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Heterogeneous Degradation of Dyes in Industrial Effluent over Fenton-Like Nano-Fe_2O_3/Goldmine Complex

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Abstract

Nano-Fe_2O_3/goldmine complex was obtained by chemical coprecipitation reaction on the surface of goldmine waste-solid. Being used as the heterogeneous catalyst in Fenton-like advanced oxidation processes (AOPs), its treatment effect was studied in the removal performance of industrial dyes effluent. Although the maximal COD removal efficiency would reach 35.4% when 5 mL NaClO was added in 100 mL industrial dyes effluent, it is found that by using nano-Fe_2O_3/goldmine system, the COD removal efficiency of 13,000 mg/L dyes wastewater could reach up to 75.5% in the presence of 30 g/L nano-Fe_2O_3/goldmine complex and 50 mL/L NaClO at 50˚C.

Keywords

Nano-Fe_2O_3/Goldmine Complex, Heterogeneous Reaction, Advanced Oxidation Processes, Industrial Dyes Effluent

1. Introduction

Synthetic dyes are widely used in food products, cosmetics, pharmaceuticals or paper printing. Due to their good solubility, synthetic dyes are also common water pollutants and they may frequently be found in trace quantities in industrial wastewater. Meanwhile, many of these dyes are also toxic and even carcinogenic. Then it is necessary to eliminate dyes from wastewater before it is discharged. However, wastewater containing dyes is very difficult to treat because the existing synthetic dyes are recalcitrant organic molecules, resistant to aerobic digestion, and stable to light, heat and oxidizing agents [1].

During the past decades, several physical, chemical and biological removal methods have been studied for the dyes wastewater purification strategies, like adsorption, filtration, coagulation, biodegradation [2]-[6]. But physical methods are limited because further treatment was demanded, where the removed dyes only being transferred from liquid phase to solid phase. Owing to the typical property of low B/C value and high salt concentration, the biological treatments also show low disposal ability in dyeing wastewater treatments. Among various techniques of dyes removal, Advanced Oxidation Processes (AOPs) is the procedure of choice and gives

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the best results as its strong oxidizing property and environmentally benign characters [7] [8].

Goldmine waste-solid contains various kinds of metallic oxides, which can play important roles in Fenton system. Then, using nano-Fe_2O_3 modified goldmine waste-solid as a natural catalyst in the heterogeneous Fenton-like system may not only be effective in dyes degradation, but also reduce the loss of ferrous ionic in the treatments of wastewater.

In this study nano-Fe_2O_3/goldmine waste-solid complexes were prepared for dyes removal of industrial effluent (COD = 13,000 mg/L). And the degradation performance of nano-Fe_2O_3/goldmine complex was determined in Fenton-like oxidation processes.

2. Experimental

2.1. Chemicals

All chemicals used here are of reagent grade and used without further purification. Iron vitriol $Fe_SO_4·7H_2O$, ferric chloride $FeCl_3·6H_2O$, Sodium hypochlorite NaClO (10%, w/v), ammonium hydroxide (25%, w/v), sulfuric acid H_2SO_4 and sodium hydroxide NaOH were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Goldmine waste-solid was obtained from Zhejiang Province Suichang Gold Mine Co. Ltd., China. The chemical composition of the goldmine waste-solid is CaO: 32.46%, MgO: 1.41%, Fe_2O_3: 20.75%, Al_2O_3: 3.26%, SiO_2: 14.11%, ZnO: 2.16%, CuO: 0.22%, PbO: 0.11%, Na_2O: 1.59%, SO_3: 15.37%.

The industrial dyes effluent was obtained from Zhejiang Runtu Co. Ltd., China. The main parameters (average values) of samples were: pH < 1, COD = 13,000 mg/L.

2.2. Synthesis of Nano-Fe_2O_3/Goldmine Complex

Raw goldmine waste-solid was pre-treated by acid-washing process, in which 20 g goldmine was mixed with 20 mL H_2SO_4 solution and stirred for 2 hours. Then the goldmine waste-solid was filtered off, washed repeatedly with distilled water and dried at 80˚C in vacuum for 2 hours. The obtained 20 g pretreated goldmine waste-solid was added to 20 mL 0.1 M $FeSO_4$ solution and stirred for 12 h under 50˚C. After the solid phase being isolated and washed with deionized water, the solid phase was added to 30 mL 0.1 M NaOH solution and stirred for 4 h. Then the modified goldmine solid was washed and dried at 80˚C. After that the solid was heated to 600˚C with a speed of 10˚C/min, and kept for 6 h in muffle furnace (Nabertherm Industrial Furnaces Ltd. Co). Upon cooling, the solid was broken to powders for the following use.

2.3. NaClO Oxidation Reaction

The experiment using NaClO as oxidant was done as follows: 100 mL industrial dyes effluent was added into Erlenmeyer flasks. Then various amount of NaClO (1.0 mL, 2.0 mL, 3.0 mL, 4.0 mL, 5.0 mL) was added to each flask by droplet and all suspensions were stirred at 30˚C for 2 hr. After being filtered, the COD value of industrial dyes effluent was measured by $K_2Cr_2O_7$ method. And the reduction of COD before and after oxidation was calculated.

2.4. Fenton Reaction

Fenton reaction in the treatment of industrial dyes effluent was done as follows: 30 mmol/L $FeSO_4$ and 100 mL dyes effluent were added into Erlenmeyer flasks individually. Then different amount of H_2O_2 (1.0 mL, 2.0 mL, 3.0 mL, 4.0 mL, 5.0 mL) was added to each flask by droplet and all suspensions were stirred at 30˚C for 2hr. After being filtered, COD of the industrial effluent was determined and the reduction before and after stirring was used to calculate the removal rate in the Fenton reaction.

