Rapid decolorization of water soluble azo-dyes by nanosized zero-valent iron immobilized on the exchange resin

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Nanosized zero-valent iron (NZVI) supported on the cation exchange resin was synthesized and applied to decompose some water soluble azo dyes. The decomposition efficiency for azo dyes was evaluated by using the aqueous suspensions and packed column of this material. Batch experiments indicated that this novel material exhibited excellent degradation ability for 0.05 g·L⁻¹ of Acid Orange 7, Acid Orange 8, Acid Orange 10, Sunset Yellow, and Methyl Orange, with decolorization ratio up to 95% in 4 min; pH value was the key factor for degradation and H⁺ was one of the reactants; adsorption of azo dyes onto the material existed at the beginning but reduced gradually until disappearing completely. For the packed column system, 58%~90% of azo dyes were decomposed in the 1st circle of solution passing through the column, and the adsorption onto the materials could accelerate the degradation azo dyes with the increasing reaction time. During the degradation process, Fe²⁺, the product of NZVI, was exchanged to the resin again and could be reduced to Fe⁰ by KBH₄ for reusing. The 10th refreshed NZVI possessed reductive activity up to 90% of the newly synthesized NZVI. Decomposing pollutants in the aqueous solution with columns packed with NZVI immobilized on the cation exchange resin is a promising technology that can solve the reclaiming and refreshing problem of NZVI.

azo-dye, nanosized-zero valent iron (NZVI), decomposition, packing column

Azo dyes, widely used in the textile and dyestuff industries, account for two-thirds of the organic colorants listed in the Colour Index if colorant precursors and sulfur dyes of indeterminate constitution are excluded. They are often designed to resist the breakdown of long-term exposure to sunlight, water, soap, and other atrocious conditions. Due to the formation of carcinogenic amines when used with textiles for body-contact end-uses, some azo dyes have been banned by some European countries in the last decades. However, many acid and direct dyes that may liberate amines, such as benzidine, *o*-tolidine, and *o*-dianisidine, are still used. The releasing of these dyes to the environment can cause acute and/or chronic effects on the exposed organisms, adsorb or reflect sunlight entering into water, and thus result in change of

food chain. Up to now, the treatment methods for azo dyes can be divided into 3 categories: (1) physical methods^[1,2], such as flocculation, adsorption, nano-filtration and ion exchange; (2) chemical methods^[3-5], such as oxidative process with Fenton's reagent, H₂O₂-ozone, H₂O₂-UV radiation, NaClO and O₃, and so on; and (3) biological degradation^[6], including aerobic and anaerobic degradation. Physical methods are unable to absolutely decompose azo dyes, and chemical methods with high cost are rarely used in the actual treatment process. Biodegradation processes, the most widely used

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methods suffered from low degradation efficiency or even no degradation for some dyes, and the requirement of a large volume of treatment equipment, so the combination of pretreatment processes, which transform azo dyes into easier bio-decomposition compounds, with biodegradation process is preferred^[7].

Zero valent iron (ZVI), an environmentally friendly strong reducing agent, has been widely studied for environmental remediation in recent years. Now, it has been used in treating and remedying waste waters contaminated with chlorinated compounds^[8,9], nitro aromatic compounds^[10], nitrates^[11] and heavy metals^[12], and even for the deoxidization of more complex anthropogenic chemicals including pesticides^[13] and dyes^[14–19]. Among these compounds, azo dyes are easier to be deoxidized than to be oxidized. Thus, deoxidization with ZVI is one of the most important paths of degradation. The degradation mechanism of azo dyes on the surface of ZVI is illustrated in Figure 1^[17,18].

Though there have been many reports on the treatment and remediation of waste water with ZVI, many pivotal technological problems have to be solved before the actual application. For example, the balance between the ZVI dispersion and treatment capacity, the residual of ZVI and the release of large amounts of Fe^{2+} in the water remain great challenges, which might be resolved with the promotion of preparation, reclaiming and refreshing technologies of ZVI.

A new method for the transformation of azo dyes into easier bio-decomposition compounds with NZVI has been developed in this study. The NZVI immobilized on the surface of cation exchange resin was prepared and

characterized. Then, some factors that influence the degradation efficiency and the reducing ability of the refreshed NZVI were studied. Results show that the refreshed NZVI possess strong activity, and immobilizing NZVI on the surface of cation exchange resin packed in a column successfully solved the problem of reclaiming and refreshing of NZVI.

