Degradation of dyes in aqueous solutions by the Fenton process

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Abstract

Degradation of 20 different dyes in aqueous solutions by the Fenton process was performed. These dyes include 6 types: acidic, reactive, direct, cationic, disperse and vat dyes. The former four types of dyes were decolorized and their TOC values were decreased greatly, while the color and TOC removals of the latter two types were lower. The catalytic activities of four metal ions on the degradation efficiencies of Vat Blue BO, which was chosen as a model dye because of its lowest color and TOC removals, were compared in the dark and under the ultraviolet light irradiation. The catalytic ability of different metals was $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ag}^+$ in the dark, and the same sequence was obtained under irradiation condition with greater degradation efficiency. Furthermore, the efficiencies of three oxidation processes, including $\text{H}_2\text{O}_2/\text{UV}$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ were compared. The results showed that the oxidation by $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ was the strongest, and even greater than the arithmetic sum of the other two processes, which suggests the synergistic effect of ultraviolet and ferrous ions on the degradation reaction.

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1. Introduction

The worldwide annual production of the dyestuffs amounts to more than 7×10^5 t (Spadaro et al., 1994).

There are many kinds of dyes on the market for various applications. In view of their chemical structures, dyes can be characterized as an azo dye, triaryl methane dye, anthraquinone dye, heterocyclic dye and phthalocyanine dye. Dyes can also be characterized according to their application method into vat dye, reactive dye, direct dye, acidic dye, disperse dye and cationic dye. Effluents from the textile industry commonly contain high concentrations of organic and inorganic chemicals and are characterized by very high COD and TOC values as well as strong color (Kurbus et al., 2003). Dye

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wastewater discharged from the textile industry can be extremely damaging to the environment if improperly disposed. The removal of dyes from industrial effluents is an area of research receiving increasing attention as government legislation on the release of contaminated effluent is becoming increasingly stringent.

Biological treatment of dye-containing wastewater is considered unsatisfactory because of the low efficiency and low reaction rate of the treatment. Consequently, dye wastewater is usually treated using physical and chemical methods (Chang et al., 2003). Flocculation and activated carbon adsorption have been used to treat dye-containing wastewater. However, sludge generation and adsorbent regeneration are the principal weakness of these processes (Slokar and Majcen Le Marechal, 1998). The Fenton process that uses Fe^{2+} to react with H_2O_2 to generate OH with powerful oxidizing ability, one of the advanced oxidation processes (AOPs), has been proposed for the degradation of organic pollutants (Chen and Pignatello, 1997; Benitez et al., 2001; Huang et al., 2002), including some dye pollutants (Kang et al., 2002; Feng et al., 2003; Swaminathan et al., 2003).

In this paper, degradation of 20 different types of dyes in aqueous solutions by the Fenton process was performed. In order to improve the degradation efficiency, catalytic activities of four metal ions on the degradation of Vat Blue BO were compared in the dark and under the UV light irradiation. Furthermore, the efficiencies of three oxidation processes, including $\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ were compared.

2. Materials and methods

2.1. Materials

The 20 dyes tested were Acidic Red B, Acidic Red G; Reactive Brilliant Red K-2BP, Reactive Brilliant Red K-2G, Reactive Yellow KD-3G; Direct Fast Black GF, Direct Fast Turquoise Blue GL, Direct Fast Red F3B, Direct Yellow RL; Cationic Pink FG, Cationic Red X-GRL, Cationic Black X-2RL, Cationic Yellow X-2GL; Disperse Red B; Disperse Violet HFRL; Disperse Brilliant Yellow 5GR; Vat Blue BO; Vat Direct Black RB; Vat Dark Blue VB and Vat Brilliant Violet RR. They were all purchased from the Eighth Dyestuff Factory in Shanghai. Copper sulfate, ferrous sulfate, manganese sulfate and silver nitrate were purchased from Beijing Chemical Reagent Factory. Distilled de-ionized water was used for all solutions and dilution. H_2O_2 (30%) and other reagents were obtained from Beijing Chemical Reagent Industrial Company. These chemicals were analytical grade.

