Iron-loaded Natural Clay as Heterogeneous Catalyst for Fenton-like Discoloration of Dyeing Wastewater

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The clay-based Fe-bearing catalyst was successfully prepared through ion-exchange reaction and applied as heterogeneous catalyst for discoloration of acid fuchsine (AF) in an aqueous solution by Fenton-like reaction. Experimental results demonstrated that the AF discoloration ratios increased by increasing Fe-loaded clay dosage and initial H_2O_2 concentration, and by decreasing the pH, respectively. The lower the initial AF concentration, the shorter the reaction time needed to achieve complete discoloration of AF. Comparative studies indicated that AF discoloration ratios were much higher in presence of Fe-loaded clay and H_2O_2 than those in presence of H_2O_2, raw natural clay or Fe-loaded clay only and raw natural clay and H_2O_2 jointly. After AF discoloration, there existed no new phases in the clay samples detected by XRD and no change in the clay crystal morphology observed by SEM. A mechanism proposed suggested adsorption and Fenton-like reaction were responsible for discoloration of AF.

Key Words: Fe-loaded clay, Acid fuchsine, Heterogeneous catalyst, Discoloration, Fenton-like reaction

Introduction

In textile industry, it was estimated that 10 ~ 15% of the dye was lost during the dyeing process and released as effluent, which constitute threat to environment.[1] Dyeing wastewater is known to contain strong color, high pH, temperature and COD, and to have low biodegradability.[2] This can lead to acute effects on exposed organisms due to the toxicity of the dyes, abnormal coloration and a resultant reduction in photosynthesis.[3,4] Due to their stability and to their xenobiotic nature, reactive azo dyes are difficult to be not totally degraded.[5] Techniques for dyeing wastewater decoloration can be grouped into physical, chemical and biological methods.[3]

Environmental catalysis performs an essential role in minimizing the emission of toxic compounds and the development of energy saving, residue-free processes.[6] Fenton's reagent [Fe(II)+hydrogen peroxide], a widely used and studied catalytic treatment system, has been applied to treat various wastes such as those found in the textile and chemical industries.[7,8] Hydroxyl radicals (·OH), a very strong and non-specific oxidant, is generated by the Fe(II)-catalyzed decomposition of hydrogen peroxide (H_2O_2). However, the common drawback of Fenton's reaction is the generation of secondary pollutants, the ferric ions.[9] To overcome this disadvantage, the use of iron types supported on an appropriate solid makes up a favorable alternative in the generation of a 'Fenton-modified' process.[6] For instance, Fenton-driven chemical oxidation of methyl tert-butyl ether (MTBE)-spent granular activated carbon (GAC) was accomplished through the addition of iron and hydrogen peroxide.[10] Iron-containing zeolite of MFI structure was used as heterogeneous Fenton-type catalyst.[11] The heterogeneous photo-Fenton-type oxidation of reactive azo dye solutions was investigated using Fe-exchanged zeolite as a heterogeneous catalyst.[12] Clays have been and continue to be one of the more important industrial minerals. The arrangement and composition of octahedral and tetrahedral sheets accounts for the major and minor differences in the properties of clay minerals and thus on their ultimate applications.[13] Still, clay minerals have commonness of ion-substitution in their structures, which makes them much easier as loaders for iron ion. Through cation exchange reaction, hydroxyl-Fe pillared bentonite was successfully prepared as a solid catalyst for UV-Fenton process.[14] The degradation and mineralization of Orange II solutions using catalysts based on pillared saponite impregnated with several iron salts was reported by Ramirez and co-workers.[15] Cheng *et al.* indicated that the iron species in layered clays were active for catalytically oxidizing synthetic dyes. Three layered clays, montmorillonite, laponite, and nontronite, were used to investigate the role of the iron species in the clays in their study.[16] However, the reports of natural kaolinite clay used as Fenton-like catalyst were still rare in wastewater treatment to the best of our knowledge.

Hence, the present investigation focuses on the preparation of iron-containing catalyst loaded by natural kaolinite clay and its catalytic performance in Fenton-like system for discoloring the active commercial dye, acid fuchsine (AF), in an aqueous solution. The affecting factors, such as contact time, catalyst dosage, H_2O_2 concentration, were studied. Changes in catalyst's crystal-chemical properties before and after discoloration have been characterized using X-ray diffraction (XRD) and Scanning electron microscope (SEM). Then, the discoloration mechanism was put forward.