2.5. Fenton-Like Reaction

The experiments for Nano-Fe_2O_3/goldmine complex as the heterogeneous catalyst in Fenton-like reaction were done as follows: 3.0 g nano-Fe_2O_3/goldmine complex and 100 mL dyes effluent were added into Erlenmeyer flasks individually. Then various amount of NaClO (1.0 mL, 2.0 mL, 3.0 mL, 4.0 mL, 5.0 mL) was added to each flask by droplet and all suspensions were stirred at 30˚C for 2 hr. After being filtered, COD of the industrial effluent was determined and the reduction before and after stirring was used to calculate the removal rate in the Fenton-like reaction.

3. Results and Discussion

3.1. NaClO Oxidation Reaction

Relationship between the degradation effect and the dosage of NaClO in the treatment process was given in **Figure 1**. It can be seen that when the content of NaClO increased from 10 to 50 (mL/L), the COD removal efficiency increased slowly from 6.2% to 35.4%, while the color removal rate show a little higher disposal ability. It is reasonable that with the increased addition of oxidants more NaClO would join the oxidation reaction of dyes components, then much higher COD removal efficiency could be obtained.

3.2. Fenton Reaction

In **Figure 2**, effects of homogeneous catalyzed Fenton reactions are investigated based on the results of COD and color removal, respectively. Being kept the concentration of $FeSO_4$ equivalent to 30 mmol/L, degradation of industrial dyes was studied under various in feed H_2O_2 concentration. And a linear enhancement of oxidation capacity was observed for COD and color with increased H_2O_2 addition. Since the removal efficiency of COD is lower than that of color during the oxidation reaction, a conclusion can be got that mineralization of dyes components in wastewater is more difficult when compared with the damage of chromophore.

3.3. Fenton-Like Reaction

Influence of NaClO concentration on heterogeneous Fenton-like processes for dyes degradation is given in **Figure 3**. By varying concentration of oxidant from 10 to 50 mL/L, COD removal efficiency of industrial dyes ef-

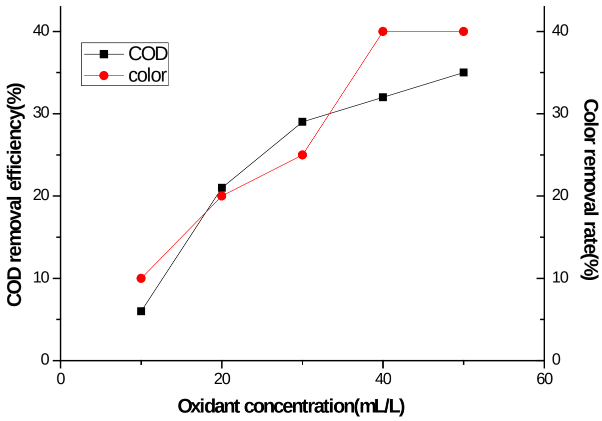

Figure 1. Effect of NaClO on COD and color degredation in industrial dyes effluent (COD = 13,000 mg/L).

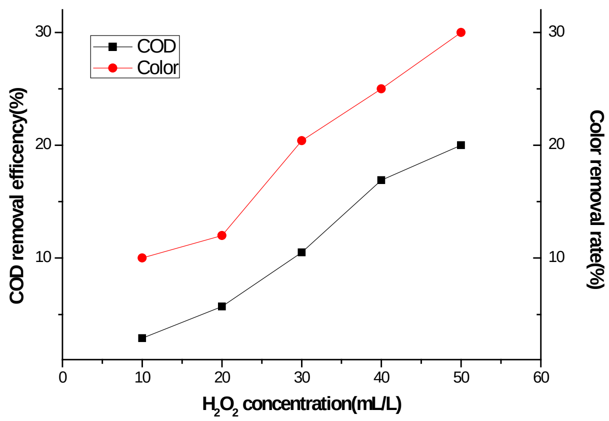

Figure 2. Effect of H_2O_2 concentration on Fenton reaction in industrial dyes effluent (COD = 13,000 mg/L, Fe^{2+} = 30 mmol/L, pH = 3.5).

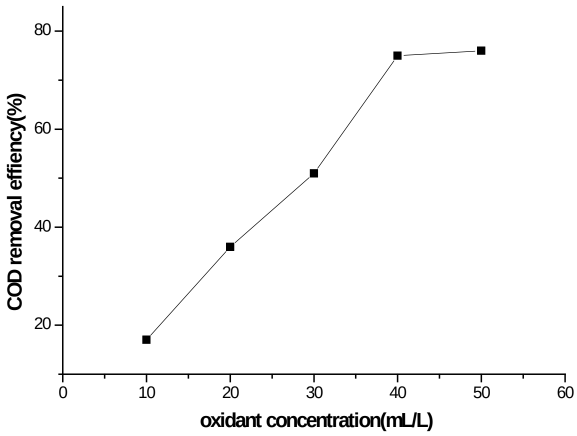

Figure 3. Effect of NaClO on Feton-like reaction in industrial dyes effluent (COD = 13,000 mg/L, nano-Fe_2O_3/goldmine complex = 30 g/L, pH = 5).

fluent was in the range of 16.9% - 75.5%. Being compared with the results treated by NaClO and Fenton reaction, it is clear that almost 2 times larger COD removal efficiency was achieved in the Fenton-like reaction when NaClO was used as oxidant in AOPs.

4. Conclusion

Nano-Fe_2O_3 modified goldmine complex can be used in advanced oxidation processes for the treatment of industrial dyes effluent. By using NaClO as oxidant, Fenton-like reaction shows highly enhanced degradation ability than by NaClO and Fenton oxidation reaction. Since different dosing steps have been found working as an important role affecting the COD removal in the oxidation process, additional effect of oxidant will be investigated in future research work.

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