2.2. Experimental procedure

The degradation of 20 dyes was carried out in graduated and plugged test tubes. Reaction mixtures were obtained by taking an appropriate amount of dye stock solution, adding ferrous ion, and adjusting pH value to 3 with 0.1 N H_2SO_4 or NaOH solution. The final volume of the reaction mixture was 50 ml. The reaction was initiated by adding H_2O_2 and was terminated instantly by adding 0.5 ml of 1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution to the reaction mixtures.

During the photo-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$) experiments, degradation of the dye in solution was carried out in a one litre cylindrical glass photo-reactor. A Hanovia model 25 W low pressure mercury lamp as a light source was located at center of the reactor. The spectral output of the lamp at 254 nm wavelength at the surface of the quartz well was 4.50 mW cm^{-2} .

The optimized conditions had been obtained for the Fenton process in the previous work (Xu et al., 1999). Therefore, the concentrations of Fe^{2+} and H_2O_2 were 5 and 50 mM and pH value was 3, respectively. The concentration of dye solutions was 150 mg l^{-1} in this experiment. The samples were withdrawn at regular time intervals and were filtered with Millipore membrane ($0.45 \mu\text{m}$) before analysis.

The experiment was conducted three separate times, and each individual assay was conducted in duplicate. The mean values were presented together with vertical error bars indicating the standard deviations of the three experiments in the figures.

2.3. Analytical methods

A TOC analyzer (TOC-500, Shimadzu, Japan) was used to measure the concentration of organic carbon in aqueous solutions. The color of solution was analyzed using a Du-650 spectrophotometer (Du-650, Beckman, USA). Each dye solution was scanned from 300 to 800 nm and its maximum absorbance was determined. The color removal was based on the change of the maximum absorbance.

3. Results and discussion

3.1. Degradation of 20 dye solutions by the Fenton process

The Fenton process employs a mixture of H_2O_2 and Fe^{2+} under acidic pH conditions, which can generate great amount of $\cdot\text{OH}$ with powerful oxidizing ability. $\cdot\text{OH}$ may react with organics (Walling, 1975; Spacek et al., 1995):

Degradation of 20 commercial dyestuffs by the Fenton process was investigated. These dyes include 6 types: acidic, reactive, direct, cationic, disperse and vat dyes

and their chemical structures include azo, triaryl methane, anthraquinone, heterocyclic and phthalocyanine. The chemical structures of 6 representative dyes, one per type, are shown in Fig. 1. The degradation results of dyes by the Fenton process are summarized in Table 1. The color removals of acidic, reactive, direct and cationic dyes were between 87% and 100%, and the TOC removals were between 56% and 79%. For disperse and vat dyes, the color and TOC removals were 30%–56% and 21%–34%, respectively suggesting that the molecules of disperse and vat dyes were more difficult to be destroyed by the Fenton process. The color removal was easier than the TOC removal indicating that the chromophoric groups were destroyed during the degradation of dyes, and were partly mineralized to CO_2 and H_2O . Although the chromophoric structures of the dye molecules are destroyed by hydroxyl radicals, some colorless degradation intermediates are formed in solution during the reaction. In most cases, adjacent aromatic ring struc-

ture is one of the intermediates (Kang et al., 1999). In addition, pH value of the solution decreased a little (about 0.1 pH unit) during the decomposition of dyes by the Fenton process.

Among all dyes tested, the color and TOC removals of Vat Blue BO were lowest. Therefore Vat Blue BO was chosen in the following experiments to compare the catalytic activity of four metal ions and the degradation efficiency of three oxidation processes.

3.2. Comparison of the catalytic activity of four metal ions

In order to improve degradation efficiency, the catalytic activity of several metal ions was compared. The catalysts used in this study were Fe^{2+} , Cu^{2+} and Mn^{2+} . The selection of metal is based on the fact that transition metals, particularly those possess two or more valency states between which there is a suitable oxidation–reduction potential, can react with H_2O_2 to produce OH.

Fig. 1. Chemical structures of 6 representative dyes.