Experimental Section

Clay collection. The original clay was a commercial type natural kaolinite, collected from Shu-Lan, Jin-Lin province, China. It was gray white in color. The mineral sample was sieved, and sample of −2 μm size range was used in the present studies. The physical properties and chemical compositions have been discussed in previous work.[17]

Catalyst preparation. Through ion-exchange reaction, the

clay-based catalyst was prepared. An aqueous dispersion of clay was prepared by adding 10 g of clay to 500 mL of H_2O under stirring for 1.5 h at room temperature. A 500 mL 0.2 M solution of ferrous sulfate ($FeSO_4 \cdot 7H_2O$, analytical grade) was added into the dispersion of clay under vigorous stirring. The suspension was stirred for 1h followed by aging at room temperature for 12 h. Then, the precipitate was filtered and dried in air at 80 °C overnight. Finally, the iron-loaded clay-based catalyst was obtained.

Testing techniques. XRD was employed to identify mineral phases and estimate crystallinity. Measurements were made on a Shimazu XD-5A instrument with Cu-K_α radiation (λ = 1.54050 Å) at 30 mA and 35 kV. SEM equipped with EDS was utilized to determine the crystal morphology and chemical element composition. Measurements were made on a JSM-5500 SEM instrument using a digital imaging process.

Discoloration methods. One commercial dye, namely, acid fuchsine (AF), with chemical formula of $C_{20}H_{17}O_9N_3S_3Na_2$ and molecular weight of 585.54, was selected as model pollutant. Its molecule structure is shown in Figure 1. A stock solution containing AF (1000 mg/L) was prepared using double distilled water, subsequently diluted to the required concentrations for the experimental work. The pH was adjusted by addition of sodium hydroxide and nitric acid to the AF solutions. The concentration of hydrogen peroxide was 30% (w/w). All chemicals were of analytical grade. Then, catalyst sample prepared previously was added into 100 mL of solution of required concentrations of AF in a conical flask. After sealing, the conical flasks were placed in a constant-temperature water-bathing retort at temperatures and contact times. The AF concentrations were measured using a 757-type ultraviolet-visible-spectrophotometer. The discoloration ratio, i.e. the removal
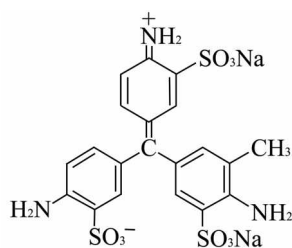
degree of color at the λ_{max} of the wastewater sample (545 nm) was calculated using DR (%) = $(C_0 - C_t)/C_0 \times 100$, where C_0 is the initial concentration of the AF wastewater and C_t the concentration at contact time t. In order to check the reproducibility of the results, random tests were done for different experimental conditions.

Results and Discussion

Sample characterization. Figure 2(a) is the XRD pattern of raw natural clay mineral. The main diffraction peaks are assigned to typical kaolinite crystallite (JCPDS78-1996), with characteristic six peaks at $2\theta = 35 - 40°$.[18] Judging from the intensity and split of peaks at $2\theta = 19 - 22°$, it can be concluded that the order degree of kaolinite mineral is poor.[19] Furthermore, there exists quartz (diffraction peak at $2\theta = 26.9°$, JCPDS1-649) as minor impurity in the natural clay. Morphological observations by SEM reveal that the kaolinite crystals are pseudo-hexagonal along with plates and some larger books, shown in Figure 3(a). The XRD pattern of Fe-loaded clay is shown in Figure 2(b), which suggests that, after Fe ions are
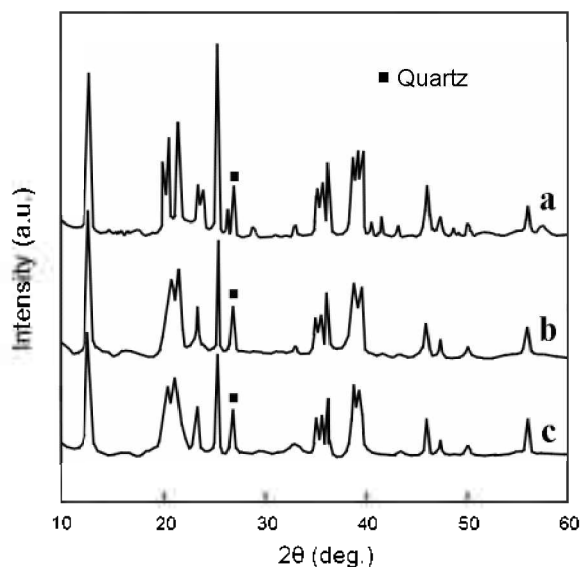

Figure 1. Molecular structure of acid fuchsine.

