Rapid treatment of atrazine-contaminated water by nickel/iron bimetallic system

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Abstract: The utility of nickel/iron in the remediation of atrazine-contaminated water was investigated. The experimental results showed that nickel/iron had effective catalytic activity in dechlorinating atrazine under acidic conditions. The dechlorination reaction approximately followed the first-order kinetics under the experimental conditions (nickel/iron: 1.0 g/250 ml; $C_{atrazine}$ = 20.0 mg/L), the reaction rate increased with decreasing pH value of the reaction solution and increasing the proportion of Ni:Fe within 2.95%. For condition with 2.95% nickel/iron, the reaction rate constants were 0.07518(R = 0.9927), 0.06212(R = 0.9846) and 0.00131 min^{-1} (R = 0.9565) at pH = 2.0, 3.0 and 4.0, respectively. HPLC analysis was used to monitor the decline of atrazine concentration.

Keywords: atrazine; nickel/iron bimetallic system; dechlorination reaction; first-order kinetics

Introduction

The widespread use of triazine pesticides in agriculture applications has resulted in extensive groundwater contamination. The triazine is a group of chemically similar herbicides including atrazine, cyanazine, propzine and simazine primarily used to control broadleaf weeds. Among these herbicides, atrazine is one of the most widely used agriculture pesticides in the world. Because it can persist in water and mobile soil, atrazine is among the most frequently detected pesticides in ground and surface water (Balmer, 1999).

In order to remediate atrazine-contaminated water, several researchers have studied elimination of this contaminant using different treatment methods. Among these methods, atrazine dechlorinated by using zero-valent Fe^0 is a promising remediation technology (Dombek, 2001; Ghauch, 2000; Monson, 1998).

There is still no report on the dechlorination of atrazine by using bimetallic system. Recently the high reactivity of Pd/Fe bimetallic system in treating low-molecule chlorinated hydrocarbons and chlorophenols has been demonstrated (Rosy, 1995; Liu, 2001), but the cost of Pd limits this technology's widely application. Nickel/iron is also proved to be effective in treatment of polychlorinated hydrocarbons (Que, 1998), but the catalytic reactivity of bimetallic system depends on organic compounds' properties (Que, 1998; Kim, 2000). Considering the reasons above-mentioned and the cost of Pd, we chose nickel/iron as a reducing agent to study its catalytic activity on the dechlorination of atrazine, the reaction kinetics was also discussed.

1 Materials and methods

1.1 Chemicals

Iron powder (99%, 40—70 mesh), NiSO$_4 \cdot$6H$_2$O was of analysis purity, methanol was HPLC reagent and atrazine was purchased from Chemical Service(USA), purity > 99%.

1.2 Preparation of nickel/iron bimetallic

Nickel/iron was prepared by weighing 30 g of iron and washing the particles in 0.1 mol/L H$_2$SO$_4$ to remove the surface oxides and contaminants, the iron was rinsed with deoxygenated water to remove the residual acidity, then immersed in certain concentration of 0.1 mol/L NiSO$_4$ solution to produce nickel/iron bimetallic system by shaking the mixture violently for appropriate time, different proportions of nickel/iron system were got by controlling the shaking time. The bimetallic system was rinsed with deoxygenated water, then filtered, dried under nitrogen protection at 80℃ for 10 h.

1.3 Reaction conditions

The desired atrazine stock concentration was prepared using methanol as the solvent. This stock solution was stored in refrigerator at about −5℃, 250 ml sample containing 20.0 mg/L of atrazine was prepared by pipetting the desired amount of the stock solution and using water as solvent. The reaction was proceeded in a 250 ml conical flask with 1.0 g pre-filled nickel/iron; the flask covered with a rubber plug was placed on the magnetic stir operating at 20℃ and stirring at 300 r/min. The pH value of the solution was regulated by adding 1.0 mol/L H$_2$SO$_4$, and controlled by pHs-29A acidity meter. The duration of the reaction was approximately 90 min during which 3.00 ml aliquots of the atrazine sample periodically were removed for HPLC analysis.

1.4 Analytic method

Atrazine and its dechlorination product were analyzed by High Performance Liquid Chromotography (HPLC). HPLC system consisted of a SPD-10Avp photodiode array detector turned to 222 nm, a SIL-10Advp automatic injector, two

HPLC pumps, a CTO-10Avp oven and Class-vp data system. The seperation column was YWG C_{18}250 mm × 4.6 mm i.d, 10 μm). The mobile phase was degassed solution of 65/35 methanol/water(unbuffered), flow rate was 0.80 ml/min.

