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Heterogeneous UV/Fenton catalytic degradation of wastewater containing phenol with Fe-Cu-Mn-Y catalyst*

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Abstract: The heterogeneous UV/Fenton process with the appropriate amount of Fe-Mn-Cu-Y as catalyst was developed and various operation conditions for the degradation of phenol were evaluated. The results indicated that by using the heterogeneous UV/Fenton process, the COD_{cr} removal rate reached almost 100% for wastewater containing phenol. Compared with the homogeneous process, the developed catalyst could be used at wider pH range in the UV/Fenton process. Comparison of various heterogeneous process showed that heterogeneous UV/Fenton process was best. The heterogeneous UV/Fenton process with Fe-Mn-Cu-Y catalyst is highly efficient in degrading various organic pollutants.

Key words: Heterogeneous catalyst, Wastewater treatment, UV/Fenton
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INTRODUCTION

For the degradation of high concentration wastewater with toxic and non-biodegradable pollutants, the UV/Fenton method has been proposed in recent years (Braun *et al.*, 1991; Bossmann *et al.*, 1998). The UV/Fenton system relies mainly on oxidative degradation reactions, where organic radicals are generated by photolysis of the organic substrate or by reaction with hydroxyl radicals. These radical intermediates are subsequently trapped by dissolved molecular oxygen and lead, via peroxyl radicals and/or peroxides; leading to enhancement of the overall degradation process and eventually to complete mineralization (to CO_2, H_2O and mineral acids) (Lei *et al.*, 1998). Hydroxyl radicals as catalyst are generated by the following steps:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\cdot \quad (1)$$

$$Fe^{3+} + H_2O_2 \Leftrightarrow Fe(OH)^{2+} + H^+ \rightarrow Fe^{2+} + HO_2\cdot + H^+ \quad (2)$$

$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + H^+ + O_2 \quad (3)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO\cdot \quad (4)$$

However, the homogeneous Photo-Fenton system's pH had to be adjusted to a limited range (3−5) and the Photo-Fenton process requires recovery of iron, so operation cost in chemicals and labor has to be added. In order to widen the application of Fenton-type oxidation processes, these drawbacks have to be overcome by immobilization of iron. Some investigators reported their research results obtained through immobilizing Fe-ions in Nafion membranes (Maletzky *et al.*, 1999; Sabhi and Kiwi, 2001), where Fe-ions were fixed and remained active in organics decomposition with H_2O_2. Moreover, these membranes do not leach out the Fe-ions even after 3000 h. However, Nafion (Sabhi and Kiwi, 2001) is too expensive for use in wastewater treatment.

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Some attempts have been made to immobilize Fe-ions in some common and cheap carriers such as zeolite, and some satisfied results were also achieved in catalytic wet air oxidation system (Centi *et al.*, 2000). But few such attempts were made in the case of the photo-Fenton process.

Investigations (Pintar and Levec, 1992; Sxriolo *et al.*, 1994) showed that other transition metal ions, due to their variety of valence can replace ferric ion and serve as a like-Fenton reagent. Furthermore, different kinds of transition metal ions and their ratio in the homogeneous UV/Fenton process will favorably affect the degradation of contamination significantly; which indicated the existence of synergistic effect among these transition metal ions. However, few studies have been carried out in the case of heterogeneous processes. It will be great practical value to use multi-component transition metals instead of single metal in the catalyst design because of their higher catalytic ability and stability as well as lower cost.

In this work, a catalyst with multi-component transition metals was developed and applied to the heterogeneous UV/Fenton process for phenol degradation. The effects of operation conditions were evaluated and compared for different UV/Fenton processes.

MATERALS AND METHODS

Preparation of catalyst

The pH of a solution prepared with a certain concentration of transition metal ions was adjusted to 4.0 and after a certain quantity of NaY zeolite was added to the solution, ion-exchange occurred for 24 hours under continuous stirring. After filtrating and washing thrice with deionized water, the catalyst was dried at 110 ºC for 6 hours and sintered at 550 ºC for 5 hours. After the concentrations of residue metal ions in the solution were measured, the amount of metal ions loaded on the catalyst was calculated. The solution was strictly controlled at pH 4.0 to prevent metal ions precipitation during ion exchange.

