Photochemically enhanced degradation of phenol using heterogeneous Fenton-type catalysts

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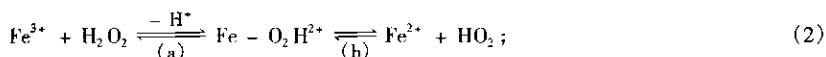
Abstract: The degradation of phenol was carried out using heterogeneous Fenton-type catalysts in the presence of H_2O_2 and UV. Catalysts were prepared by exchanging and immobilizing Fe^{2+} in zeolite 13X, silica gel or Al_2O_3. The concentration of phenol solution was 100 mg/L. The amount of H_2O_2 added was the stoichiometric amount of H_2O_2 required for the total oxidation of phenol. Under the irradiation of medium pressure light (300 W) phenol was mineralized within 1 h in the presence of Fe^{2+}/zeolite 13X. The COD removal rate was enhanced in the presence of Fe^{2+}/zeolite 13X compared to that of Fe^{2+}/silica gel or Fe^{2+}/Al_2O_3. Analogous homogenous photo-Fenton reaction with equivalent Fe^{2+} was also carried out to evaluate the catalysis efficiency of Fe^{2+}/zeolite 13X. Results showed that the COD removal rate was near to that of homogeneous Fenton, while heterogeneous Fe^{2+}/zeolite 13X catalyst could be recycled.

Keywords: phenol degradation; photo-Fenton process; heterogeneous Fenton; Fe^{2+}/zeolite

Introduction

The treatment of phenolic organics is an important environmental issue and has attracted considerable attentions. Many industries such as chemical plastic plants and oil refineries are the sources of this kind of pollutants(Wu, 2001). Phenolic organics are not easily biodegraded due to the resistance to common microorganisms. Thus alternative methods such as extraction, activated carbon adsorption and chemical oxidation(Urtiaga, 1997; Abuzaid, 1994; Grigoropoulou, 1997) were usually chosen.

Recently, advanced oxidation processes(AOPs), especially photo-Fenton process, because of its high efficiency and cheapness(Pousek, 1996; Bauer, 1997), based on the generation of ·OH radicals have been extensively studied for the treatment of phenolic pollutants(Legrini, 1993; Chen, 1997), Fenton reagent is a common source of ·OH radicals in acidic media, and it has been shown to be enhanced by the UV light due to the photo-active $Fe(OH)^{2+}$ leading to the addition of ·OH radicals(Walling, 1975; Sun, 1993). In this ferric system, Fe^{3+} acts as a catalyst via the following steps:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \cdot OH ; \tag{1}$$

$$Fe^{3+} + H_2O_2 \underset{(a)}{\overset{-H^+}{\rightleftharpoons}} Fe - O_2H^{2+} \underset{(b)}{\rightleftharpoons} Fe^{2+} + HO_2 ; \tag{2}$$

$$Fe^{3+} + HO_2 \cdot \longrightarrow Fe^{2+} + H^+ + O_2 ; \tag{3}$$

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + \cdot OH. \tag{4}$$

However, pH has to be adjusted to a limited range (pH 3.0—5.0) to perform the photo-Fenton process in homogeneous system, and regeneration of iron is needed. This means that operation cost has to be increased in chemicals and labor. 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 through immobilizing Fe-ions in Nafion membranes(Fernandez, 1999; Maletzky, 1999; Sabhi, 2001), where Fe-ions were fixed and remained active in organics decomposition with H_2O_2. Moreover, Nafion membranes do not allow leaching out of the Fe-ions even after 3000 h. However, Nafion is a kind of expensive membrane, its use for wastewater treatment is very limited. Meanwhile, some attempts have been made to immobilize Fe-ions in some usual and cheap carriers such as zeolite. Some interesting results were also achieved in catalytic wet air oxidation system(Centi, 2000).