Figure 2. XRD patterns of (a) raw natural clay, (b) Fe-loaded clay and (c) Fe-loaded clay after AF discoloration.
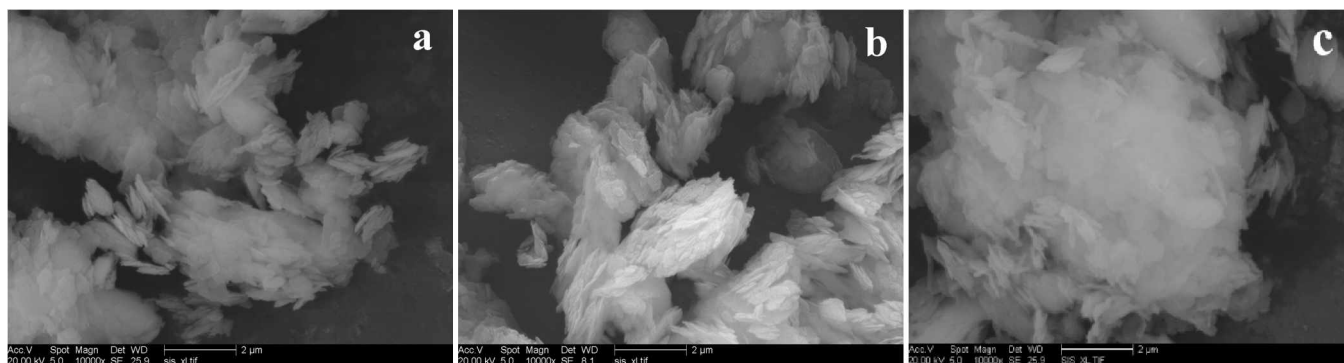

Figure 3. SEM micrographs of (a) raw natural clay, (b) Fe-loaded clay and (c) Fe-loaded clay after AF discoloration.

loaded. the clay mineral still holds the crystal structure of kaolinite. Different from raw natural clay, the order degree of kaolinite loaded by Fe becomes poorer. And, there is no change in the crystal morphology of Fe-loaded clay observed by secondary electron imaging of SEM (Figure 3(b)).

Fenton-like discoloration of AF. Figure 4 shows the AF discoloration ratios versus time under different H_2O_2 concentration conditions. The data clearly indicate that the AF discoloration ratio increases with increasing H_2O_2 concentration, which suggests the more H_2O_2 concentration is, the more OH radical generation is.[20] So, the increase of H_2O_2 concentration leads to higher system reactivity. When the addition of H_2O_2 concentration is more than 3.0 mL/L, only 10 minutes are required for AF discoloration ratio above 90%. Figure 5 shows the AF discoloration ratios versus time under different Fe-loaded clay dosage conditions, which suggests that the reactivity of the system increases by increasing Fe-loaded clay dosage. The more the catalyst dosage, the more active Fe sites on the catalyst surface for accelerating the decomposition of H_2O_2
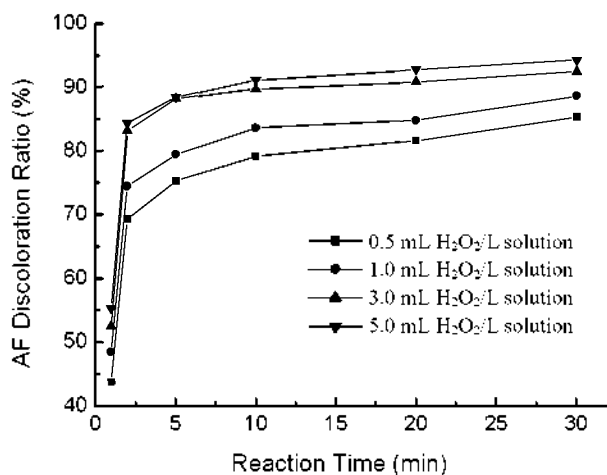
(heterogeneous catalysis), and the more Fe ion leaching in the solution, leading to an increase in the number of OH radicals (homogeneous catalysis).[21] When the dosage of Fe-loaded clay is 10 g/L, the AF discoloration can reach 90% only after five-minute's reaction time. Figure 6 shows the AF discoloration ratios versus time under different initial AF concentration conditions. It can be found that the lower the initial AF concentration, the shorter the reaction time needed to achieve complete discoloration of AF, which is the normal phenomenon for pollutant discoloration.[21] Figure 7 shows the AF discoloration ratios versus time under different pH conditions. The AF discoloration ratio increases by decreasing the pH value in the solution. The possible reason for this phenomenon is that, at acidic pH, more Fe ion is dissolved in the solution from Fe-loaded clay catalyst, which then catalyzes H_2O_2 to generate more OH radicals, resulting in a faster discoloration of AF, and homogeneous catalysis is responsible for this process at alkaline pH, because there is less Fe ion leaching in the solution, it is proposed that H_2O_2 is catalyzed by active Fe sites on the

