

Heterogeneous catalytic degradation of polyacrylamide solution

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Abstract

Degradation of polyacrylamide (PAM) in aqueous solution was studied by using $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ as heterogeneous catalyst in the presence of H_2O_2 . Effects of catalyst preparation conditions such as impregnated materials and adding different trace metal elements to catalyst activity were studied, respectively. It was observed that compared with FeSO_4 , the Fe(III) catalyst prepared with $\text{Fe}(\text{NO}_3)_3$ as the impregnated material showed better catalyst activity. Modified with trace metal elements, the catalytic activity of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ could be changed greatly. Among various trace metal elements, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts modified with Co and Cu showed great increase on catalytic activity.

Keywords: Fenton-like; polyacrylamide; heterogeneous catalyst; Fe(III) catalyst.

1. Introduction

“Produced water” is the largest volume of waste generated by the oil industry (Liu *et al.*, 2008). In China, the most oil fields have entered a stage of tertiary oil recovery. A kind of new produced water containing polyacrylamide (PAM) was produced with the conducting of polymer flooding in tertiary oil recovery processes. However, the method of treating the produced water is discharged by re-injection into the subsurface, which has caused severe contamination to the ground water wells. Nevertheless, the existing methods are very difficult to deal with it. Thus, the treatment of produced water containing PAM has become a key problem in China.

Many methods had been developed for treating PAM, including ultrasonic degradation (Vijayalakshmi *et al.*, 2005; Yen, 2003), pulsed laser degradation (Vijayalakshmi *et al.*, 2005), thermal degradation (Yang, 1998; Yang, 2000), photo-catalytic degradation (Vinu *et al.*, 2008) and so on. However, some of these methods are too expensive to achieve industrialization, and it was found that the degradation ratio of PAM in aqueous solution was slow by using physical and biological methods. Recently, some studies used the successful application of advanced oxidation processes for PAM treatment. Fenton reaction, regarded as a very effective approach, has been used in the degradation of many organic compounds. However, as the homogeneous reaction, Fenton reaction has a disadvantage that the removal of Fe ions in the solution after the reaction is a rather costly process. Therefore, many efforts have been made to explore new heterogeneous catalysts. In recent years, there have been reports on the heterogeneous catalyst instead of Fe ions catalyzed decomposition of hydrogen peroxide, such as Metal Oxide, known as the Fenton-like (Barreiro *et al.*, 2007; Xu, 2009) reaction. Compared with Fenton reaction, Fenton-like reaction has obvious advantages: catalysts are easy to be recovered and a negligible amount of metal ions into the liquid phase. Liu *et al.* (2008) prepared heterogeneous Fe(III)- SiO_2 catalysts for the photo-Fenton degradation of PAM in aqueous solution successfully, and about 94% degradation of PAM and 70% TOC is removed in 180min at an initial pH of 6.8. Dantas *et al.* (2006) reported the treatment of textile wastewater using $\text{Fe}_2\text{O}_3/\text{carbon}$ can be carried out at initial pH above 3.0 and lower hydrogen peroxide consumption than in the homogeneous Fenton process is needed. Neamtu *et al.* (2004) evaluated the degradation of a reactive azo dye, procion Marine, by Fenton-like process with Fe-exchanged Y zeolite as catalyst, and found more than 96% removal of color of 100mg/L dye could be removed in 30min at pH 5, $T=50^\circ\text{C}$. However, the degradation of organic pollutants with high concentration by Fenton-like process at general conditions or without other special equipment is not satisfactory.

Many investigators have been trying to improve the catalytic activity and stability of heterogeneous oxidation catalysts (Laat *et al.*, 2006; Baldrian, 2006; Kitis and Kaplan, 2007; Zelmanov and Semiat, 2008). In this paper, the Fe(III) catalyst was prepared as

a heterogeneous catalyst for the degradation of PAM in aqueous solution. The catalytic activity was investigated at general conditions (atmospheric pressure, pH=7.2, T=60°C). In order to improve the catalytic activity, effects of catalyst preparation conditions as impregnated materials and adding trace elements to catalyst activity were studied in detail.

2. Experimental

2.1 Materials: The analytical grade PAM, H₂O₂ (30%, w/w), Fe(NO₃)₃·9H₂O, FeSO₄·7H₂O, ZnSO₄·7H₂O, CuSO₄·5H₂O, CoCl₂·6H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, MnSO₄·H₂O and Mn(NO₃)₂·6H₂O were used for this experiment without further purification. The average molecular weight of PAM was 7 000 000Da. The carrier used in the study was Al₂O₃ granule (60-80 mesh) supplied by Tianjin Kewei Chemical Company, China.