In this work, we investigated the degradation of phenol using three different heterogeneous systems, in which Fe-ions were immobilized in zeolite 13X, silica gel or Al_2O_3, respectively. Their degradation efficiencies were evaluated by comparing with the homogeneous photo-Fenton process in the presence of UV and H_2O_2.
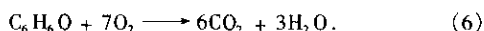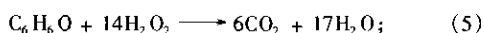
1 Experimental section

1.1 Materials

$FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3 \cdot 11H_2O$, H_2O_2, H_2SO_4, $KMnO_4$, phenol, 1,10-phenanthroline acetonitrile and acetic acid were all analytical grade. Catalase was purchased from Worthington. Each catalyst carrier, including zeolite 13X, silica gel, Al_2O_3, was about 150 screen mesh. Water is of double-distilled quality.

1.2 Photoreactor and photodegradation procedure

All photolysis experiments were carried out in a batch reactor. The experimental apparatus are shown in Fig.1. It consisted of a reservoir ($V = 1.00$ L), a flow-through annular photoreactor ($V = 0.30$ L) equipped with a mercury medium pressure lamp (Philips, GGZ 300) and a quartz filter. The solution was recirculated (250 ml/min) by a pump (Masterflex). The phenol solution was continuously purged (in the reservoir) by compressed air during the entire reaction time. The photolysis experiments were performed for 60 min. The reaction temperature was kept at 30℃ by means of cooling water.

The total volume of the photolysis solution was 1.25 L. The initial concentration of phenol solution was 100 mg/L. 375 mg Fe^{2+}/zeolite 13X was added in phenol solution before H_2O_2 added. The amount of H_2O_2 added was the stoichiometric amount of H_2O_2 required for the total oxidation of phenol as calculated according to Eq.(5).

$$C_6H_6O + 14H_2O_2 \longrightarrow 6CO_2 + 17H_2O; \quad (5)$$
$$C_6H_6O + 7O_2 \longrightarrow 6CO_2 + 3H_2O. \quad (6)$$

The pH was adjusted by using H_2SO_4 to the initial value of 3.0. The analysis was performed immediately after the samples were taken to avoid further reaction. Oxidation was monitored by measurement of chemical oxygen demand (COD). Residual H_2O_2 was consumed by enzyme catalase to prevent interference to COD analysis.

Fig.1 Photochemical batch reactor employed in all irradiation experiments

1.3 Analytical methods

UV/VIS (8500 spectrophotometer, Techcomp) was used to measure the concentration of phenol solutions, while pH was measured by Rex-pH-analyzer (PHS-25). H_2O_2 concentration was analyzed by classic $KMnO_4$ titration(Jander, 1984).

The analysis of the COD was carried out using a titrimetric method. Analysis of ferrous irons was conducted by using the modified 1.10-phenanthroline colorimetric method at 510 nm.
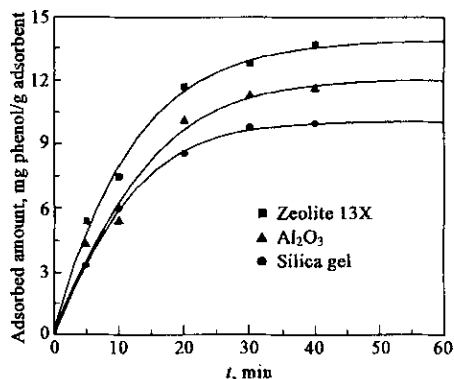
1.4 Preparation of catalysts

