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Rapid dechlorination of chlorinated organic compounds by nickel/iron bimetallic system in water[*]

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Abstract: Detoxification of chlorinated organic compounds via reaction with nickel/iron powder was implemented in aqueous solution. Compared to iron, nickel/iron bimetallic powder had higher hydrodechlorination activities for both atrazine (ATR) and *p*-chlorophenol (*p*CP); nickel/iron (2.96%, w/w) was shown to have the largest specific surface area and the optimum proportion for the dechlorination of both ATR and *p*CP. Electrochemical measurements showed that the adsorbed hydrogen atom on the nickel must have been the dominant reductive agent for the dechlorination of both ATR and *p*CP in this system.

Key words: *p*-Chlorophenol, Atrazine, Nickel/iron, Catalytic reduction dechlorination
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INTRODUCTION

In the chemical process industry toxic and non-biodegradable chlorinated organic compounds, such as solvents, pesticides, medicine intermediates, etc., are produced in large quantities that present a major environmental problem. Different methods have been developed to treat water containing chlorinated organics. Reductive dechlorination technology using zero-valent iron is considered to be a promising remediation method (Schlimm and Heitz, 1996; Balmer and Sulzberger, 1999; Claudia *et al.*, 2000; Ghauch and Suptil, 2000).

The reduction potential of Fe^0 (the standard corrosion potential: −0.441 V) for the dechlorination of some chlorinated organic compounds is too high to be feasible (Graham and Jovanovic, 1999), so some bimetallic system based on zero-valent iron was investigated recently. For example, palladium/iron has high reactivity for treating low-molecule chlorinated hydrocarbons and chlorinated phenols (Rosy *et al.*, 1995; Wei J.J. *et al.*, 2004), nickel/iron also proved effective for treatment of polychlorinated hydrocarbons (Quan *et al.*, 1998). However, some works showed that the catalytic reactivity of bimetallic system always depends on the properties of chlorinated organic compounds (Quan *et al.*, 1998; Kim and Carraway, 2000).

Our previous work addressed the effect of Ni/Fe molar ratio and different pH on the dechlorination efficiency of ATR, but we still have not studied the characteristics of Ni/Fe catalyst and the dechlorination mechanism of ATR (Wei H. *et al.*, 2004). For the above reasons and the cost of palladium, we studied the relationship between surface characteristics of Ni/Fe catalyst and its catalytic activity on the dechlorination of both chlorinated heterocyclic compound–atrazine (ATR) and chlorinated aromatic compound–*p*-chlorophenol (*p*CP). The dechlorination mechanisms of ATR and *p*CP were also investigated.

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MATERIALS AND METHODS

Iron powder: (99%, 40~70 mesh), $NiSO_4{\cdot}6H_2O$ was of analytic purity; methanol was HPLC reagent; ATR was purchased from Chemical Service (USA, purity>99%) and *p*CP from Shanghai Reagent Factory (China, purity>99%). Nickel/iron bimetallic powder was prepared according to Wei H. *et al.*(2004).

Except otherwise specified, the concentrations of ATR and *p*CP were 20 mg/L and 200 mg/L, respectively. Stock solution (300 ml) was used in each experiment with the added amount of nickel/iron catalyst being 9.0 g/L. The pH of the solution was controlled by 809 Titrando (Metrohm) maintained at 2.0 with 1.0 mol/L H_2SO_4. Corresponding sample (3.00 ml) was removed periodically and filtered through 0.45 μm membrane for HPLC analysis. All the experiments were conducted at room temperature.

Linear voltammetry measurements were performed in a three-electrode cell using a Model 273A potentiostat. The reference electrode was saturated calomel electrode (SCE); the counter electrode and working electrode were Pt flake and stainless steel (or porous nickel), respectively. The apparent area of working electrode was always 1.0 cm^2. The solutions were deaerated with N_2 for 30 min before every electrochemical measurement and protected by N_2 during all the experiments.