Experimental setup and operation of heterogeneous UV/Fenton process

Fig.1 shows the experimental apparatus for heterogeneous UV/Fenton process. The standard conditions and process of the experimentation were as follows: After 500 ml 100 mg/L simulated wastewater and 0.2 g catalyst were added into the reactor, the magnetic stirrer and UV lamp were turned on; and then one multiple of the theoretical amount of H_2O_2 (Q_{th}) was added to start the reaction. The temperature of the reaction system was maintained at 45 ºC by a thermostat during the entire process. The conditions and process of the experimentation were noted in the results and discussion part of the article when they were different from the standard one.

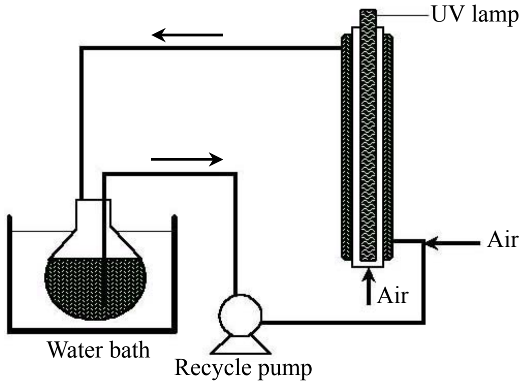

Fig.1 Photochemical batch reactor employed in all irradiation experiments

The amount of H_2O_2 added is the stoichiometric amount of H_2O_2 required for the total oxidation of phenol as calculated according to Eq.(5).

$$C_6H_6O + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O \qquad (5)$$

Following standard experimentation practice, one multiple of Q_{th} means 1.32 ml H_2O_2 solution of 30% (W/W) concentration.

Analytical methods

Phenol concentration was measured by aminopyrine colorimetric method (Xi *et al.*, 1989). The degradation rate, η, of phenol was defined as:

$$\eta = 1 - C/C_o \qquad (6)$$

where, C and C_o were phenol concentration at time t and time zero, respectively. PHS-25 type pH meter was used to measure the pH value (Xi *et al.*, 1989). The metal ion concentrations were determined by spectrophotometric method (Xi *et al.*, 1989). Analysis of the COD_{cr} was carried out using a titrimetric method (Xi *et al.*, 1989).

RESULTS AND DISCUSSION

Ion-exchange isotherms of Fe^{2+}, Cu^{2+} and Mn^{2+} with NaY zeolite

The ion-exchange isotherms of Fe^{2+}, Cu^{2+} and Mn^{2+} with NaY zeolite were measured and the results are given in Fig.2 and Table 1 showing that the ion-exchangeability of three kinds of metal ions on the NaY zeolite was in the order: $Cu^{2+} > Fe^{2+} > Mn^{2+}$. The isotherms were correlated with Langmuir's equation

$$q = q_{\max}C/ (b + C) \tag{7}$$

where, q and $q_{\max}$ represent the amount and maximum amount of ion exchange on the NaY zeolite, respectively, and b is a constant. The simulated $q_{\max}$ and b values are listed in Table 1.

Preparation and comparison of multi-component metal-ion catalysts

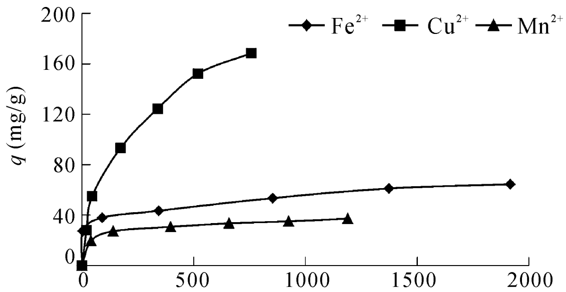

Fig.2 The isotherms of Fe^{2+}, Cu^{2+}, Mn^{2+}

Table 1 Comparative study on the isotherm of Fe^{2+}, Cu^{2+}, Mn^{2+}

	$q_{\max}$ (mg/g)	b (L/g)	R^2
Fe^{2+}	65.8	0.01029	0.9900
Cu^{2+}	196.1	0.006718	0.9853
Mn^{2+}	38.2	0.01498	0.9959

