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Degradation behavior and kinetics of dinitrotoluene in simulated wastewater by iron–carbon microelectrolysis

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ABSTRACT

Dinitrotoluene (DNT) removal strategies suffer from high costs or slow conversion rates. The effects of initial pH, mass ratio of iron–carbon, mass concentration of anhydrous sodium sulfate, and residence time on DNT removal rate were investigated. Results showed that the degradation efficiency of DNT reached 55.98% under the optimum conditions: an initial value of pH 3, an iron dosage of 10 g/L, a mass ratio of iron–carbon of 1, and a Na_2SO_4 concentration of 200 mg/L. The degradation kinetics of DNT by iron–carbon micro-electrolysis in the studied temperature range was a pseudo-first-order reaction.

Keywords: Dinitrotoluene; Wastewater; Iron–carbon micro-electrolysis; Kinetics; Pseudo-first-order reaction

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1. Introduction

Dinitrotoluene (DNT) is an industrial compound widely used in the production of medicines, dyes, high-polymer materials, explosives, and propellants. Therefore, DNT is typically found as an environmental contaminant [1] and has been listed as a priority pollutant by the US Environmental Protection Agency [2]. In most cases, DNT-containing wastewater is always characterized as complex composition, high toxicity [3,4], high chromaticity, and high chemical oxygen demand, so that it cannot be biodegraded readily. Researches on various technologies used for the degradation of DNT-containing wastewater have been conducted. These technologies include active carbon (AR) adsorption [5], advanced chemical oxidation processes [6], electrochemical reaction [7], and biodegradation [8]. However, many of these technologies are costly, unefficient, and unable to treat highly concentrated DNT-containing wastewater. Therefore, it is necessary to develop an efficient and low-cost treatment strategy of DNT-containing wastewater.

Iron–carbon micro-electrolysis is an effective water treatment method which has been widely used in treating poorly biodegradable wastewaters containing nitrobenzene, pharmaceuticals, heavy metals, and dyes as its low cost and high efficiency [9–13]. Based on the electrochemical corrosion of metals, massive microscopic galvanic cells will be formed by the iron chips and a carbon component in the electrolyte solution [14,15]. Electrode products released from the microscopic galvanic cells reaction include hydroxyl, nascent hydrogen, and Fe^{2+} [16]. These products are highly active in decomposing contaminants, especially

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in transforming the original substituent group. The iron–carbon micro-electrolysis reactions are proposed as follows [17]:

Anode reaction:

$$\mathrm{Fe} - 2\mathrm{e} \rightarrow \mathrm{Fe}^{2+} \quad \text{(Acidic)} \quad E^{\theta} = -0.44\ \mathrm{V} \tag{1}$$

$$2\mathrm{OH}^- + \mathrm{Fe}^{2+} \rightarrow \mathrm{Fe(OH)}_2 \tag{2}$$

$$3\mathrm{OH}^- + \mathrm{Fe}^{3+} \rightarrow \mathrm{Fe(OH)}_3 \ \text{(Neutral to alkaline)} \tag{3}$$

Cathode reaction:

$$2\mathrm{H}^+ + 2\mathrm{e} \rightarrow 2[\mathrm{H}] \rightarrow \mathrm{H}_2 \quad \text{(Acidic)} \quad E^{\theta} = 0\ \mathrm{V} \tag{4}$$

$$\mathrm{O}_2 + 4\mathrm{H}^+ + 4\mathrm{e} \rightarrow 2\mathrm{H}_2\mathrm{O} \quad \text{(Acidic)} \quad E^{\theta} = 1.23\ \mathrm{V} \tag{5}$$

$$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e} \rightarrow 4\mathrm{OH}^- \quad \text{(Neutral to alkaline)} \quad E^{\theta} = 0.40\ \mathrm{V} \tag{6}$$

This research aimed to establish the kinetic model of iron–carbon micro-electrolysis reduction in DNT-containing wastewater. The effects of initial pH, mass ratio of iron–carbon, mass concentration of anhydrous sodium sulfate (Na_2SO_4), and residence time on DNT reduction were investigated. This article will provide a definite theoretical basis and present potential application for treating DNT-containing wastewater in iron–carbon micro-electrolysis system.