2.2 Catalyst preparation: The catalyst was synthesized by impregnation methods and the concrete prepared process as follows: carrier were added into aqueous solution of Fe(NO₃)₃ or FeSO₄ and kept stirring for 1 h after 12 h at room temperature, the samples were dried for 4h at 100 °C. Then the samples were calcined at a high temperature for 4h. Finally, the Fe(III) heterogeneous catalysts were obtained. The catalysts prepared in different conditions are showed in Table 1.

Table 1. The catalysts prepared in different conditions

name	carrier	impregnated material	calcination temperature(°C)
Al-Fe/1	Al ₂ O ₃	Fe(NO ₃) ₃	400
Al-Fe/2	Al ₂ O ₃	FeSO ₄	800

Note: The above catalysts do not contain any trace elements

2.3 Characterization of catalyst: The surface morphology of the samples was investigated using a JSM-6380 analyzer. Brunauer-Emmett-Teller(BET) specific surface area and total pore volume of the Fe(III) heterogeneous catalysts were measured by adsorption of nitrogen, by using automated volumetric adsorption instrument (Quantachrome Quadrosorb SI). XRD analysis was carried out using a Rigaku D/max-rB system with Cu K α radiation operating at 45 kV and 40 mA. The 2 θ ranged from 10° to 90°.

2.4 Catalytic activity: All solution was prepared with distilled water. The experiments were conducted in a batch reactor with mechanical stirring. The initial pH of reaction solution was about 7.2. The pH variation during the reaction was less than ± 0.1 pH unit. The reactions were initiated by injecting Fe(III) heterogeneous catalyst to the mixed solution of H₂O₂(0.6g/L) and PAM(400mg/L), the temperature of the solution was 60°C. The degradation ratio of PAM, M, was calculated by the intrinsic viscosity of PAM solution, and the intrinsic viscosity was measured by Ubbelohde viscometer. M was calculated and defined as below:

$$M = \frac{M_0 - M_t}{M_0} \times 100\%$$

where M₀ and M_t refer to the M of PAM at reaction time 0 and t.

3. Results and Discussion

3.1 BET and SEM analysis of catalysts: The BET surface area and total pore volume of the investigated catalysts were listed in Table 2. Al-Fe/1 and Al-Fe/2 catalyst reduced the surface area from 296.8 to 209.0 m²/g and 176.3 m²/g, respectively, and due to the introduction of Fe, the total pore volume of the catalysts also reduced compared with the carrier. In addition, Al-Fe/1 catalyst shows more BET surface area and total pore volume compared with Al-Fe/2 catalyst. The dispersion of Fe₂O₃ particles on the surface of Al-Fe/1 and Al-Fe/2 catalysts is as showed in Fig. 1. It can be seen that slight aggregates of Fe₂O₃ particles are observed on the surface of Al-Fe/2 catalyst from Fig. 1 (a), but the better dispersion can be achieved in Al-Fe/1 catalyst as shown in Fig. 1 (b).

Table 2. Results of BET tests

Name	BET surface area(m ² /g)	Total pore volume(mL/g)
Al ₂ O ₃	296.8	0.4521
Al-Fe/1	209.0	0.4330
Al-Fe/2	176.3	0.3356