Table 1

The removals of color and TOC of 20 dyes used^a

Dye	$\lambda_{\max}$ (nm) ^b	Color removal (%)	TOC removal (%)
Acidic Red B	530	100 ± 1	67 ± 3
Acidic Red G	530	100 ± 1	62 ± 1
Reactive Brilliant	530	98 ± 2	76 ± 4
Red K-2BP			
Reactive Brilliant	530	100 ± 1	72 ± 3
Red K-2G			
Reactive Yellow KD-3G	420	96 ± 2	79 ± 2
Direct Fast Black GF	580	90 ± 3	66 ± 3
Direct Fast Turquoise	620	92 ± 1	74 ± 4
Blue GL			
Direct Fast Red F3B	530	87 ± 2	72 ± 2
Direct Yellow RL	420	91 ± 4	78 ± 1
Cationic Pink FG	540	96 ± 2	61 ± 3
Cationic Red X-GRL	550	98 ± 1	68 ± 2
Cationic Black X-2RL	580	92 ± 3	60 ± 3
Cationic Yellow X-2GL	470	94 ± 1	56 ± 1
Disperse Red B	520	56 ± 2	34 ± 4
Disperse Violet HFRL	640	47 ± 3	26 ± 2
Disperse Brilliant	420	41 ± 2	30 ± 3
Yellow 5GR			
Vat Blue BO	620	30 ± 1	21 ± 1
Vat Brilliant Violet RR	640	46 ± 2	27 ± 2
Vat Direct Black RB	580	37 ± 1	30 ± 3
Vat Dark Blue VB	630	39 ± 3	28 ± 2

^a Reaction time = 120 min, pH = 3, Temperature = 20 ± 1 °C.^b $\lambda_{\max}$ = wavelength of the maximum absorbance.

In addition, these transition metals are easily obtainable, inexpensive, and relatively low in toxicity. Furthermore, Ag^+ was also chosen to test its catalytic activity. Vat Blue BO was used as a model dye. The results of the color and TOC removals are shown in Fig. 2. Without addition of metal ions, both color and TOC removals were very low, indicating that Vat Blue BO was difficult to be oxidized by H_2O_2 . It can be found that when catalysts were added into the reaction mixture, both color and TOC removals of Vat Blue BO were obviously enhanced. Metal ions can catalyze H_2O_2 to produce $\cdot\text{OH}$ with strong oxidizing ability. Hydrogen peroxide with an oxidation potential of 1.77 V has a less oxidizing power than hydroxyl radicals (2.80 V). The catalytic activity of Mn^{2+} was comparable with Fe^{2+} initially but gradually deviated from Fe^{2+} . Cu^{2+} showed a good catalytic ability during the degradation of Vat Blue BO although at the beginning of the degradation, its catalytic activity was comparatively lower than Fe^{2+} and Mn^{2+} . At the end of the degradation, its catalytic activity was almost equal to that of Fe^{2+} . Ag^+ was the least effective of the four tested metal ions. Catalytic activity of metal ions was found to be in the following sequence: $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ag}^+$.

Fig. 2. Effect of four metal ions on the color (a) and TOC (b) removals of Vat Blue BO. [Vat Blue BO] = 150 mg l⁻¹, [metal ions] = 5 mM, [H_2O_2] = 50 mM, pH = 3. (◆): Fe^{2+} ; (+): Cu^{2+} ; (▲): Mn^{2+} ; (○): Ag^+ ; (×): no metal.

3.3. Comparison of the catalytic activity of four metal ions under UV light irradiation

The oxidation of Vat Blue BO by the above mentioned metal ions and H_2O_2 was carried out under the UV light irradiation. The results are presented in Fig. 3. Removals of color and TOC were obviously enhanced under the UV light irradiation compared with results without irradiation. Without metal ions but with UV light, color and TOC removals were 26% and 15%, respectively after 120 min of reaction. It indicated that degradation of Vat Blue BO was sensitized by the presence of UV light due to the favorable adsorption spectrum of H_2O_2 . The direct photolysis of H_2O_2 , requiring $\lambda < 360$ nm, generates $\cdot\text{OH}$. $\cdot\text{OH}$ is known to react with organic chemicals by H-abstraction from alkyl or hydroxyl groups (Walling, 1975) or by an electron transfer process (Bossmann et al., 1998). In the presence of Fe^{2+} , H_2O_2 and UV light, the best color and TOC removals were obtained. Up to 64% of color and 45% of TOC of Vat Blue BO were removed after 120 min.

Under the irradiation of UV light, the same sequence of the catalytic activity of the metal ions was obtained. The sequence of catalytic ability for metal ions alone and metal ions assisted by UV light was $\text{Fe}^{2+}/\text{UV} > \text{Cu}^{2+}/\text{UV} > \text{Mn}^{2+}/\text{UV} > \text{Ag}^+/\text{UV} > \text{Fe}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ag}^+$.