2. Materials and methods

2.1. Materials

2,4-DNT (chemically Pure, CP), anhydrous Na_2SO_4 (Analytical Reagent, AR), sodium hydroxide (NaOH, AR), concentrated hydrochloric acid (HCl, AR), sulfuric acid (H_2SO_4, AR), AR, and other reagents were all purchased from Taiyuan Chemical Reagent Company (Taiyuan, China). DNT-containing wastewater was prepared by dissolving certain 2,4-DNT into deionized water.

Cast iron chips were obtained from a metal machining mill. The size of the chips was 0.3–2.5 mm in length and 1.5 mm in width. The cast iron chips were degreased in 10% NaOH solution, soaked in a diluted 5% HCl solution, and then washed with deionized water for several times. The AR were sieved to 16–20 mesh, then immersed in raw wastewater to reach saturated adsorption.

2.2. Experimental methods

The batch experiments were conducted with a ZR4-6 Intelligent Jar Tester with six agitators (Shenzhen Zhongrun Water Industry Technology Development Co., Ltd). 300 mL certain concentration of DNT-containing wastewater was added into 600-mL beakers, then adjusted to a desired pH. For each beaker, certain amount of cast iron chips, AR, and Na_2SO_4 were added. The stirring speeds of the agitators ranged from 10 to 1,000 rpm, and the reactions were proceeded at ambient temperature. The degradation kinetics of DNT by iron–carbon micro-electrolysis was investigated in a constant temperature water bath.

2.3. Analytical methods

The concentrations of DNT were analyzed by high-performance liquid chromatography (HPLC; Dionex's Ultimate 3000, USA) with a C_{18} reversed-phase column (250 mm × 4.6 mm, 5 μm). The detection wavelength was at 246 nm, the mobile phase was methanol and water (50/50, v/v). The flow rate, oven temperature, and sample volume were 1.5 ml/min, 40°C, and 20 μL, respectively.

The removal efficiency of DNT was defined as the following equation:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \tag{7}$$

where C_t represents the concentration of DNT at a specific time t and C_0 represents the initial concentration of DNT.

3. Results and discussion

3.1. Effect of initial pH

The effect of initial pH on the removal efficiency of DNT was investigated and pH was adjusted using 10% NaOH and 5% H_2SO_4. The mass concentration of iron was 20 g/L, and the mass ratio of iron–carbon was controlled at 2. During the experiment, the stirring speed was 300 rpm and reaction temperature was maintained at 25°C. The residence time was controlled at 60 min, the mass ratio of iron–carbon was controlled at 2, and the mass concentrations of Na_2SO_4 electrolyte was 200 mg/L. Six beakers with different initial pH (2–7) were examined during the experiment. The effects of pH on the removal efficiency of DNT are presented in Fig. 1.

Fig. 1 shows that the removal efficiency of DNT decreased with increasing pH. The degradation performance of DNT strongly depended on the pH. The results implied an acid-promoted reaction between cast iron chips (Fe^0) and DNT. A more rapid and complete reaction may be due to the lower pH, which could enhance the efficiency of the micro-electrolysis system. Under acidic conditions, higher concentration of hydrogen ion resulted in higher potential generated at the cathode. This phenomenon leads to an increase in electromotive force and concentration of Fe^{2+} and [H]. And these nascent Fe^{2+} and [H] have much higher reduction activity than Fe^0 and H^+, and they can convert nitro aromatic compounds into amino compounds efficiently [16,18]. It is clear that the lower the pH, the higher the removal efficiency of DNT. However, a lower pH may lead to a faster corrosion rate of the iron and the reaction apparatus. Take into account of these aspects, the pH of the iron–carbon system was chosen at 3.

