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Degradation of Reactive Blue 19 dye in aqueous solution using iron-modified fly ash

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Abstract: Reactive Blue 19 dye in aqueous solutions was removed by heterogeneous Fenton-like process using iron-modified fly ash. Under the suitable conditions including catalyst dose of 0.6 g/L, hydrogen peroxide dose of 4 mM, pH3, the RB19 degradation efficiency can be achieved ca. 92% and 97% in 6 h and 24 h, respectively. The catalyst can be reused without the reduction of degradation performance.
Keywords: Reactive Blue 19 dye, Fly Ash.

1. Introduction

Wastewater from the textile industry has become a serious environmental problem in many countries [1-6]. Textile wastewater is causing multidimensional problems not only to the land mass fertility but also to the natural flora, fauna, as well as the aquatic bodies. Therefore, it is very necessary to remove the dyes from textile wastewater before discharge. Among the treatment technologies, advanced oxidation processes (AOPs) have received widespread attention for degradation of dyes in textile wastewater [1]. Homogeneous Fenton oxidation, which involves the generation of hydroxyl radical via a reaction between hydrogen peroxide and ferrous ion, is the most widely used technique for destroying dyes in aqueous solution. However, the homogeneous Fenton technique has some significant disadvantages, including (i) requirement for large amount of chemicals, (ii) cost for huge amount of sludge-containing ferric ions that need to be treated, and (iii) inactivation of ferrous ion by interacting with ions such as phosphate or some intermediate oxidation products in aqueous solutions, which restrict its application [2]. These disadvantages of the homogenous process can be overcome by the heterogeneous Fenton-like process, in which oxidating agents and iron immobilized on a solid support are used. In contrast to the homogeneous Fenton process, the heterogeneous one provides the possibilities to recover and reuse solid catalysts and operate in broader pH range. Wu et al. developed the functional iron nanoparticles by tea extracts and used as a catalyst for the Fenton-like oxidation of malachite green (MG). The authors reported that more than 85% of MG was removed under the suitable conditions [1]. Herney-Ramirez et al. used response surface methodology to optimize the conditions for the oxidation of Orange II dye by iron-impregnated saponite. As reported, more than 99% colour and 90% TOC can be removed under the optimum conditions [3]. Shao-hua and Dong-yun studied the degradation of n-butyl xanthate using fly ash combined with hydrogen peroxide [7]. The authors found that over 97% chemical oxygen demand (COD) removal and 97% n-butyl xanthate conversion can be achieved within 120 min under suitable conditions. However, to the best of our knowledge, little information is available regarding the utilization of fly ash as the heterogeneous Fenton-like catalyst for degradation of reactive dyes in aqueous solutions.

In the present work, fly ash was modified and used as a heterogeneous Fenton-like catalyst for degradation of Reactive Blue 19 dye (RB19) in aqueous solutions. Effects of catalyst dose, the dose of hydrogen peroxide, and pH on the decolorization efficiency were investigated and discussed.

2. Experimental section

Materials

Fly ash used in this study was collected from Uong Bi thermal power plant in Quang Ninh province, Vietnam. The sample was dried in an oven at 105 °C for 24 h, and stored in a sealed jar at room temperature for experiments.

Fly ash was loaded with iron by the incipient impregnation method followed by thermal treatment. For a typical procedure, 4 g of $Fe(NO_3)_3 \cdot 9H_2O$ (98%) was dissolved in 20 mL of distilled water. Then, 10 g of fly ash was added to the solution. The mixture was stirred using a magnetic stirrer at the speed of 20 rpm and heated at 100 °C until the water was completely evaporated. The collected solid was dried overnight in an oven at 100 °C. The catalyst, denoted as Fe-FA, was obtained after heating the solid at 400 °C for 3 h.

Characterization

The texture parameters Fe-FA were characterized via N_2 adsorption-desorption isotherm at 77 K on a volumetric sorption analyzer (ASAP2420, Micrometrics, USA). The element components of the materials were determined by an energy dispersive X-ray spectroscopy (EDS) with FESEM-EDS S-5000 (Hitachi, Japan) at an accelerating voltage of 25 kV.

Degradation experiment

RB19 used in this study with the chemical structure as shown in Fig. 1 was purchased from Shimi Boyakhsaz Co., Iran. Degradation experiments were conducted by adding a specific amount of Fe-FA to an agitated reactor. 500 mL of 200 mg/L of RB19 containing aqueous solution with adjusted pH by the addition of HCl or NaOH was injected into the agitated reactor. pH was measured using pH meter. The catalyst was mixed well with the aqueous RB19 dye solution at 200 rpm in the agitated reactor. Then, aqueous hydrogen peroxide solution (30wt%) was added to the mixture to start to degrade RB19.