1 Experimental section

1.1 Chemicals

All chemicals were used without further purification. Acid Orange 7, 1-amino-2-naphthol hydrochloride, and sulfanilic acid were purchased from Acros (NJ, USA). Acid Orange 8 was purchased from Aldrich (CAS 5850-86-2). Acid Orange 10, Methyl Orange, and Sunset Yellow were all purchased from TCI (Tokyo Kasei Kogyo Co., Ltd.). The structures of the five studied azo dyes are listed below.

Aqueous stock solutions ($2.5 \text{ g} \cdot \text{L}^{-1}$) were prepared by dissolving corresponding mass of reagents in 250 mL water, respectively. The cation exchange resin (exchange capacity $\geq 4.2 \text{ mmol} \cdot \text{g}^{-1}$, granularity (0.3–1.2 mm) $\geq 95\%$, water content 46%–52%) was purchased from Shanghai Curatorial Factory (China). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (99%) was purchased from Tianjin Reagent Co. Ltd. (China). KBH_4 (99%) was purchased from Langfang Reagent Co. Ltd. (China).

1.2 Synthesis of NZVI immobilized on cation exchange resin

The cation exchange resin supported NZVI was pre-

(Illustration: This picture shows the structure of azo dyes)

Figure 1 Azo dyes degradation schematic using ZVI.

pared by the method of reducing iron salt in aqueous solutions^[20] with some modifications. Briefly, the resin was firstly treated with 4 mol·L⁻¹ HCl for 30 min to replace Na⁺ with H⁺ and washed with plenty of water to remove the residual HCl. FeCl₂·4H₂O and the treated resin were mixed in aqueous solutions at a 1:5 mass ratio and stirred for 30 min to ensure that Fe²⁺ could be exchanged on the surface of the resin, and then the resin was washed again with deionized water to remove the residual Fe²⁺.

To reduce the Fe²⁺ to NZVI, 20 g of the above prepared resin was transferred to a 500 mL clean beaker containing 100 mL ice water and the reaction was initiated by slow addition of 100 mL KBH₄ solution (0.2 mol·L⁻¹, prepared in ice water) under magnetic stirring. The resin quickly transferred to grey from buff, and then to black, coupling with many H₂. About 30 min later, the resin was washed again to remove the rest of KBH₄ and conserved in weaker basic solutions for use.

1.3 Surface characterization

The new NZVI, the used NZVI and the refreshed NZVI were all washed with deionized water to remove the impurities and then dried in N₂ at ambient temperature. The characterization was carried out on an S-3000 (Hitachi) scanning electron microscope (SEM) coupled with energy dispersive spectroscopy (EDS). The SEM was conducted under the following conditions: Accelerating voltage 15.0 kV, working distance 5.3 mm, and high vacuum mode. For EDS, the operating conditions were 15.0 kV accelerating voltage, and 15.0 mm working distance under high vacuum mode.

1.4 Degradation in batch system

2 g of the prepared cation exchange resin supported NZVI was added into a group of 50 mL of 0.05 mg·mL⁻¹ azo dye solutions and the reaction started. After an interval of several minutes, one of them was stopped and the supernatant was collected for analysis by UV-vis spectroscopy.

1.5 Degradation in packing column system

The packing column, with inner diameter of 0.6 cm and length of 15 cm, was packed with the prepared cation exchange resin supported NZVI (about 0.4 g iron). The initial 200 mL of azo dye solution (0.05 g·L⁻¹, pH 5.3) was pumped with a peristaltic pump through the column, where the degradation reaction happened, at a flow rate of 80 mL·min⁻¹ and the effluent was directly analyzed for evaluating the degradation efficiency or taken back to the same container for another circle.

1.6 Activation of NZVI

The used resin was washed with deionized water to remove the adsorbed impurities and treated with KBH₄ solution to reduce Fe²⁺ to NZVI again. For the column system, refreshing could be realized by pumping KBH₄ solution through the packed column under circulatory mode. For evaluating the activity of the refreshed NZVI, the experiments described above (part 1.4 or 1.5) were repeated.

1.7 Analysis of azo dyes and their degradation products

All the samples were diluted 10 times before analysis. The concentrations of azo dyes were determined with an

UV-3000 (Shimazu) spectroscope under the scanning mode. A HPLC-UV (Agilent 1100) equipped with a J'sphere ODS-H80 (S-4 μm , 8 nm, 150 $\times$ 4.6 mm) column was used for the determination of azo dyes and their relevant products. The mobile phase was the mixture of methanol and water (80 + 20) and the flow rate was 1.0 mL $\cdot$ min⁻¹.