1. Fe-Mn-Y catalyst

Fe^{2+} and Mn^{2+} concentration ratio was changed, while keeping the concentration of total metal ions at 900 mg/L. The obtained catalysts were evaluated in the heterogeneous UV/Fenton process. The experimental procedure was as follows: 0.2 g catalyst and 1/4 Q_{th} of H_2O_2 were added to 500 ml solution with 250 mg/L phenol to start the reaction with results as shown in Fig.3. It was obvious that the COD_{cr} removal capabilities with two-component metal-ion catalysts were higher than that with single metal-ion catalysts. The optimal Fe^{2+} to Mn^{2+} ratio of 2:1 was obtained for COD_{cr} removal. After 40 min reaction, the COD_{cr} removal rate reached 76.7%, which was 30.5% and 28.6% higher than that catalyzed by single Fe^{2+} and Mn^{2+} catalysts, respectively. It indicated that synergistic effect should exist between Fe^{2+} and Mn^{2+} in heterogeneous UV/Fenton reaction. The synergistic effect among these transition metal ions may be due to their differing redox potential, which may enhance the deoxidizing of high valence ion to low valence ion and result in production of peroxyl radicals.

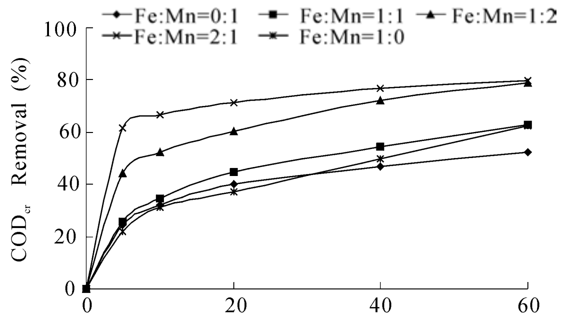

Fig.3 COD_{cr} removal rate vs time

2. Fe-Mn-Cu-Y catalyst

The initial compositions of metal ions, Fe^{2+}, Mn^{2+} and Cu^{2+} in the solution are listed in Table 2.

After ion exchange, the six kinds of Fe-Mn-Cu-Y catalysts were obtained and used for the degradation of wastewater containing phenol. The experimental conditions remained the same as above, except that the amount of catalyst added was 0.1 g/L. The experimental data on COD_{cr} removal and phenol removal rates are summarized in Figs.4 and 5, respectively. It was observed that the Fe:Mn:Cu ratio

Table 2 Concentrations of various metal ions

	Fe^{2+} (mg/L)	Cu^{2+} (mg/L)	Mn^{2+} (mg/L)
1	300	600	900
2	300	900	600
3	600	300	900
4	600	900	300
5	900	300	600
6	900	600	300