Fig.2 Adsorption histories of phenol with initial phenol concentration of 100 mg/L on zeolite 13X silica gel and Al_2O_3, performed under pH = 3
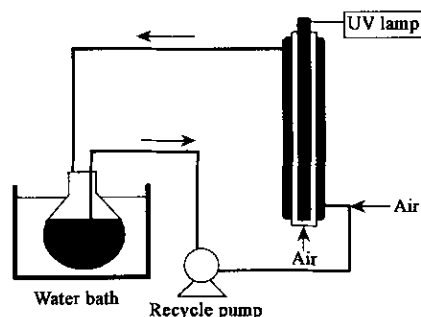
The Fe^{2+}/zeolite 13X, silica gel and Al_2O_3 were all prepared by an ion exchange process. Ion exchange was carried out at room temperature using 0.01 mol/l aqueous solution of $FeSO_4 \cdot 7H_2O$. pH was kept in a limited range (3.0—4.0) in this process to prevent the formation of ferric hydroxide precipitation. The ion exchange process lasted 150 min and at a stirring speed of 200 r/min. The amount of iron introduced into the zeolite 13X was 7.6 wt.%. The amounts of iron introduced into silica gel and Al_2O_3 were both 6.9 wt.%. After filtration and washing with double-distilled water, the sample was dried in 100℃ overnight.

1.5 Leaching test

Leaching test was carried out by the following steps. The same amount of Fe^{2+}/zeolite 13X used in later experiments was

weighed and added into 500 ml water. After stirring 2 h, Fe^{2+} concentration of the final solution was measured. Around 0.02 mmol ferrous ion was detected after this test.

2　Results and discussion

2.1　Adsorption of phenol by the catalyst carriers

Zeolite 13X, silica gel and Al_2O_3 have a good adsorption capacity. In order to evaluate Fenton-type oxidation efficiency, the original adsorption amount by carrier has to be eliminated. Adsorption experiments of these three carriers were conducted. After stirred by magnetic stirrer for 1 h, the final concentration of phenol solutions was measured, and the results are shown in Fig.2.

From Fig.2, it can be seen that phenol adsorption reached equilibrium after 0.5 h and the adsorbed phenol amount per unit catalyst carrier was limited. After adsorption equilibrium, the adsorbed phenol amount was 13.8 mg for per gram zeolite 13X, 12 mg for per gram Al_2O_3 and 10 mg for per gram silica gel respectively. Since the amount of catalyst (300 mg catalyst for 1000 ml solution) added was low, the adsorption of organic by the zeolite 13X (4.1 mg phenol/L solution), silica gel, (3.6 mg phenol/L solution), and Al_2O_3 (3.0 mg phenol/L solution) could be negligible with comparison to Fenton-type oxidation.

2.2　Degradation of phenol with different heterogeneous catalysts

Under the same experimental conditions, the degradation of phenol was conducted by using three heterogeneous Fenton-type catalysts. The reason why we choose zeolite silica gel and Al_2O_3 as the carriers was that they were usual catalyst supports, and moreover they had good luminous transmittance. Because of their nearly equal amounts of exchanged iron, the comparability is also favorable. The degradation of phenol in the presence of UV/H_2O_2 was also conducted to evaluate the effect of H_2O_2 in heterogeneous Fenton systems. Another important heterogeneous photo catalysis system as UV/TiO_2 was evaluated but no H_2O_2 was added(Fig.3).

From Fig.3, it was evident that zeolite 13X was a better carrier than silica gel and Al_2O_3. The results also showed that after 30 min 83% of COD removal was achieved in Fe^{2+}/zeolite 13X Fenton-type system. Compared to UV/H_2O_2, the function of Fe^{2+}/zeolite 13X in degradation process was very significant, because only 36.5% of COD was achieved in UV/ H_2O_2 system within the same reaction time. So the fixed Fe-ions in zeolite remained active in H_2O_2 decomposition. However, the function of silica gel or Al_2O_3 was not as visible as zeolite 13X especially Al_2O_3. This perhaps can be explained by the different structure of these three catalyst carriers. The chemical composition of zeolite 13X can be expressed as Na_{86} ($Al_{86}Si_{106}$ O_{384}) · $264H_2O^{16}$. Compared to silica gel ($SiO_2 \cdot nH_2O$) and Al_2O_3, zeolite has better ion-exchange capability in acidic media. With no H_2O_2 added, UV/TiO_2 had a low efficiency in the oxidation of phenol solutions; only 38% COD removal was achieved even after 60 min because of the fast recombination of hole/electron pairs photogenerated in TiO_2. Compared to Fenton-type reactions, UV/TiO_2 was not suitable for the treatment of phenol solutions, especially at a high concentration.