1.8 The determination of Fe²⁺

Fe²⁺ concentration, released into the solution from the oxidation of the NZVI in the degradation process of azo dyes, was determined by using the *o*-phenanthroline hydrate- spectrophotometric method.

2 Results and discussion

2.1 Characterization of NZVI immobilized on cation exchange resin

Figure 2 shows the SEM images and the energy spectrum of NZVI. The left part illustrates that the diameters of the new, used, and refreshed NZVI were about 100–160 nm and they dispersed evenly on the surface of the resin with many ravines (especially for the new NZVI) which increased the surface area.

The right part is the semi-quantitative information (chosen from the entire eyeshot, not a spot) of the new NZVI, which shows the elemental formation of the material. As the iron layer is so thin that the electron beam can penetrate through it and arrive at the surface of the resin, high contents of S, C, and O that were composed of the cation resin was shown in the EDS. K is ex-

changed onto the resin during the NZVI formation process. The energy spectrum indicates that NZVI is the only reducing reagent in the degradation process.

2.2 Degradation of azo dyes

Figure 3 illustrates the degradation efficiency of Acid Orange 7 in the batch system at different pH values. The initial reaction rate is very fast, but it decreases quickly with the increasing of time and shows no obvious change 5 min later. Figure 3 also shows that the decolorization ratio decreases with the increasing of pH. The maximum degradation efficiency is only 70%–85% at pH $\geq$ 6.2, but it could increase and even reach up to 100% with the addition of acids into the system. Therefore, it can be concluded that H⁺ is one of the reactants. This result agreed with the reaction mechanism shown in Figure 1, i.e., the azo dyes adsorbed onto the surface of NZVI interact with H⁺ to form a transitional product, which is then transformed into the terminal product (amine compounds) under the interaction of another H⁺[17,18].

Figure 4(a) shows the decolorization ratio of azo dyes with the increase of reaction time: Acid Orange 8 had the highest rate, followed by Sunset Yellow and Acid Orange 7, while Acid Orange 10 and Methyl Orange had the lowest rates. Among the five azo dyes, Acid Orange 10 and Methyl Orange are the most hydrophobic (see molecular structure in Figure 1) and their products have lower aqueous solubility. This may result in the relatively low diffusing away rate and thus higher content of terminal products on the NZVI surface, which reduced the reaction rates from transitional products to terminate

Figure 2 Scanning electron microscopy (SEM) image and EDS of NZVI. (a) New NZVI; (b) used NZVI; (c) refreshed NZVI; (d) energy dispersive spectroscopy (EDS) spectrum of new NZVI.

Figure 3 Effect of pH on the decolorization of Acid Orange 7. Concentration: $0.05 \text{ g} \cdot \text{L}^{-1}$; Mass of as-prepared material: 2 g (wet weight).

products. Although Acid Orange 8 has lower hydrophilicity than Acid Orange 10 and Methyl Orange, it still had the highest decolorization rate, and up to 97% of Acid Orange 8 was decolorized in 4 min. This is because the methyl radical of Acid Orange 8 has stronger ability of electron offering that accelerates the formation of the transitional product of Acid Orange 8 with iron.

In the packing column system, the degradation rate was influenced not only by the solution acidity, but also by the flow rate and the design of the column. Figure 4(b) shows the increase of decolorization ratio with increasing circular times of the azo dye solutions. As can be seen, Acid Orange 10 and Methyl Orange still had the lowest decolorization ratio, but Acid Orange 8 had lower decolorization ratio than that of Acid Orange 7 and Sunset Yellow. After the 1st circle, the decolorization ratio was 79% for Acid Orange 8, 89% for Acid Orange 7, and 88% Sunset Yellow, which were lower than that in the batch system. Probably in the column system, the reactants and products were taken away quickly which

decreased the reaction time and thus the decolorization ratio. At a fixed flow rate, the compounds with higher adsorption capacity can stay on the NZVI in the packing column for a longer time that promoted the formation of the transitional and terminal products. Therefore, the adsorption of azo dyes on the surface of ZVI is also an important factor that affects the degradation rate in the packing column. Figure 4(b) also indicates that the decolorization had no significant change after 2 circles. This is because the consumption of H^+ in the solution, and the degradation ratio decreased very quickly with the acidification of the solution. Obviously, this result accorded with the mechanism shown in Figure 3 and further demonstrated that H^+ is one of the reactants.