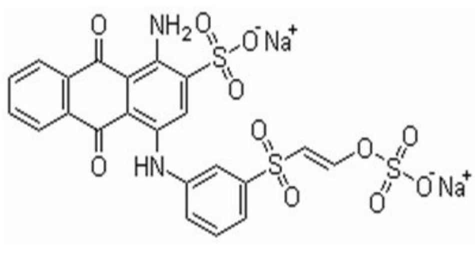

Fig. 1. Chemical structure of RB19 dye.

Table 1. Physical properties of RB19 dye

Dye properties	
Color index	Reactive Blue 19
Molecular formula	$C_{22}H_{16}N_2Na_2O_{11}S3$
Molecular weight	626.54
λ_{max}	593.0 nm
Antraquinone groups	1

Analytical procedures

The concentration of RB19 in aqueous solutions was determined by the photometric method at 593 nm. Dye removal performance, *H* (%), was determined using the following formula:

$$H = 100\times(C_0 - C_t)/C_0 \qquad (1)$$

where C_0 and C_t (mg/L) are concentrations of RB19 in the aqueous solutions before the degradation and after the reaction for *t* (min), respectively.

3. Results and Discussions

3.1. Characterization of materials

The elemental composition of the catalyst was verified using an energy dispersive EDX analysis to obtain the additional information on the catalyst performance. After impregnation with iron salt, the iron content in fly ash is greatly increased from 4.43% to 9.76%, which is evident from the SEM-EDS spectra of fly ash and Fe-FA in the panels a and b of Fig. 2, respectively. This result indicated that iron was impregnated into fly ash successfully. The SEM-EDS spectra also indicated that Si, Al, Fe, and C are the main elements in the fly ash. This result is in good agreement with the XRD patterns of fly ash which show three main compounds in the sample including quartz, mullite, and hematite [4,8].

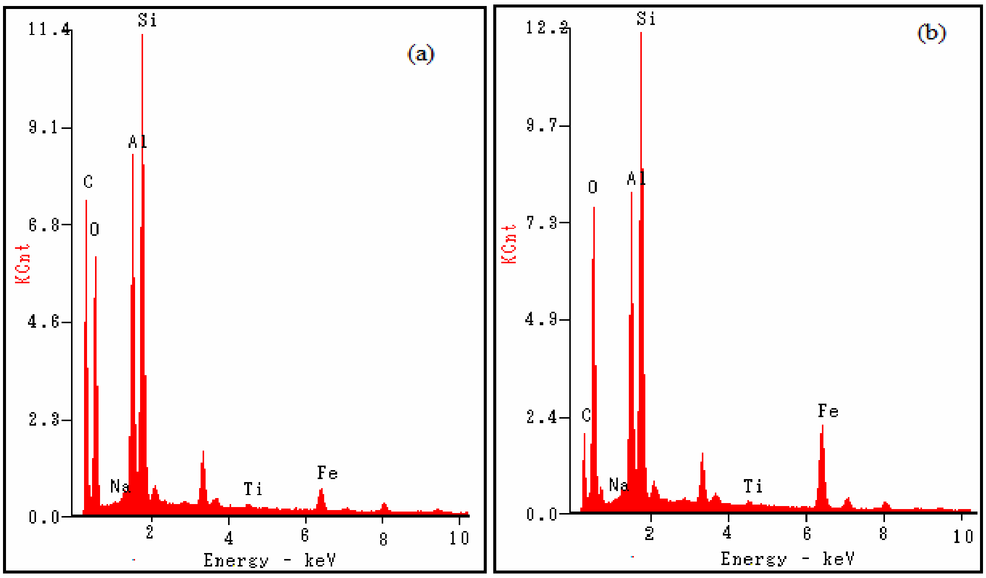

Fig. 2. EDS spectra of RFA (a) and Fe-FA (b).

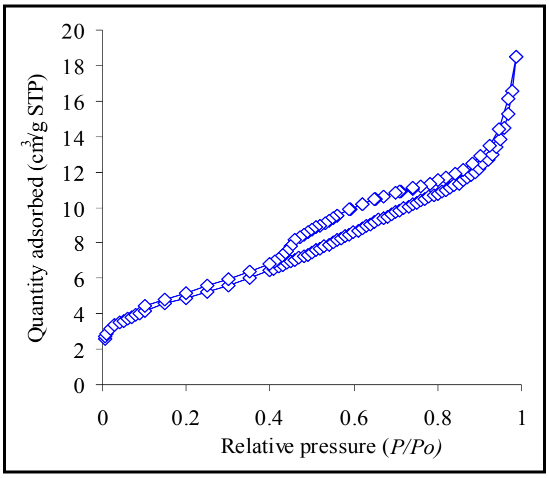

Fig. 3. N_2 adsorption-desorption isotherms of Fe-FA at 77 K.