2.3　Degradation of phenol in homogeneous Fenton system

In Fig.4, the degradation of COD was compared between homogeneous and heterogeneous Fenton-type oxidation. The test with homogeneous Fenton catalyst was carried out analogously by adding $FeSO_4 \cdot 7H_2O$ salt to the solution. The amount of iron in the test was 5.1×10^{-4} moles Fe^{2+} and thus was nearly equivalent to the total amount of Fe^{2+} ions present in the zeolite. Homogeneous Fenton with the same Fe^{2+} amount had a better efficiency in the initial period of phenol degradation. This can be explained by that hydrated iron ions could react with H_2O_2 completely and received light directly. However, fixed Fe-ions encountered much resistance in mass transfer. But in the end of the reaction, similar removals were achieved in two systems. Phenol was mineralized in 1 h both in heterogeneous and homogeneous Fenton systems.

In the end of the homogeneous reaction, brown colloid was found, showing that 0.51 mmol/L ferrous ion resulted in the formation of ferric hydroxide precipitation even at pH 3.0 and having effect on the COD removal. However, with the fixation of Fe^{2+}, coagulation problem did not exist as only 0.02 mmol/L ferrous ion was detected after the leaching test. The recycling of heterogeneous catalysts was possible. Compared to about 30 mg/L Fe-ions in homogeneous Fenton system, the secondary pollution generated by Fe^{2+} was avoided.

Photo-Fenton process using heterogeneous Fenton-type catalysts such as zeolite 13X may be a promising technology for

the treatment of organic wastewaters. But the preparation of catalyst needs to be improved to reduce the problems such as limited amount of Fe^{2+} exchanged and the leaching of iron ions.
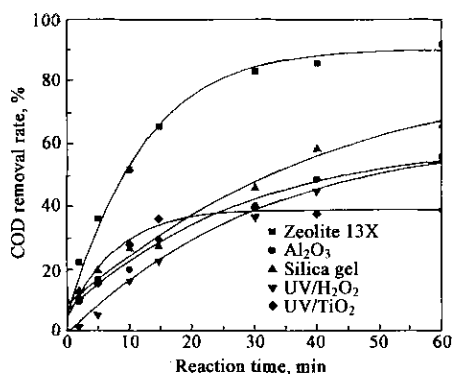

Fig. 3   Phenol degradation in different heterogeneous photochemical systems, performed under standard conditions (100% stoichiometric amount of H_2O_2, phenol of 100 mg/L)
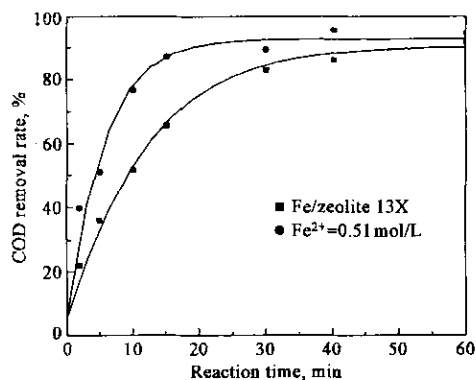
Fig. 4   Comparison in phenol degradation between heterogeneous and homogeneous Fenton systems, performed under standard conditions (Fe^{2+} = 0.51 mmol/L)

3   Conclusions

Several heterogeneous Fenton-type catalysts were prepared and tested. The leaching and adsorption of these catalysts were negligible. The COD removal in the presence of heterogeneous catalysts in photo Fenton oxidation of phenol solutions showed that zeolite 13X was a good carrier in the immobilization of Fe^{2+}. Fe^{2+}/zeolite 13X had a higher rate of COD removal than other catalysts. Analogous homogeneous Fenton showed a better efficiency in the degradation of phenol than Fe^{2+}/zeolite 13X, but Fe ion could not be recycled in homogeneous Fenton oxidation.