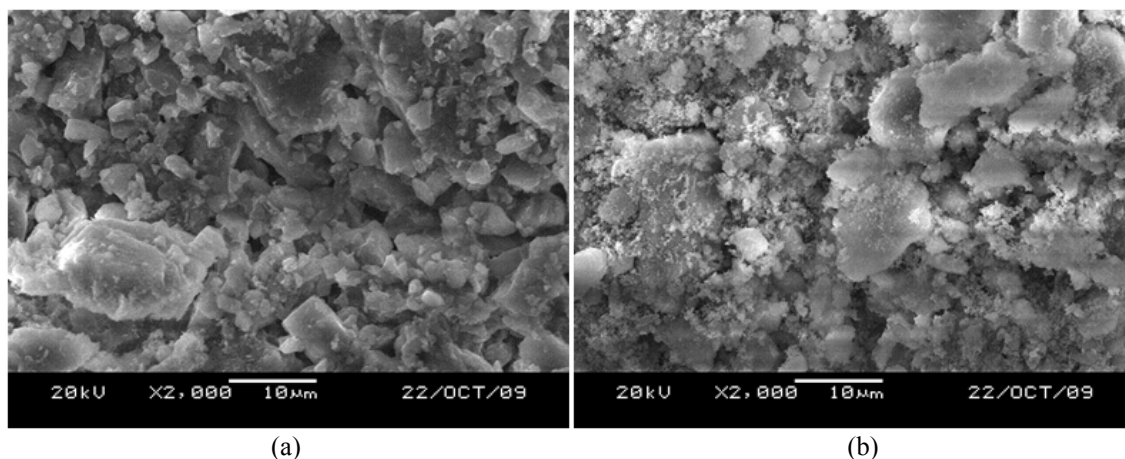


Figure 1. SEM image of catalysts: (a) Al-Fe/2; (b) Al-Fe/1

3.2 XRD analysis and catalyst: The XRD patterns of Al_2O_3 carrier, Al-Fe/1 and Al-Fe/2 catalyst are shown in Fig. 2. Al_2O_3 phase can easily be seen in its pattern. The peaks characterizing Fe_2O_3 crystal can be seen in the pattern of Al-Fe/1 and Al-Fe/2 catalysts.

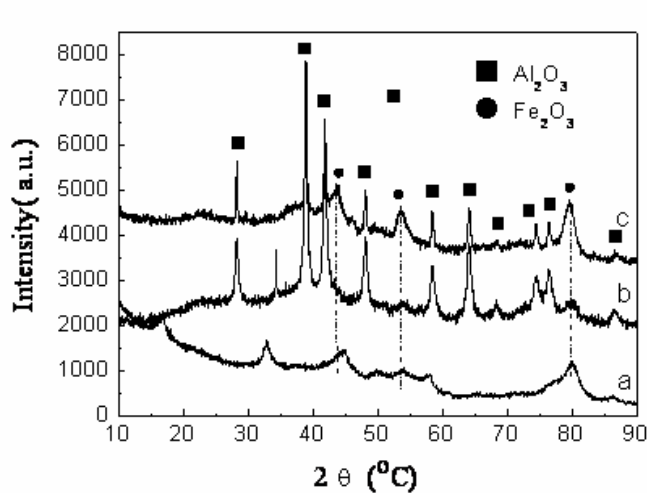


Figure 2. XRD patterns of catalysts: (a) Al_2O_3 ; (b) Al-Fe/1; (c) Al-Fe/2

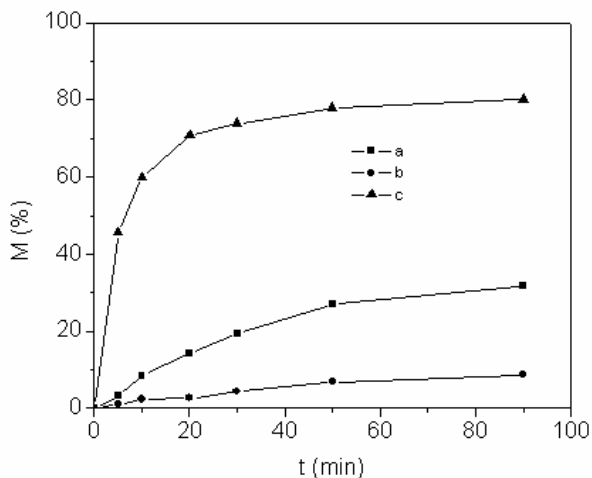


Figure 3. Degradation ratio of PAM under different conditions: (a) 600mg/L H_2O_2 , (b) 2g/L Al-Fe/1 catalyst, (c) 600mg/L H_2O_2 +2g/L Al-Fe/1 catalyst

3.3 Degradation of PAM in aqueous solution: The evaluation of the Fe(III) heterogeneous catalyst was measured in the degradation of 400 mg/L PAM aqueous solutions in the presence of 600 mg/L H_2O_2 and the results are showed in Fig. 3. It can be seen that with 600 mg/L H_2O_2 about 31% degradation ratio of PAM in solution was observed, indicating that the direct oxidative degradation ratio of PAM solution is limited. With 2.0 g/L Al-Fe/1 catalyst, degradation ratio of PAM was less than 8%, which was caused by the physical adsorption of PAM on the surface of Al-Fe/1 catalyst. The result implies that the adsorption of PAM on Al-Fe/1 catalyst is insignificant. With 600mg/L H_2O_2 2g/L Al-Fe/1 catalyst, the degradation ratio of PAM increased up to 80% after 90min. Experiment results indicate that the Al-Fe/1 catalyst exhibits a good activity in the degradation of PAM in aqueous solution.