Weighed nickel/iron sample 0.1 g, dissolved in the solution of 2 : 1 (HCl : HNO₃) and diluted to an appropriate concentration, then the amount of nickel and iron powder could been determined by atom absorption analysis (Analytik Jena GmbH, Germany).

2 Results and discussion

2.1 Evolution of HPLC and UV absorption spectra

Fig.1 shows the variation of HPLC chromatogram and UV spectra of atrazine during the reaction. In Fig.1a, the retention time of atrazine is 10.039 min, and that of its dechlorination by-product is 3.025 min; in Fig.1b, the specific atrazine band at 222 nm disappears gradually with the band appearance of its dechlorination by-product. These results are in accord with the references (Dombek, 2001; Ghauch, 1999; 2000; Monson, 1998). At the end of reaction the opalescence produced when a few drops of HNO₃-AgNO₃ agent was added into the solution, which confirmed that atrazine was dechlorinated by nickel/iron system.
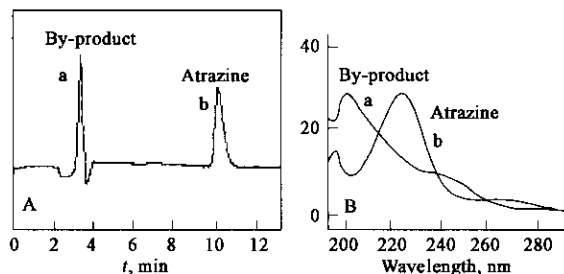

Fig.1   HPLC chromatogram(a); UV spectra of atrazine solution 20 mg/L(b) with nickel/iron 1.0 g, reaction time = 45 min, pH = 3.0

2.2 Increase of atrazine dechlorination efficiency with the loading of nickel

The presence of nickel on iron powder speeds up the dechlorination efficiency of atrazine greatly, which is due to the larger surface of nickel/iron than that of iron and the presence of nickel makes H₂ be a strong reducing agent(Wei, 2004). Fig.2 shows that the dechlorination efficiency of atrazine increases with the loading of nickel when its proportion is within 2.95%, then decreases slowly when the amount of nickel is larger than 2.95%. 2.95% nickel/iron is proved to be optimum under these experimental conditions. And the experimental results showed that the dechlorination efficiencies of atrazine decrease with the increasing of the initial concentration of atrazine(Fig.3).

2.3 Effect of pH on the dechlorination efficiency of atrazine

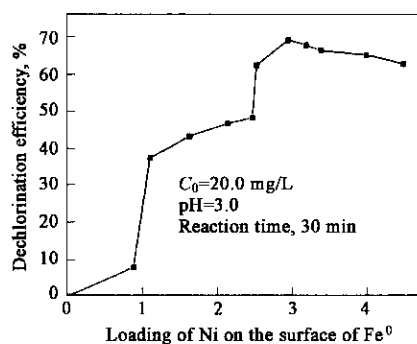Fig.4 shows the changes of pH of uncontrolled solution during

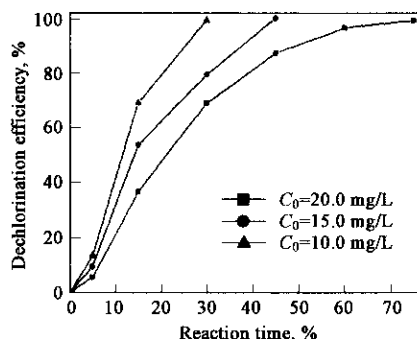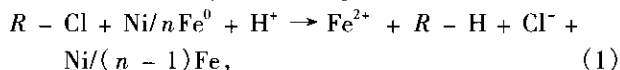Fig.2   Effect of nickel/iron proportion on the declorination efficiency of atrazine