Nitrogen adsorption-desorption isotherm of the catalyst in Fig. 3 showed that Fe-FA had BET surface area, pore size, and pore volume of 17.14 m^2/g, 124. 08 $\overset{o}{A}$, and 0.02 cm^3/g, respectively. This analysis also indicated that Fe-FA exhibited typical type IV according to the IUPAC classification.

3.2. Effect of catalyst dose

A heterogeneous Fenton-like process requires higher amount of catalyst than homogeneous Fenton-like processes which have been being worked well in the presence of low quantities of iron ions. Effect of catalyst dosage on the degradation performance in this work was conducted by changing the initial catalyst dosage from 0.4 g/L to 2.0 g/L. As shown in Fig. 4, the degradation efficiency of RB19 increased with increase in load of Fe-FA from 0.4 to 0.6 g/L due to the increase of active sites for producing hydroxyl radicals. After 6 h of treatment, about 79% and 92% of RB19 were removed under the catalyst doses of 0.4 g/L and 0.6 g/L, respectively. However, the RB19 degradation performance reduces to ca. 79% and 78% in 6 h for 1.0 and 2.0 g/L Fe-FA, respectively, suggesting that Fe-FA acts as $OH^{\bullet}$ scavengers at high iron amount. Comparing to Reactive Blue 181, the required time for the degradation of RB19 is longer [4]. Considering lower Fe-FA loading and better catalysis performance, the Fe-FA loading of 0.6 g/L was chosen in the rest experiments. Under the optimum conditions, the degradation efficiency can be increased to ca. 97% in 24 h.

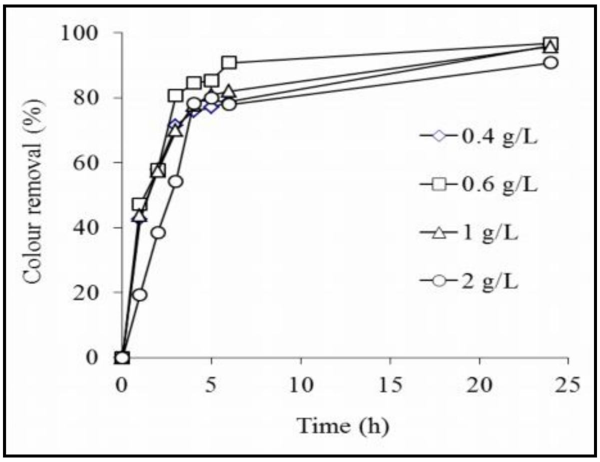

Fig. 4. Effect of catalyst dosage on the decolorization of RB19.

3.4. Effect of hydrogen peroxide dose

Hydrogen peroxide plays an important role as a source of $OH^{\bullet}$ generation in Fenton, Fenton-like processes, and its concentration is one of the most important factors which affects on the treatment efficiency for dyes degradation by both homogeneous and heterogeneous Fenton techniques. The effect of H_2O_2 dose on the decolorization of RB19 was carried out from 2 mM to 5 mM at pH 3, catalyst dose of 0.6 g/L, and RB19 concentration of 200 mg/L. The results in Fig. 5 showed that the treatment efficiency increased with the increasing of H_2O_2 dose in the range of 2 mM to 4 mM, but decreased at higher concentration of H_2O_2. The most suitable concentration of H_2O_2 in this study is 4 mM for the degradation of RB19. At low concentration, H_2O_2 could not generate enough hydroxyl radicals, and the treatment performance is logically slow. The increase of hydroxyl radicals due to an increasing H_2O_2 concentration enhanced the degradation efficiency. However, at a concentration of H_2O_2 higher than 4 mM, the treatment efficiency decreased, attributed to the recombination of free radicals, scavenging of $OH^{\bullet}$ radicals by H_2O_2 and incremental generation of $HO_2^{\bullet}$ also consumes $OH^{\bullet}$, and due to the auto-decomposition of H_2O_2 to water and oxygen [9]:

$H_2O_2 + OH^{\bullet} \longrightarrow H_2O + HO_2^{\bullet}$	(1)
$HO_2^{\bullet} + OH^{\bullet} \longrightarrow H_2O + O_2$	(2)
$2OH^{\bullet} \longrightarrow H_2O_2$	(3)
$2H_2O_2 \longrightarrow H_2O + O_2$	(4)

