction

Figure 1 XRD patterns of (a) $\text{Fe}_{78}(\text{Si}, \text{B})_{22}$ ribbons obtained by melt-spinning and (b) crystalline ZVI, inset: image of $\text{Fe}_{78}(\text{Si}, \text{B})_{22}$ ribbons obtained by melt-spinning.

time at room temperature are shown in Figure 2(a). The strong absorbance peak at $\lambda_{\text{max}} = 484 \text{ nm}$ in the visible region originates from a conjugated structure formed by the azo bonds, the intensity of which denotes the dye concentration in the solution. The other two bands at 230 and 310 nm in the ultraviolet region are ascribed to the benzene and naph

Figure 2 (a) UV-vis spectra as a function of reaction time at room temperature; (b) C_t/C_0 as a function of reaction time at room temperature. Initial Orange II concentration, 100 mg/L; ribbon dosage, 0.062 m^2/L ; initial pH 6.

thalene rings of the dye, respectively [25,26]. The changes in the peaks reflect the evolution of the chromophores of Orange II and so useful information can be obtained from the analysis of the UV-vis spectra. The bands at $\lambda_{\max}$ became weaker, because of the cleavage of the azo bonds and the decrement of Orange II in the solution. Along with the cleavage of the azo bonds, $-\text{NH}_2$ groups were also formed, as shown by the increasing intensity of the absorbance peak at 246 nm in Figure 2(a).

Figure 2(b) shows the change in C_t normalized by C_0 with reaction time, where C_0 and C_t are the current and initial dye concentration, respectively. Nonlinear curve fitting shows that the degradation process fits very well to first order exponential decay kinetics as proposed by Nam and Tratnyek [14]:

$$C_t/C_0 = \exp(-k_{\text{obs}}t), \quad (1)$$

where k_{obs} (min^{-1}) is the observed rate constant, and t is the reaction time. Thus, the k_{obs} of the degradation process by $\text{Fe}_{78}(\text{Si}, \text{B})_{22}$ is 0.125 min^{-1} .

Table 1 summarizes rate constants from various works. Nam and Tratnyek [14] observed color removal rate constants of 0.380 and 0.380 min^{-1} for 300 $\mu\text{mol/L}$ Orange II and 300 $\mu\text{mol/L}$ Crocein Orange G, respectively, by adding 200 g L^{-1} microscale iron. Although a much lower mass dosage of NZVI particles [19,20] can produce rate constants of the same order of magnitude as the results of Nam and Tratnyek, the higher rate constants are probably attributed to the superior surface area of NZVI particles.

Cao et al. [28] have shown that the rate constants of Orange II reduction are linearly dependent on iron surface area concentration, and thus surface area normalized rate constants (k_{SA}) can better reflect the essential degradation ability of different materials. Based on this, k_{SA} can be estimated from the values of k_{obs} reported by dividing by ρ_a , which gives $k_{\text{SA}} = 2.0 \text{ L m}^{-2} \text{ min}^{-1}$ at room temperature for the disappearance of Orange II in this study. This value is one to two orders of magnitude larger than those reported previously for the degradation of similar azo dyes with ZVI or NZVI. That is to say, if the same dosage was added, the degradation rate produced by the ribbons in our work would be one order of magnitude larger than that by ZVI or NZVI, just as k_{SA} shows. There is little doubt that this phenomenon

is attributed to the peculiar short-range ordered structure and non-equilibrium state of the glassy ribbons. Another issue should be noted is that k_{SA} of NZVI is one order of magnitude lower than that of Micro-ZVI; this is perhaps caused by heavy passivation and aggregation of NZVI, leading to a sharp decrease in its efficiency for the degradation of dyes.

Generally speaking, chemical reactions are very sensitive to changing temperature, and the temperature effect can provide important insight into the reaction mechanism. In the present work, experiments were carried out over a temperature range of 25–50°C to study the effect of temperature on the degradation of Orange II, and the results are presented in Figure 3(a). By nonlinear regression, the degradation rate constants could be obtained, and based on the obtained kinetic rate constants at different temperatures, the observed activation energy (E_a) for the degradation process of Orange II by amorphous ribbons can be calculated according to the Arrhenius equation:

$$\ln k = -E_a/RT + \ln A. \quad (2)$$

The plot of $\ln k$ versus $1/T$ is shown in Figure 3(b), and is clearly linear. It was calculated that the activation energy was 27.9 kJ/mol for the degradation process of Orange II by the ribbons over the temperature range of 25–50°C. Considering the fact that the activation energies for ordinary thermal reactions are usually between 60 and 250 kJ/mol [12], our result implies that the degradation of Orange II by the ribbons required a relatively low energy.