Figure 4. Effect of initial H_2O_2 concentration on the discoloration of 100 mg/L AF under pH = 5, 10 g/L of Fe-loaded clay catalyst dosage and room temperature.
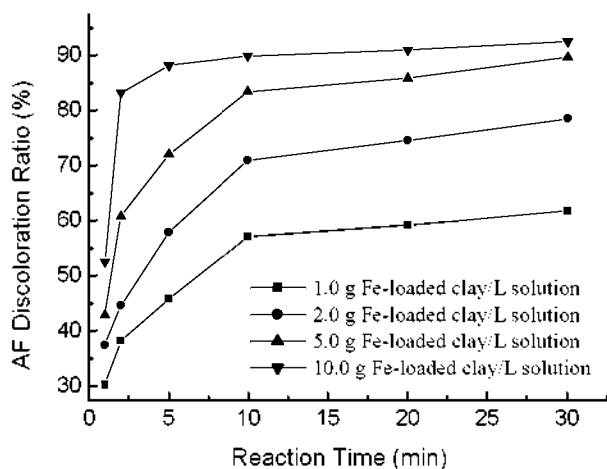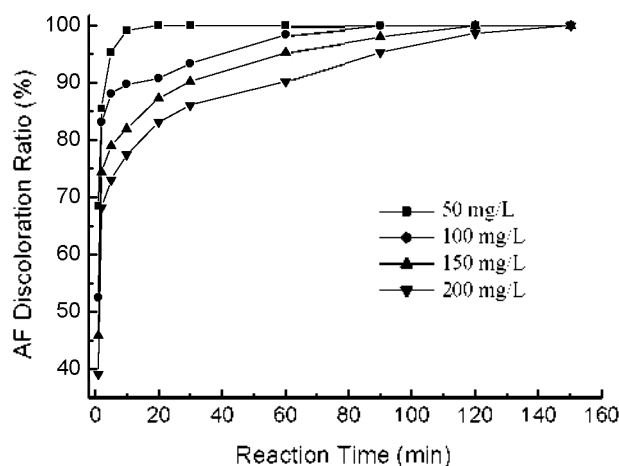

Figure 6. Effect of initial AF concentration on the discolorationof AF under pH = 5, 3.0 mL/L of initial H_2O_2 concentration, 10 g/L of Fe-loaded clay catalyst dosage and room temperature.
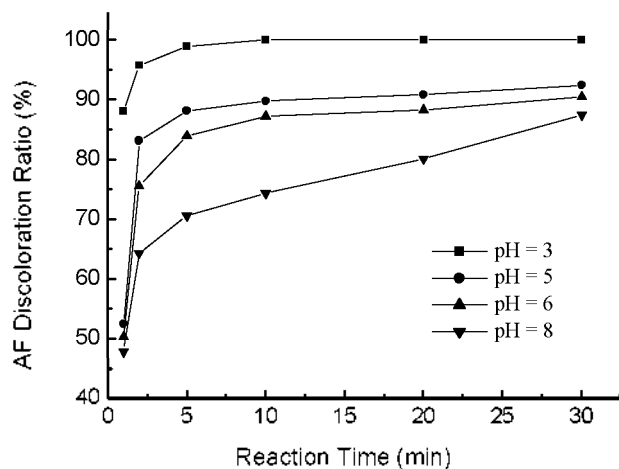

Figure 5. Effect of Fe-loaded clay catalyst dosage on the discoloration of 100 mg/L AF under pH = 5, 3.0 mL/L of initial H_2O_2 concentration and room temperature.