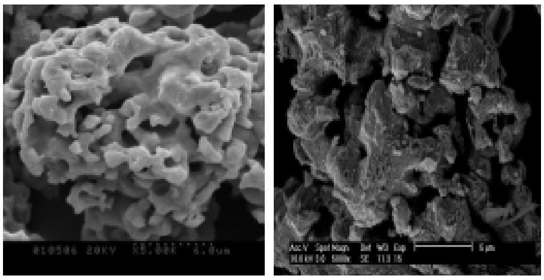
ATR's concentration was analyzed by HPLC (Shimadzu LC-10Advp). The separation column was YWG C_{18} (10 μm), and the mobile phase was 65:35 methanol/water solution, flow rate was 0.80 ml/min; *p*CP concentration was analyzed by HPLC (Waters1525-2996). The separation column was Symmetry C18 (5 μm), and the mobile phase was 50:50 methanol/4% acetic acid solution (V/V), flow rate was 0.80 ml/min.

The amount of nickel loading on iron was determined by atom absorption spectrometry (AAS, Analytik Jena GmbH, Germany); the morphological structure of nickel/iron was viewed with a scanning electron microscope (SEM, Model S-570, Hitachi); and its surface area was measured by N_2-BET (Model ST-03, Beijing).

RESULTS AND DISCUSSION

Characterization results of nickel/iron powder

Matheson and Tratnyek (1994) reported that the reactive sites on the metal surface were involved in dechlorination reactions, so metal surface area and condition would strongly influence the reductive rate of chlorinated organic contaminant. The surface morphological characteristics of iron and nickel/iron (2.96%, w/w) powders are shown in Fig.1 showing that the surface of 2.96% nickel/iron was sponge-like with the nickel dispersed on iron surface, so the load of nickel could probably enlarge the specific surface area of the iron powder and present more reactive sites.



(a) (b)

Fig.1 SEM image of iron powder (a) and 2.96% Ni/Fe (b)

To confirm the possibility of the above conjecture, the specific surface areas of different nickel/iron catalysts were measured by N_2-BET. Fig.2 shows clearly that the specific surface areas of nickel/iron bimetallic powders varied with the increase of nickel's loading and that the catalyst of 2.96% nickel/iron had maximum specific area (11.671 m^2/g).

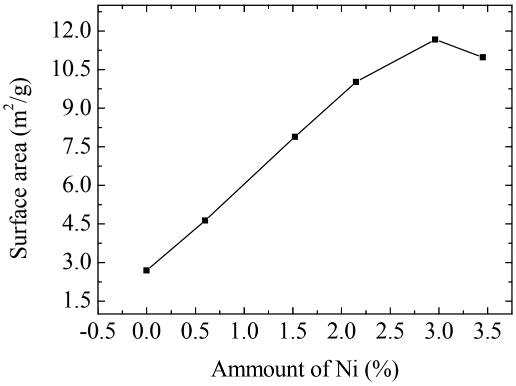


Fig.2 Specific surface areas of catalysts with different nickel/iron proportions

Effect of nickel/iron proportion on dechlorination efficiencies of both ATR and *p*CP

The ATR and *p*CP dechlorination efficiencies achieved by different nickel/iron catalysts are shown in Fig.3 and Fig.4, respectively. Fig.3 and Fig.4 indicate that dechlorination efficiencies of both ATR and *p*CP maximized at 2.96% nickel/iron, which accorded with the results obtained with various of specific surface area of different nickel/iron catalysts. The above results also indicate that the dechlorination efficiencies of both ATR and *p*CP on nickel/iron bimetallic particles could increase when more catalyst were added to the solution. For example, the dechlorination efficiencies of ATR by 2.96% nickel/iron catalyst loaded with 3.0 g/L, 6.0 g/L and 9.0 g/L in 20 min were 30.2%, 63.5% and 95.5% under the same conditions, respectively; the *p*CP dechlorination efficiencies obtained by different concentrations of 2.96% nickel/iron catalyst had similar results. After comparison of Fig.3 and Fig.4, it can be concluded that dechlorination of chlorinated aromatic compound is more difficult than that of chlorinated heterocyclic compound under the same conditions.