Fig.3   Dechlorination efficiencies of atrazine at different initial concentrations by using 2.95% nickel/iron

dechlorination process in 90 min(from 5.74 to 6.74), which can be explained by the following reactions(Eq (1)—(3)):

$$R - Cl + Ni/n Fe^0 + H^+ \rightarrow Fe^{2+} + R - H + Cl^- + Ni/(n - 1)Fe, \tag{1}$$

$$2H_2O + 2e \rightarrow 2OH^- + H_2, \tag{2}$$

$$O_{2(g)} + 2H_2O + 4e \rightarrow 4OH^-. \tag{3}$$

Eq.(1) shows the direct dechlorination of atrazine by Ni/nFe⁰, water and dissolved oxygen may compete for the electrons provided by Fe⁰ according to Eq.(2)—(3), with the production of OH⁻, pH value of the solution increases with reaction time as shown in Fig.4.
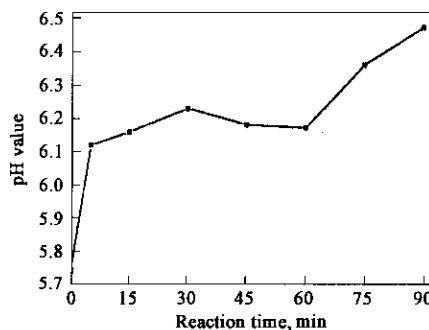

Fig.4   Variation of pH value with reaction time

Our previous work has indicated that nickel/iron (≤ 1.22%) almost have no catalytic dechlorination effect when pH ≥ 4.0 (Wei, 2003). Now the 2.95% nickel/iron was chosen to study the dependence of its catalytic activity on pH value because of its sufficient dechlorination efficiency as

shown in Fig. 2, addition of catalyst was 1.0 g in each experiment, and the catalytic activity of nickel/iron is shown in Fig.5, atrazine was entirely dechlorinated in 60 min at pH = 2.0, but no more than 6.0% at pH = 4.0 and in uncontrolled system. These results indicated that the reaction was greatly affected by pH value of the solution under our experimental conditions. The degree of iron's corrosion and atrazine's protonation at different pH values are probably the reasons for this.
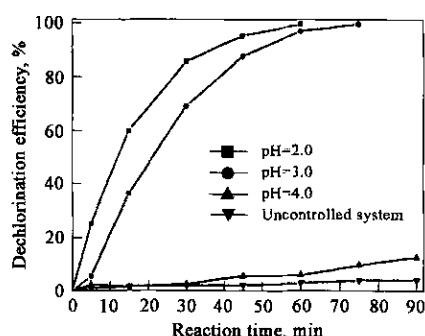

Fig.5   Dechlorination efficiency of atrazine at different pH value

2.4   The reaction constants

Rearranging the data shown in Fig. 5 with a linear decrease of $\ln(C/C_0)$ over time was obtained as shown in Fig.6. This linear relationship revealed a pseudo-first order reduction regarding the atrazine concentration. The reaction rate constants (K) can be determined from Fig. 6 as 0.07518, 0.06212 and 0.00131 $\min^{-1}$ for pH = 2.0, 3.0 and 4.0, respectively. The correlation coefficients (R) for the determined rate constants were 0.9927, 0.9846, 0.9565, respectively.
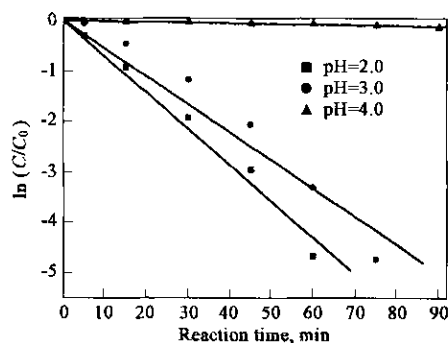

Fig.6   Dechlorination efficiency of atrazine at different pH value

The dependence of reaction rate constant on pH value was affected by several factors: the first one was the

enhanced corrosion of iron at low acidity (Eq. (1)); the second one was due to atrazine's protonation, approximately 33% of the atrazine was protonated at pH of 2.0, and only 1% at pH = 4.0; in addition, the amount of H_2 absorbed on nickel/iron surface also contributed a lot to this reaction (Wei, 2003). The variation of the reaction rate constants obtained here can presumably verify this.

3   Conclusions

Nickel/iron had great catalytic activity on the treatment of atrazine-contaminated water, the dechlorination efficiency is dependent on both the nickel loading and pH values of the solution. 2.95% nickel/iron was proved to be optimum and pH value of the solution must be less than 4.0. The reaction approximately followed first-order kinetics under the experimental conditions, the rate constants at pH = 2.0, 3.0 and 4.0 were 0.07518, 0.06212 and 0.00131 $\min^{-1}$, respectively.

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