3.4 Effect of the impregnated materials on catalysts activity: The degradation ratio of PAM by heterogeneous Fenton-like process under various catalysts prepared by different materials was shown in Fig. 4. When the catalyst was prepared with the impregnated materials of FeSO_4 , the degradation ratio of PAM was under 50% after 90 min. However, when the impregnated material change to $\text{Fe}(\text{NO}_3)_3$, the degradation ratio of PAM increase to more than 74%. This indicate that the Fe(III) heterogeneous catalyst prepared with $\text{Fe}(\text{NO}_3)_3$ has better catalytic activity. This is consistent with the above conclusions that better dispersion and smaller size of Fe_2O_3 crystal can be achieved in Al-Fe/1 catalysts.

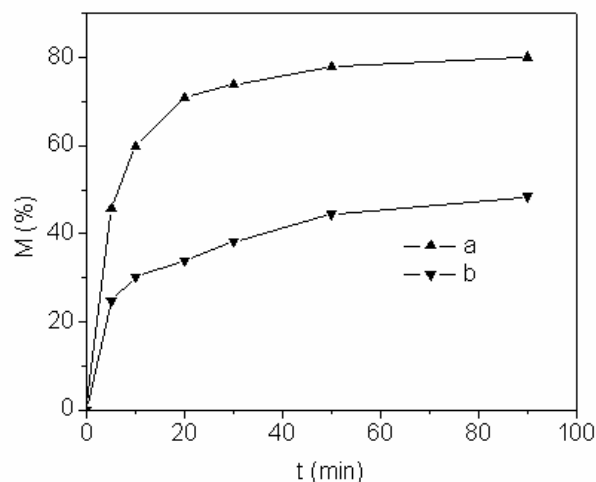


Figure 4. Degradation ratio of PAM with different catalysts: (a) A-Fe/1, (b) Al-Fe/2

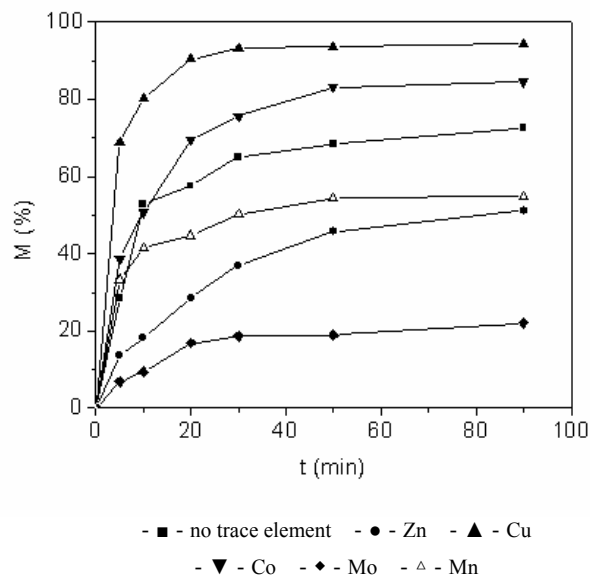


Figure 5. Degradation ratio of PAM with the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts containing trace elements.

3.5 Effect of adding trace elements on catalysts activity: Degradation ratio of PAM with the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts containing trace elements was shown in Fig. 5. It could be seen that the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts containing Co and Cu showed better catalytic activity, compared with other trace elements. In the present of 2g/L $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst containing Cu and 600 mg/L H_2O_2 , about 94% of PAM was removed after 90min, indicating that Cu is conducive to the improvement of catalytic activity. The reason may be that the addition of Cu changed the crystalline structure of catalysts; Cu is oxidized into CuO in the calcination process. The $\text{Fe}_2\text{O}_3/\text{CuO}/\text{Al}_2\text{O}_3$ catalyst was more conducive to catalytic decomposition of H_2O_2 into $\cdot\text{OH}$. Liu and Sun (2007) have also reported the effect of Ce doping on catalytic activity of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst for CWPO of azo dyes. It was found that better dispersion could be achieved by adding Ce, and the content of chemisorbed oxygen could also be increased on the surface of catalyst.

4. Conclusions

The Fe(III) catalyst was used as a heterogeneous catalyst for the degradation of PAM in aqueous solution. The results show that preparation conditions (the impregnated material and trace elements) have great effect on the catalyst activity. Compared with FeSO_4 , the Fe(III) catalyst prepared with $\text{Fe}(\text{NO}_3)_3$ as the impregnated material showed better catalyst activity. And $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts containing trace elements Cu showed higher catalyst activity.

Nomenclature

PAM Polyacrylamide
 M_0 The molecular weight of PAM at reaction time '0'.
 M_t The molecular weight of PAM at any reaction time 't'.

Acknowledgement

We would like to acknowledge the Science and Technology Development Foundation of Tianjin Municipal High Education (No. 20080516) for financial support.

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Received April 2010

Accepted August 2010

Final acceptance in revised form September 2010