Figure 7. Effect of pH value on the discoloration of 100 mg/L AF under 3.0 mL/L of initial H_2O_2 concentration, 10 g/L of Fe-loaded clay catalyst dosage and room temperature.
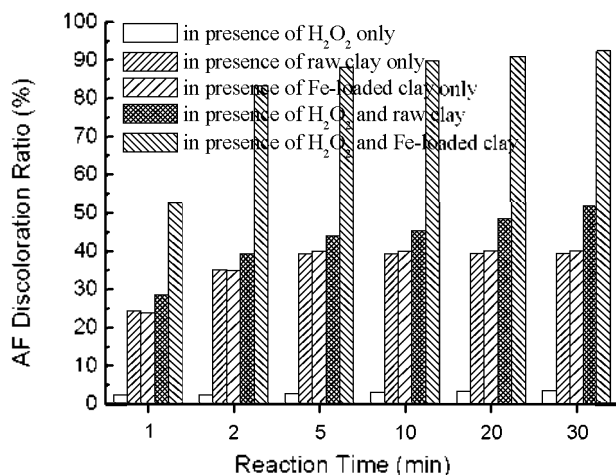
Figure 8. Comparative analyses for the discoloration of 100 mg/L AF under different reaction time at condition of pH = 2 and room temperature.

surface of Fe-loaded clay catalyst, and heterogeneouscatalysis governs this process.[22]

Mechanism for AF discoloration. In order to gain an insight into the process of the AF discoloration by Fe-loaded clay catalyst, comparative experiments were undertaken in presence of (i) H_2O_2 only (initial H_2O_2 concentration = 3.0 mL/L), (ii) raw natural clay only (clay dosage = 10 g/L), (iii) Fe-loaded clay only (clay dosage = 10 g/L), (iv) raw natural clay and H_2O_2 (clay dosage = 10 g/L and initial H_2O_2 concentration = 3.0 mL/L), and (v) Fe-loaded clay and H_2O_2 (clay dosage = 10 g/L and initial H_2O_2 concentration = 3.0 mL/L). The results are shown in Figure 8, where it can be observed that, in the (i) condition, the discoloration ratio of AF is lowest, in the (ii) and (iii) condition, the discoloration ratio is nearly equivalent, in the (iv) condition, the discoloration ratio is little higher than that of the (ii) and (iii) condition, but in the (v) condition, the AF wastewater can be discolored significantly, approaching 95%. In the presence of H_2O_2 only, the AF discoloration ratio is nearly null. In the presence of raw natural clay only and Fe-loaded clay only, less than 40% of AF can be discolored, due to adsorption of AF by solid sample, which can reach adsorption equilibrium after 5 minutes of reaction time. In the presence of raw natural clay and H_2O_2, little higher AF discoloration ratio is achieved because, besides adsorption, Fenton-like reaction might occur, catalyzed by trace amount of Fe ion in the clay structure. When both H_2O_2 and Fe-loaded clay are present, it is discolored significantly, due to the Fenton-like reaction.

A further investigation using XRD and SEM to characterize the Fe-loaded clay after AF discoloration shows the following results that there exist no new phases in the clay samples, which can be detected by XRD (Figure 2(c)) and there is no change in the clay crystal morphology observed by secondary electron imaging of SEM after AF discoloration (Figure 3(c)).

So, the reaction mechanism of AF discoloration is put

forward in our present study. Adsorption and Fenton-like reaction govern the process.

Conclusion

The clay-based Fe-bearing catalyst was successfully prepared and used as heterogeneous catalyst in Fenton-like system for discoloration of acid fuchsine wastewater. A number of batch discoloration experiments under various conditions strongly indicated that the optimized conditions for 100 mg/L AF discoloration ratio approaching 100% were as follows: the initial H_2O_2 was 3 mL/L, the reaction time was 10 min, the Fe-loaded clay dosage was 10 g/L and the solution pH was 5. Adsorption and heterogeneous Fenton reaction governed the fast discoloration of AF. After AF discoloration, there existed no new phases in the clay samples detected by XRD and no change in the clay crystal morphology observed by SEM.

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