3.2. Effect of iron dosage

The effect of iron dosage on the removal efficiency of DNT is shown in Fig. 2 under the following operating conditions: pH of 3, mass ratio of iron–carbon of 2, Na_2SO_4 concentration of 200 mg/L, the reaction temperature of 25℃, the stirring speed of 300 rpm, and the residence time of 60 min. As shown in Fig. 2, the removal efficiency of DNT increased with increasing iron dosage and increased sharply to 35.3% from 20.3% when iron dosage increased from 2 to 10 g/L. This phenomenon may be ascribed to the fact that higher iron dosage results in larger surface area; thus, more DNT could be absorbed on the reactive sites of the iron [19,20], then the redox reactions of DNT were accelerated. When the dosage of iron exceeded 10 g/L, the removal efficiency of DNT tended to be flat. This might due to that with the dosage of iron increased to a certain amount, accumulation between iron and carbon exhibited obviously, then the exposure of reactive sites on the surface of iron were reduced. Therefore, the removal efficiency of DNT did not increase with an increase in iron dosage. The dosage of iron was fixed at 10 g/L for the following investigation.

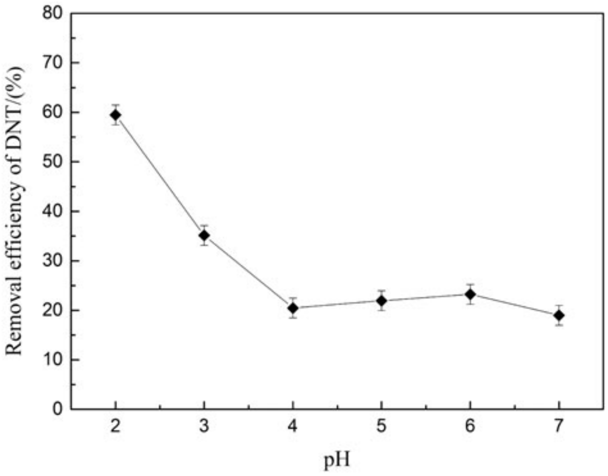

Fig. 1. Effect of initial pH on the removal efficiency of DNT.

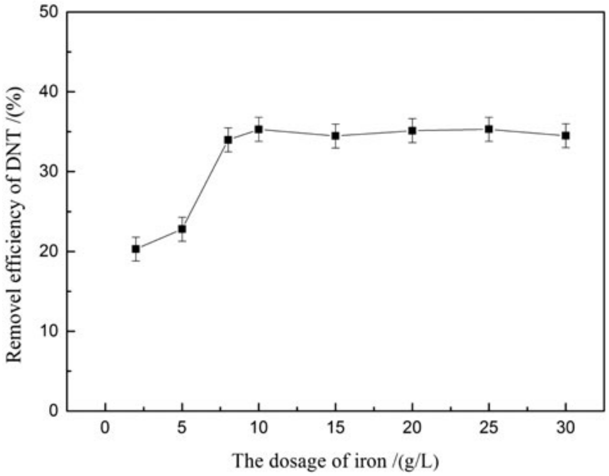

Fig. 2. Effect of dosage of iron on the removal efficiency of DNT.

3.3. Effect of mass ratio of iron–carbon

Fig. 3 shows the removal efficiency of DNT as a function of mass ratio of iron–carbon that ranged from 0.25 to 3 at a Na_2SO_4 concentration of 200 mg/L, an iron dosage of 10 g/L, a pH of 3, a stirring speed of 300 rpm, a reaction temperature of 25℃, and the residence time of 60 min. As shown in Fig. 3 that with an increasing mass ratio of iron–carbon, the removal efficiency of DNT initially increased and then decreased. In general, the mass ratio mainly affected the numbers of microscopic galvanic cells, more microscopic galvanic cells result in quicker and more efficient redox reaction [21]. When the mass ratio of iron–carbon was controlled to 1, the removal efficiency of DNT reached a peak value. This might be due to that with the mass ratio of iron–carbon approximated to 1, the mass concentration of iron and carbon were optimum to form the greatest numbers of microscopic galvanic cells, so the reduction of DNT was enhanced. The mass ratio of iron–carbon was fixed at 1 for the following investigation.