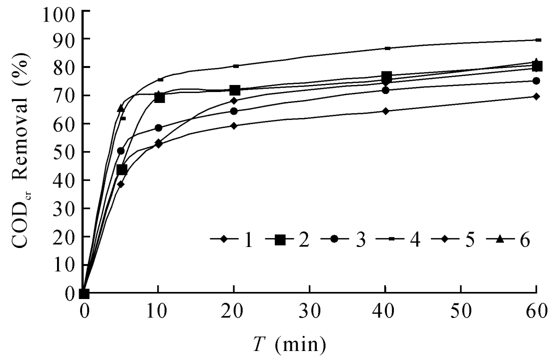

Fig.4 The COD_{cr} removal rate of various catalysts

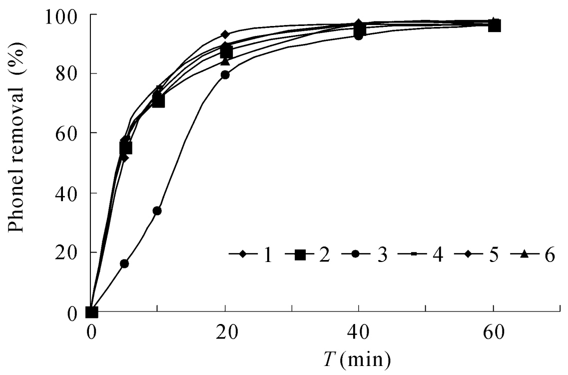

Fig.5 The phonel removal rate of various catalysts

ratio did not affect the phenol removal rates very much; but the ratio's effect on the COD_{cr} removal rate was obvious. The No.4 catalyst, with Fe:Cu:Mn ratio of 2:3:1, yielded highest COD_{cr} removal rate. After reaction for 40 min, the COD_{cr} removal rate reached 86.8%, which was higher than that with Fe-Mn-Y catalyst. Therefore, the No.4 catalyst was further evaluated in the next part of the investigation. The positive function of Cu^{2+} in Fe-Mn-Cu-Y catalyst also indicated the existence of synergistic effect.

Evaluations of heterogeneous UV/Fenton process

1. Effect of amount of H_2O_2 on the COD_{cr} removal rate catalyzed by Fe-Mn-Cu-Y

Fig.6 on the results of COD_{cr} removal rate catalyzed by the No.4 Fe-Mn-Cu-Y catalyst under the standard condition of the heterogeneous UV/Fenton process except H_2O_2 amount shows that with increase of H_2O_2 amount, COD_{cr} removal rate increased when H_2O_2 amount was 2 Q_{th}, the COD_{cr} removal rate was almost 100% after reaction for 40 min. Further increase in H_2O_2 to 4 Q_{th}, affected little COD_{cr} removal. The function of H_2O_2 in the UV/Fenton process is to provide free radicals for the oxidation reaction. Because of self-degradation of H_2O_2 during reaction, excess H_2O_2 amount was required for the complete degradation of phenol.

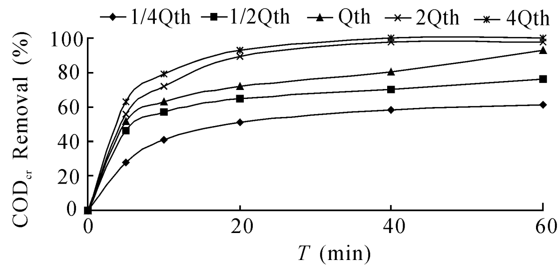

Fig.6 The effect of H_2O_2 amount on COD_{cr} removal rate

2. Effect of initial pH value on the COD_{cr} removal rate

The effects of initial pH value on the heterogeneous UV/Fenton process catalyzed by the No.4 Fe-Mn-Cu-Y catalyst were evaluated and the results are shown in Fig.7. Between pH 2.0 and pH 10.0, the COD_{cr} removal rate remained very high, but the removal rates were lower in the initial stage when the initial pH value was pH 2.0 or pH 10.0.

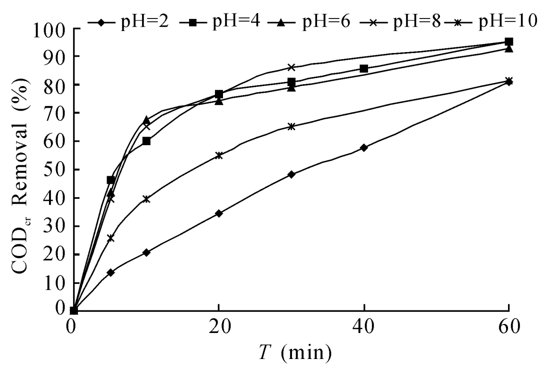

Fig.7 The COD_{cr} removal rate in various pH solution

It is well known that the pH value should be controlled to lower than 5 to prevent Fe^{2+} precipitation in the homogeneous UV/Fenton process. That means operation cost in chemicals and labor has to be added. Therefore, it is an advantage to apply heterogeneous UV/Fenton process in the wide pH range instead of narrow one in the homogeneous process.