Catalytic reduction mechanism

The above experimental results show that ATR and *p*CP can be catalytically reduced effectively by nickel/iron system, and that the reducing agents including Fe^0 and adsorbed hydrogen atom on the nickel might be responsible for their dechlorination. To clarify the mechanism of their dechlorination of nickel/iron, the linear sweep voltammetrical curve was measured using model 273A potentiostat. Figs.5a and 5b show voltammetrical curves of ATR on the electrodes of stainless steel and porous nickel electrodes. It can be seen that hydrogen gas was formed obviously on these two electrodes at –0.6 V (vs SCE)

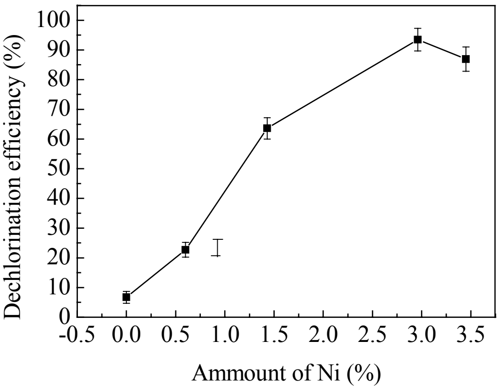


Fig.3 Effect of nickel/iron proportion on the dechlorination efficiency of ATR

Reaction time: 20 min; pH: 2.0; catalyst loaded: 9.0 g/L

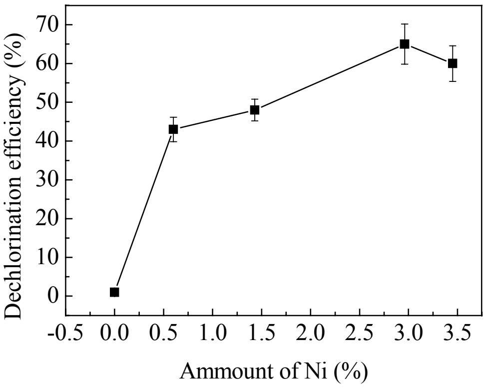
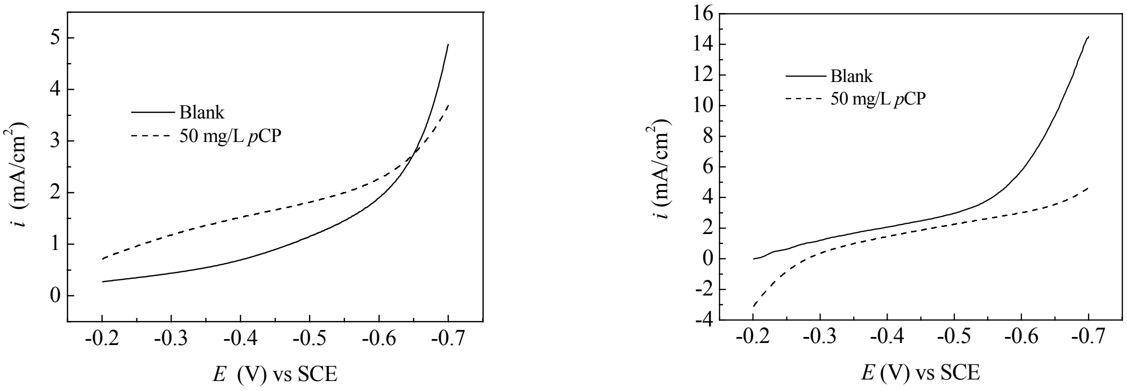


Fig.4 Effect of nickel/iron proportion on the dechlorination efficiency of *p*CP

Reaction time: 90 min; pH: 2.0; catalyst loaded: 9.0 g/L

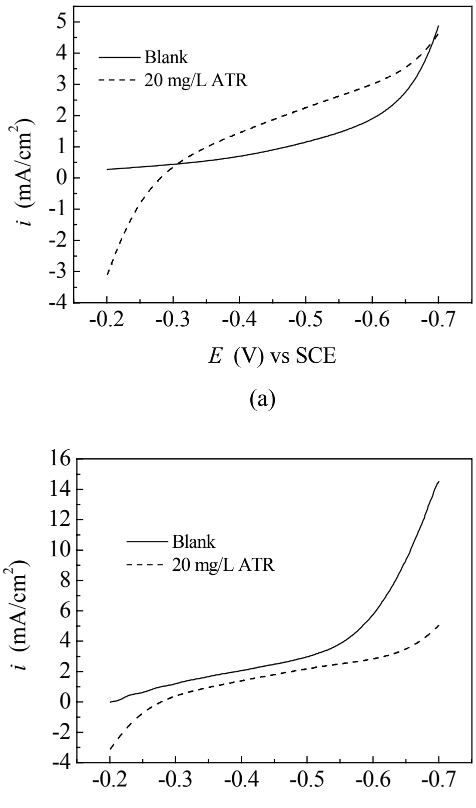


(a) (b)