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Research Fields:

Aquatic Environmental Quality

It is to develop advanced sciences of water quality process and high technology, study the mechanisms of water quality process of natural waters and water treatment. As well as to develop high technology and techniques for water treatment, so as to push the development of environmental water quality research in China, and provide sciences supports for water quality resource utilization. The research is focused on the following:

1. Speciation and identification of water quality;
2. Bio- and chemical interfacial process of water quality;
3. New high-tech and principles of water treatment;
4. Water quality/safety assessment and its methodologies;
5. Safety guarantee technology for drinking water.

Environmental Chemistry and Ecotoxicology

Study on analysis, environmental chemical behavior and ecotoxicological effect of persistent toxic substances (PTS). The research focuses on the needs of the state in the field of environmental safety of PTS and provides support to decision-making of pollution control. The major research contents are as follows:

1. Study on methodology of persistent toxic substances analysis;
2. Screen methodology of endocrine disruptors;
3. Major environmental chemical process and biological process of toxicants;
4. Eco-toxicological effect of chemicals and their effects on human health;
5. Abatement technologies and pollution control strategies of PTS in China.

Systems Ecology and Ecological Engineering

Studying on dynamics mechanism and controlling principles of social-economic-natural complex eco-systems at various scales, and establishing sustainable development theory on the basis of ecology, eco-economics, system sciences and developing urban ecology, landscape ecology and ecological engineering technology. The main research contents are as follows:

1. Urban and industrial ecology;
2. Complex ecosystems analysis and sustainable development;
3. Landscape patterns and ecological process;
4. Ecological assessment and plan;
5. Pollution ecology and ecological remediation;
6. Environmental policy and national status analysis.

Atmospheric Chemistry and Air Pollution Control

The objective is to study science and technology related to air pollution, involving atmospheric chemistry, air pollution mechanism, kinetic process and heterogeneous catalysis, materials science, surface science and applied technology involved in emission control from mobile sources, industry sources, closed environment, and control strategies. The major research contents are as follows:

1. Atmospheric pollution chemistry;
2. Technology for catalytically cleaning automobile exhaust gas;
3. Acid precipitation and control;
4. Environmental catalysis and purification materials.

Water Pollution Control Technology

Water pollution control mainly works on research and application of theory and technology on water pollution control. Based on national demand and developing direction in the field of water science in the world, the innovation and integration of technologies on water pollution control, water quality transfer and wastewater reuse are carried out. The research contents mainly include:

1. Water pollution control and reclamation of aquatic environment;
2. Safety guarantee technologies for drinking water;
3. High technology for wastewater treatment and wastewater reuse;
4. Integration of high efficacy technologies for water pollution control and water treatment.

Soil Environmental Science

Based on the unique eco-environments and rich soil resources and biodiversity in China, soil environmental research in RCEES focuses on soil-plant interactions. Through the fundamental and applied research on the changes in soil environmental quality: factors and manipulation, and the interactions between soil and other environmental components, it is expected that the research will provide basic knowledge and technical support for food safety and quality, and regional eco-environmental construction in China. Main research topics are:

1. Soil environmental quality and human health;
2. Soil contamination and remediation;
3. Eco-balanced fertilization;
4. Soil eco-toxicology;
5. Soil/plant ecology and revegetation in degraded environments.

Environmental Biotechnology

The activities of R & D are focused on environmental friendly product, green chemistry processes and detection of transgenic food by applying modern biotechnological principles and methods. Principle research areas are as follows:

1. New pesticides production by fermentation technology or chemical synthesis;
2. Synthesis of oligosaccharides with high bioactivity and its application;
3. Mini-modulate plant growth regulators;
4. Separation materials for application in environment analysis, bioengineering and pharmacy;
5. Detection of transgenic food;
6. Pyrolysis and bioconversion of cellulose biomass.

(YANG Ke-wu)