In the degradation process, ZVI is considered to be both the electron donor and the catalyst (surface catalysis) for the cleavage of the $-\text{N}=\text{N}-$ bonds [14–20]. From the viewpoint of thermodynamics, amorphous materials are always metastable, and usually lie at a higher energy level than their crystalline counterparts, so amorphous ZVI is expected to be more active than crystalline micro-ZVI or NZVI. In chemical reactions involving pure metals or alloys acting as reductants, reaction thermodynamics and chemical kinetics always depend on the properties of the electrons in the outermost electronic shell. These electrons are called free electrons or valence electrons. In crystalline metals or alloys, the activity of valence electrons is constrained by metallic cations arranged periodically according to metallic bond

Table 1 Comparison of rate constants from various studies ^{a)}

ZVI type	Mass dosage (g L^{-1})	Area dosage ($\text{m}^2 \text{ L}^{-1}$)	Dye	C_0 ($\mu\text{mol/L}$)	Temp. ($^{\circ}\text{C}$)	pH	k_{obs} (min^{-1})	k_{SA} ($\text{L m}^{-2} \text{ min}^{-1}$)	Reference
Micro-ZVI	200	1.42	Orange II	300	20–30	7.0	0.380	0.268	[14]
Micro-ZVI	200	1.42	Crocein Orange G	300	20–30	7.0	0.380	0.268	
Micro-ZVI	66.6	—	Orange II	290	30	6.0	0.016	—	[27]
NZVI	0.165	23.2	Acid Black 24	137	20–30	6.7	0.199	0.009	[19]
NZVI	0.5	>23.2	Methyl Orange	306	30	6.0	0.511	<0.022	[20]
Amorphous ZVI	9–12	6.2×10^{-2}	Orange II	290	20–30	6.0	0.125	2.0	this work

a) Micro-ZVI, Zero-valent iron with micron scale particles; NZVI, zero-valent iron with nanometer scale particles; Amorphous ZVI, zero-valent iron frozen into amorphous ribbons.

Figure 3 (a) Effect of temperature on the degradation of Orange II and (b) Arrhenius plot of $\ln k$ versus $1/T$ for the degradation of Orange II by amorphous ribbons: initial Orange II concentration, 100 mg/L; ribbon dosage, 0.0833 m²/L; initial pH 6.

theory. In contrast, in amorphous alloys, metallic cations are in a disordered arrangement; the absence of periodicity in the atomic arrangement weakens the constraint from the cations on the valence electrons, thus these electrons should be more active in chemical reactions than those electrons of their crystalline counterparts.

To determine the effect of the alloy structure on the relative positions of the valence band (VB) edges and empty band (EB) widths, total densities of states of VBs of crystalline ZVI and amorphous ribbon containing ZVI were measured by virtue of XPS (Figure 4(a)). Spectrograph parameters and experimental conditions for the two samples were kept the same to enable the results to be compared. Examining the VB edges indicates that, in contrast to crystalline ZVI, the ZVI in the amorphous ribbon presents a VB maximum down-shifted from -1.23 to -1.39 eV, as well as the EB itself being widened. Clearly, a unique electronic structure featuring a depressed VB maximum and a widened EB is established in the amorphous ribbon, as shown in the schematic diagram (Figure 4(b)). Intriguingly, the downward shift of the VB maximum by 0.16 eV makes it easier for electrons from the $4s$ electronic shell to jump over the VB maximum into the EB, which means more electrons

Figure 4 (a) Total densities of states of valence bands of crystalline ZVI and amorphous ribbon containing ZVI; (b) schematic diagram of the different electronic structures of crystalline ZVI and amorphous ribbon.

would participate in oxidation-reduction reactions per unit time. This unique electronic structure gives amorphous ZVI much better reductive ability compared with that of its crystalline counterpart.

The degradation process of Orange II is supposed to be surface-mediated [29], and the activation energy and reactive sites are the two factors determining the reduction rate. The activation energy for the degradation process by amorphous ribbons was calculated according to the Arrhenius equation as mentioned above. For the amorphous ribbons, the atoms are in their amorphous state, which is a higher energy state compared with that in the crystalline ZVI. That is to say, the electron needs less energy to pass the barrier. This agrees well with the lower activation energy presented in this study (27.9 kJ/mol for the degradation process of Orange II by amorphous ribbons over a temperature range of 25 – 50°C); while the activation energies for azo dye degradation by micro-ZVI or NZVI are much higher [20]. Accordingly, the higher degradation rate was exhibited for the amorphous ribbons compared with previously reported results for ZVI. Besides that, as mentioned above, the atoms in amorphous alloys are grouped on a scale of several angstroms to several nanometers, and these atoms are highly coordinatively unsaturated. The surface of an amorphous alloy therefore has more unsaturated coordination than its crystalline counterpart, and hence can provide more reactive sites for the degradation reaction. More reactive sites bring

more chances for a reaction between ZVI and the dye molecules, and thus may accelerate the degradation process.

3 Conclusions

In summary, $\text{Fe}_{78}(\text{Si},\text{B})_{22}$ amorphous ribbon produced by melt-spinning was found to substantially enhance the reductive degradation of Orange II aqueous solution. The degradation process followed first order exponential decay kinetics, and the surface-area normalized rate constant k_{SA} was up to $2.0 \text{ L m}^{-2} \text{ min}^{-1}$ at room temperature. According to the Arrhenius equation, the activation energy of the degradation process was 27.9 kJ/mol over the temperature range $25\text{--}50^\circ\text{C}$, much lower than previously reported values. Valence band measurement indicated that a depressed valence band maximum and a widened empty band had been established in the amorphous ribbon. These phenomena were suggested to be because of the peculiar short-range ordered and long-range disordered structure and the non-equilibrium state of the amorphous alloys, which could reduce the activation energy of the degradation process and enhance the activity of the electrons. Our finding indicates Fe-based amorphous alloys are promising candidates in remediation of groundwater or wastewater contaminated with azo dyes, chlorinated solvents, nitrates and other oxidative contaminants.

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