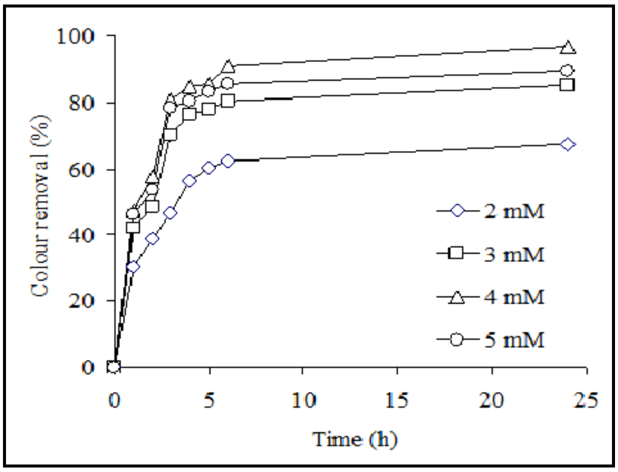

Fig. 5. Effect of hydrogen peroxide dosage on the decolorization of RB19.

3.3. Effect of pH

Generally, pH has significant effect on the degradation of organic pollutant in aqueous solutions by hydroxyl radicals in Fenton and/or Fenton-like processes. The effect of initial solution pH on the degradation of RB19 using Fe-FA catalyst was also investigated in a range of initial pH of solution varied from 2 to 5. The experimental results, as shown in Fig. 6, confirm that pH plays an important role on the degradation of RB19 by heterogeneous with Fe-FA. As seen, the degradation efficiency of RB19 decreased with the increase of pH. After 6 h of treatment, the degradation performance under pH 4 and pH 5 is much lower than those at pH 2 and 3. At pH > 3, the decomposition of H_2O_2 and the deactivation of Fe-FA lead to the reduction of hydroxyl radicals, and the degradation performance decreased as a result [7, 10].

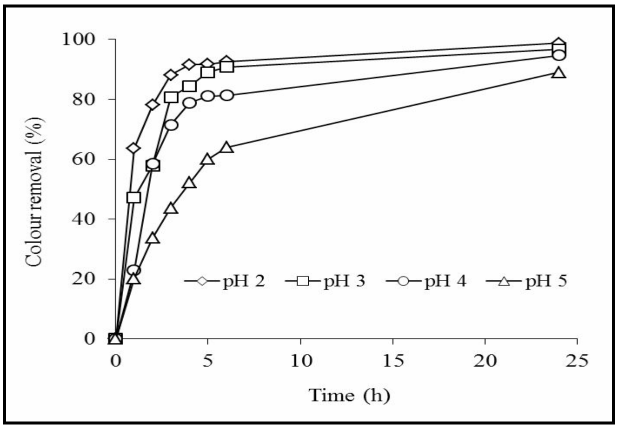

Fig. 6. Effect of pH on the decolorization of RB19.

3.4. Reusability

The stability and recyclability of Fe-FA catalyst for the degradation of RB19 was evaluated by recycling and reusing the catalyst over four consecutive cycles. After each run, the catalyst was separated from the solution by filtration, and then dried for the next degradation experiment. After 6h of treatment, about 92% decolorization efficiency was achieved in all four cycles (Fig. 7). The experimental results indicated that Fe-FA can be reused for successive treatments.

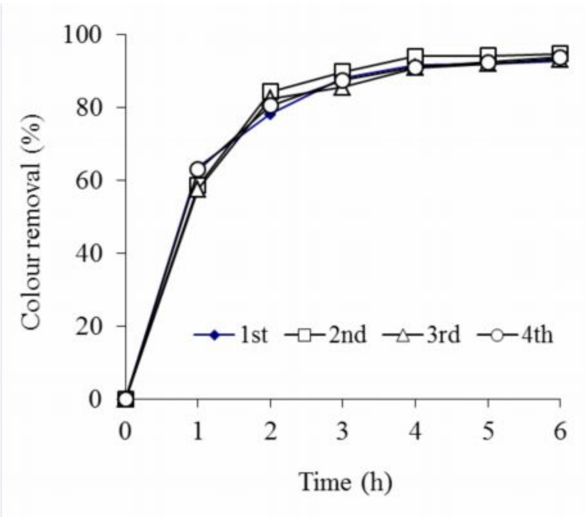

Fig. 7. The degradation performance of RB19 over 4 reused cycles of Fe-FA.

4. Conclusions

The iron impregnated fly ash has been prepared as a heterogeneous Fenton-like catalyst for the removal of reactive dye RB19 in aqueous solutions. Under the suitable conditions including catalyst dose of 0.6 g/L, hydrogen peroxide dose of 4 mM, and pH3, about 92% and 97% of RB19 were removed in 6 h and 24 h, respectively. The catalyst can be reused for successive decolorization.

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