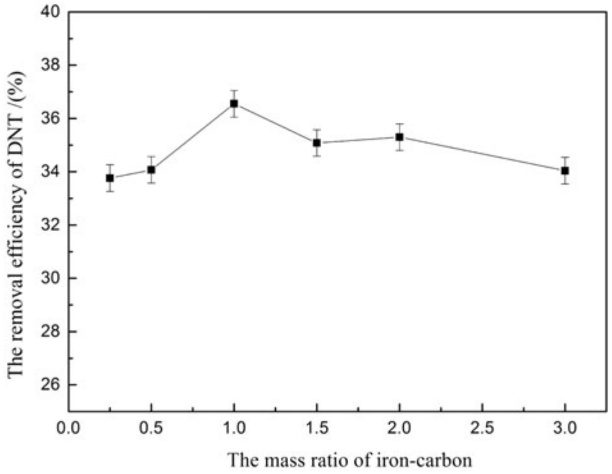

Fig. 3. Effect of mass ratio of iron–carbon on the removal efficiency of DNT.

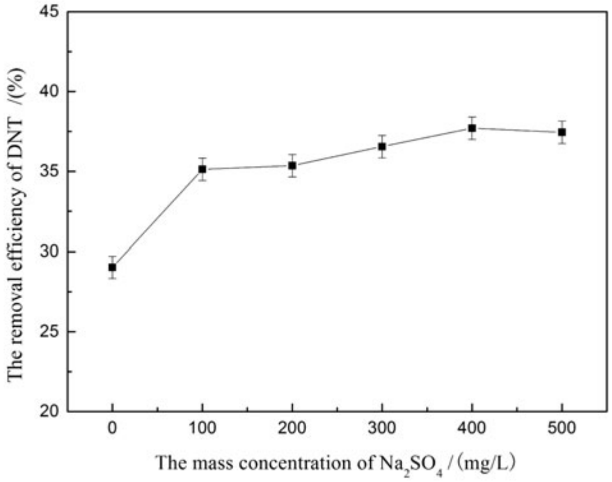

Fig. 4. Effect of Na_2SO_4 concentration on the removal efficiency of DNT.

3.4. Effect of mass concentration of Na_2SO_4 electrolyte

The effect of mass concentration of Na_2SO_4 electrolyte on the removal efficiency of DNT was investigated at an iron dosage of 10 g/L, a pH of 3, a mass ratio of iron–carbon of 1, a temperature of 25℃, a stirring speed of 300 rpm, and the residence time of 60 min. Fig. 4 shows the effect of mass concentration of Na_2SO_4 on the removal efficiency of DNT. In the micro-electrolysis system, adding electrolytes could improve the electrical conductivity of wastewater and then accelerate the electrochemical oxidation corrosion [20]. The electron transfer between metal iron and nitro compounds during the reaction process was reinforced and then the degradation efficiency of DNT was improved. As shown in Fig. 4 that the removal efficiency of DNT increased with the increasing mass concentration of Na_2SO_4 electrolyte. But the variation tendency of the removal efficiency of DNT tended to be flat when the Na_2SO_4 concentration exceeded 200 mg/L. This might be due to that though the presence of electrolyte can improve the transfer of electron between iron and nitro compounds, the production of electron during a certain period was limited. Therefore, the transfer of electron did not increase linearly with an increase in the concentration of electrolyte, so the variation tendency of the removal efficiency of DNT tended to be flat while the Na_2SO_4 concentration exceeded 200 mg/L.

3.5. Effect of residence time

The effect of residence time (20–160 min) on the removal efficiency of DNT was observed under the following conditions: an iron dosage of 10 g/L, a mass ratio of iron–carbon of 1, a pH 3, a stirring speed of 300 rpm, a Na_2SO_4 concentration of 200 mg/L, and a reaction temperature of 25℃. Fig. 5 shows that the removal efficiency of DNT increased with the increasing residence time. These results might attribute to the variation in the concentration of hydrogen electrons under an acidic environment. In the first 60 min, numerous electrons were released from the anode reaction to reduce DNT. Under an acidic environment, the system generated a large amount of nascent activated hydrogen [H] and other active groups [22]. When the residence time exceeded 60 min, an increase in the removal efficiency of DNT became slightly as