Fig. 3. Effect of four metal ions on the color (a) and TOC (b) removals of Vat Blue BO under the irradiation of UV light. [Vat Blue BO] = 150 mg l⁻¹, [metal ions] = 5 mM, [H₂O₂] = 50 mM, pH = 3. (◆): Fe²⁺; (+): Cu²⁺; (▲): Mn²⁺; (○): Ag⁺; (×): no metal.

3.4. Comparison of H₂O₂/UV, H₂O₂/Fe²⁺ and H₂O₂/Fe²⁺/UV processes

In order to compare the efficiency of the advanced oxidation processes on the degradation of Vat Blue BO, the following advanced oxidation processes were carried out, namely H₂O₂/UV, Fe²⁺/H₂O₂ and Fe²⁺/H₂O₂/UV. The results of the color and TOC removals are shown in Fig. 4. The color and TOC removals of Vat Blue BO were lower by Fe²⁺/H₂O₂ or H₂O₂/UV processes alone than by Fe²⁺/H₂O₂/UV. For a reaction time of 120 min, color and TOC removals were obtained as the followings: Fe²⁺/H₂O₂/UV: 64% and 45%; Fe²⁺/H₂O₂: 30% and 21%; H₂O₂/UV: 26% and 15%, respectively. The degradation rate of Vat Blue BO by Fe²⁺/H₂O₂/UV was also faster than by Fe²⁺/H₂O₂ or H₂O₂/UV processes. The rapid degradation is related to the enhanced decomposition of H₂O₂ to powerful oxidizing ·OH under photo-Fenton conditions. The degradation rate of organic compounds can be strongly accelerated by irradiation with ultraviolet light (Ruppert and Bauer, 1993; Fukushima et al., 2000). The increased efficiency of the photo-Fenton is attributable to the photo-reduction of the Fe³⁺ formed during the Fenton process.

Fig. 4. The color (a) and TOC (b) removals of Vat Blue BO in three homogeneous systems. [Vat Blue BO] = 150 mg l⁻¹, [Fe²⁺] = 5 mM, [H₂O₂] = 50 mM, pH = 3. (◆): Fe²⁺/H₂O₂; (■): H₂O₂/UV; (▲): Fe²⁺/H₂O₂/UV; (×): Fe²⁺/H₂O₂+H₂O₂/UV.

During photo-reduction, an additional ·OH is generated and the reproduced Fe²⁺ react with H₂O₂ to produce Fe³⁺ and ·OH so that the cyclic reaction can continue.

The higher efficiency observed with the Fe²⁺/H₂O₂/UV process for the degradation of Vat Blue BO can be explained by the fact that OH radicals are generated by multiple reactions: photolysis of H₂O₂, reaction of H₂O₂ with Fe(II) which leads to a generation of Fe(III) and photolysis of Fe(III). The contribution of each of these reactions to the production of ·OH depends on the relative concentrations of Fe(II) and H₂O₂.

Furthermore, it is necessary to point out that the color and TOC removals by Fe²⁺/H₂O₂/UV were higher than the arithmetic sum of those by Fe²⁺/H₂O₂ and H₂O₂/UV indicating the synergistic effect of UV and Fe²⁺ on the degradation reaction.

4. Conclusions

Degradation of 20 dyes in aqueous solutions by the Fenton process was performed. These dyes include 6 types: acidic, reactive, direct, cationic, disperse and vat dyes. The former four types of dyes were decolorized and their TOC values were decreased significantly, while the color and TOC removals of the latter two types were lower. The catalytic abilities of four metal ions in the dark and under UV light irradiation were in the

sequence of $\text{Fe}^{2+}/\text{UV} > \text{Cu}^{2+}/\text{UV} > \text{Mn}^{2+}/\text{UV} > \text{Ag}^+/\text{UV} > \text{Fe}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ag}^+$. The color and TOC removals of dye solution by $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ were higher than by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ or $\text{H}_2\text{O}_2/\text{UV}$ processes and greater than the arithmetic sum of the latter two, suggesting the synergistic effect of UV and Fe^{2+} on the degradation reaction. The Fenton process could be used to enhance biotreatment of the dye wastewater in the sewage treatment plant.

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