Fig.5 Voltammetrical curves of *p*CP solution at different electrodes. Scan rate: 20 mV/s

(a) Stainless steel; (b) Porous nickel

in the blank solution (pH=2.0 of H_2SO_4). However, no reductive peak was also observed on both electrodes at the potential of higher than –0.6 V when ATR was added to the solution. Voltammetry measurement for *p*CP showed similar results as shown in Figs.6a and 6b. The above results indicated that Fe^0 was not the cause of dechlorination of ATR and *p*CP because of its high reduction potential, the adsorbed hydrogen atom on the nickel must be the main reductive agent for their dechlorination under these experimental conditions. The above results were also reported by Kulikov *et al.*(1996) and Lin and Tseng (1999).



(a)

(b)

Fig.6 Voltammetrical curves of ATR solution at different electrodes
Scan rate: 20 mV/s; (a) Stainless steel; (b) Porous nickel

Without regard to dehclorinated products of ATR and *p*CP, the dechlorination mechanisms of the above two chlorinated organic compounds can be expressed by following chemical reactions:

$$\mathrm{Ni^0}/n\mathrm{Fe^0} + \mathrm{H^+} \rightarrow \frac{1}{2}\mathrm{Fe^{2+}} + \mathrm{H_{atom}} - \mathrm{Ni^0}\Big/\left(n-\frac{1}{2}\right)\mathrm{Fe^0} \tag{1}$$

$$\mathrm{H_{atom}} - \mathrm{Ni^0}\Big/\left(n-\frac{1}{2}\right)\mathrm{Fe^0} + \mathrm{R-Cl} \rightarrow \mathrm{Ni^0}\Big/\left(n-\frac{1}{2}\right)\mathrm{Fe^0} + \mathrm{R-H} + \mathrm{Cl^-} \tag{2}$$

$$\mathrm{H_{atom}} - \mathrm{Ni^0}\Big/\left(n-\frac{1}{2}\right)\mathrm{Fe^0} + \mathrm{H^+} \rightarrow \frac{1}{2}\mathrm{Fe^{2+}} + \mathrm{Ni^0}/(n-1)\mathrm{Fe^0} + \mathrm{H_2}\uparrow \text{ (Side reaction)} \tag{3}$$

$$\mathrm{Ni^0}/n\mathrm{Fe^0} + 2\mathrm{H^+} \rightarrow \mathrm{Fe^{2+}} + \mathrm{H_2}\uparrow + \mathrm{Ni^0}/(n-1)\mathrm{Fe^0} \text{ (Side reaction)} \tag{4}$$

$$\mathrm{O_2(g)} + 2\mathrm{H_2O} + 4\mathrm{e} \rightarrow 4\mathrm{OH^-} \tag{5}$$

According to this mechanism, dechlorination reactions of these two types of chlorinated organic compounds have the same reductive agent (adsorbed hydrogen atom on the nickel). Except Eq.(1), it is also possible to generate adsorbed hydrogen atom when hydrogen gas becomes dissociatively sorbed onto the nickel/iron catalyst. The dependence of catalytic reactivity of bimetallic system on the properties of chlorinated organic compounds for their dechlorination should be attributable to mainly the stability of their C-Cl bond. Eq.(5) also indicates that the dissolved oxygen in water may compete for the electrons provided by Fe^0 reaction with H^+, which lowers the dechlorination efficiency, so deoxygenation in water can improve the dechlorination rate of chlorinated organic compounds.

CONCLUSION

Nickel/iron had great catalytic efficiency for the dechlorination of both ATR and *p*CP in water, and the dechlorination efficiency depended very much on both nickel/iron proportion and the catalyst concentration. The experimental results revealed that 2.96% nickel/iron had largest specific surface area and was the optimum proportion for dechlorination of both ATR and *p*CP. Electrochemical measurements showed that the adsorbed hydrogen atom on the nickel must have been the dominant reductive agent for their dechlorination in water. The dependence of catalytic reactivity of bimetallic system on the properties of chlorinated organic compounds for dechlorination should be mainly attributable to the stability of their containing C-Cl bond.

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