Comparisons of various processes

The following degradation processes were evaluated for phenol degradation: Fenton, UV/Fenton, UV/Fenton/air, UV/H_2O_2, H_2O_2 and UV. For these experimentations, Fenton means the No.4 Fe-Mn-Cu-Y catalyst and H_2O_2. The reagents and process of the experimentation were same as the standard one. The results are shown in Fig.8. It was observed the COD_{cr} removal rate was UV/Fenton/air >UV/Fenton>UV/H_2O_2>Fenton>UV>H_2O_2. When H_2O_2 was used alone, no visible degradation of phenol was observed. The degradation rate with UV/Fenton/air and UV/Fenton system were higher than that in UV/H_2O_2 and Fenton system, indicating that the Fe-Cu-Mn catalyst together with UV was a highly efficient catalyst for oxidizing phenol. The existence of UV was necessary for high degradation rate; and oxygen as well as H_2O_2 supply could accelerate the process.

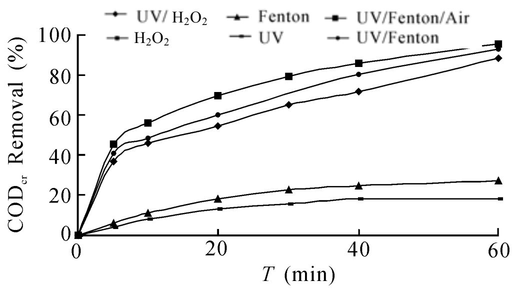

Fig.8 COD_{cr} removal of various Fenton systems

Comparisons for the degradation of different pollutants

Six kinds of pollutants and two kinds of industry wastewater from chemical as well as dyeing and printing industries were studied in the Fe-Cu-Mn-Y catalyst heterogeneous UV/Fenton process. The results are presented in Fig.9 showing that the highest COD_{cr} removal rate for degradation of resorcinol, whose COD_{cr} removal rate reached almost 100% after 60 min reaction. The COD_{cr} removal rates for other pollutants were also quite high and ranged from 30% to 80% after 60 min reaction, except for NaAC, whose relatively low COD_{cr} removal rate may be due to its low UV absorbing ability.

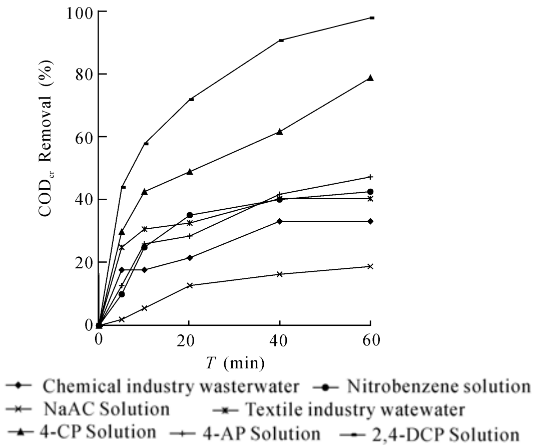

Fig.9 Treatment of various wastewaters

CONCLUSUION

The heterogeneous UV/Fenton process with Fe-Mn-Cu-Y catalyst was developed and various operation conditions were evaluated for the degradation of phenol and other pollutants. The results indicated that the COD_{cr} removal rate reached almost 100% for phenol. The catalyst could be used at wider pH range compared with the homogeneous process. Because metal ions were ion-exchanged on the zeolite matrix, the catalyst is expected to be feasibly applicable for repeated or continuous without secondary contamination of metal ions. The heterogeneous UV/Fenton process with Fe-Mn-Cu-Y catalyst has high efficiency in degrading various organic pollutants.

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