2.3 Mass balance in the decolorization process

It is well known that nano-materials have a large ratio of surface area to volume and strong adsorption capacity for reactants and products. If the degradation ratio of a compound is calculated based on the mass difference of the reactant mass before and after the reaction, the adsorption mass will be regarded as the degradation mass and results in positive error. In order to investigate influence of the adsorption on the calculation of degradation ratio, the mass of reactants and products are determined and calculated according to their molar ratio. Figure 5(a) shows the mass balance of Acid Orange 10 in the batch system. From the total mass curve it is clear that the adsorption did exist at the beginning of reaction and reached up to 18% in 1 min, then it decreased gradually and disappeared finally. Figure 5(b) and 5(c) shows mass balance of Acid Orange 10 and Acid Orange 7 in the packing column system. After the 1st circle, the adsorption mass of Acid Orange 10 and Acid Orange 7 was 12% and 17%, respectively. The adsorption almost

Figure 4 Decolorization ratio of the five azo dyes. (a) Batch system; (b) packing column system.

Figure 5 Mass balance curve. (a) Acid Orange 10(Batch system); (b) Acid Orange 10(Column System); (c) Acid Orange 7(Column system).

disappeared from the 2nd circle for Acid Orange 10, whereas it existed all the while and decreased slowly in the following circles for Acid Orange 7. The results of these two systems indicate that the decolorization mainly resulted from the deoxidization of ZVI instead of adsorption.

Figure 5(b) and Figure 5(c) also show the different adsorption ability of NZVI for the two azo dyes. This adsorption ability depends not only on the hydrophilicity and the spacial structure of azo dyes, but also on the positive charge on the surface of NZVI resulting from the hydrogen bond interaction between the metal hydroxy groups of NZVI and H^+ . For a packed column system with fixed acidity and flow rate, the larger the mass of the adsorbed azo dyes on the surface of NZVI, the higher the odds of formation of transitional and terminal products, which results in higher decolorization ratio. Thus, adsorption can not only accelerate decolorization, but also promote decomposition.

2.4 Refreshing of NZVI

All the refreshed NZVI can quickly decompose the azo dyes (see Figure 6), though the decolorization efficiency decreased slightly with the increasing of refreshing times. Even after the 10th refreshing, the decomposition efficiency of the refreshed NZVI was 90% of that of the

Figure 6 Activity of the refreshed NZVI.

new NZVI, and satisfactory decomposition ratio was obtained in 8 min.

With the mixing of NZVI and excess amount of dyes, the Fe^{2+} concentration increased with the time increasing and then kept constant until all the NZVI were consumed, as shown in Figure 7. This is because most of the Fe^{2+} , released from the oxidation of NZVI, are exchanged onto the surface of the resin and only small amounts stay in the aqueous solution. Thus, when the

resin with Fe^{2+} is reduced with KBH_4 after the decomposition reaction, NZVI is formed again and it is ready for decomposing azo dyes. There is no obvious difference between the new and the refreshed NZVI in the micro-morphology, i.e., the refreshed NZVI is still spheres with ravines (See Figure 2(c)). The resin acts as both the supporter of NZVI and the collector of Fe^{2+} , which obviously reduces Fe^{2+} release and its potential negative effect on the environment.

Figure 7 Fe^{2+} released into the aqueous solution. NZVI immobilized on resin (2 g of wet weight, with about 0.1 g Fe^0) and excess azo dyes were mixed in 50 mL solution volume.

3 Conclusion

NZVI immobilized on the surface of cation exchange resin was synthesized, and their applications in the degradation of azo dyes were studied in both the batch system and the packing column system. It was found that $0.05 \text{ g}\cdot\text{L}^{-1}$ of azo dyes can be reduced to a very low level in several minutes or circles. The decomposition efficiency of azo dyes depends strongly on structure of dyes, pH reaction solution, and adsorption of reactants. It was demonstrated that the decomposing efficiency increases with hydrophilicity, H^+ is one of the reactants, and adsorption promotes decomposition. Furthermore, Fe^{2+} can be exchanged onto the surface of the cation exchange resin, the supporter of NZVI, during the decomposition process, and the Fe^{2+} on the resin can be reduced to form refreshed NZVI for reusing. Thus, decomposing pollutants in aqueous solution with columns, packed with NZVI immobilized on the cation exchange resin, is a promising technology that can solve the reclaiming and refreshing problem of NZVI.

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