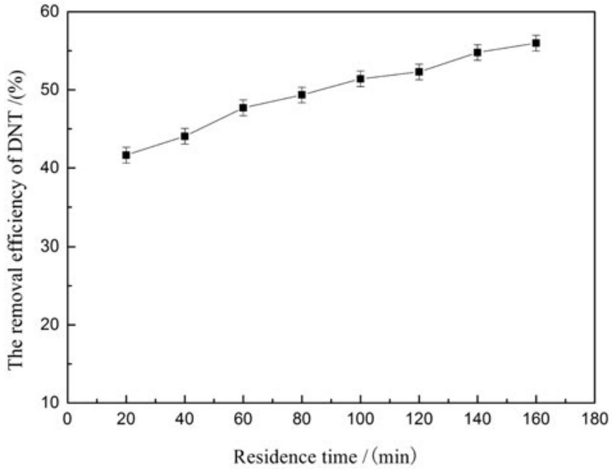

Fig. 5. Effect of residence time on the removal efficiency of DNT.

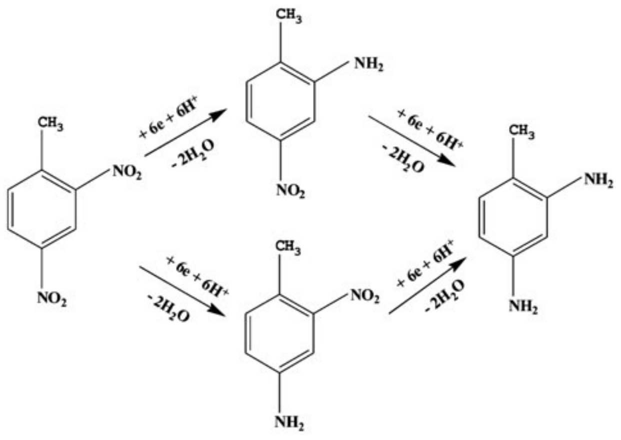

Fig. 6. Degradation pathway of DNT by micro-electrolysis.

the concentration of hydrogen ion gradually reduced. With the residence time prolonged, Fe^{2+}, Fe^{3+}, and OH^- easily formed a hydroxide layer on the iron surface [23,24], thereby, the degradation of DNT was inhibited.

3.6. Degradation kinetics of DNT

The reduction kinetics of DNT in aqueous systems was investigated to elucidate the mechanism of the iron–carbon micro-electrolysis reaction. The DNT concentration obtained at different times for the experiments was plotted on a semilogarithmic plot of C_t/C_0 vs. the residence time, where C_t represents the concentration at a specific time t and C_0 represents the initial concentration of DNT. From the previous study [25,26], DNT can be reduced to 2,4-diaminotoluene 2,4-DAT with 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene as intermediates, the degradation pathway can be described as the following mechanism (Fig. 6).

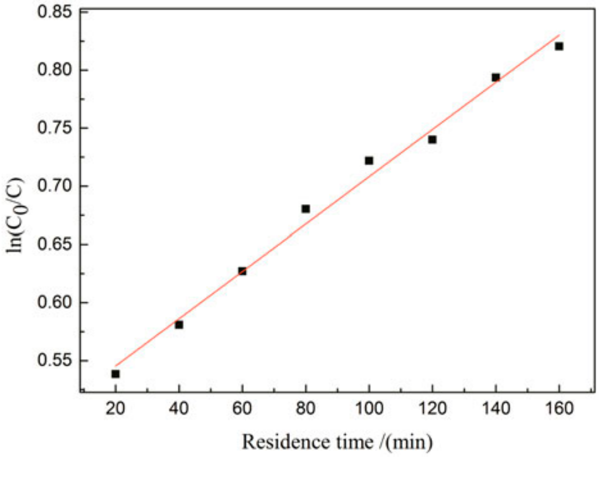

Fig. 7. Degradation kinetics of iron–carbon micro-electrolysis reaction.

Fig. 7 shows the analysis of the first-order reaction linear regression. According to the fitting results, the value of the linearly dependent coefficient R was 0.995 and the rate coefficient was 0.00203. However, this reaction not only included redox, but also adsorption and deposition. Water, hydrogen ions, dissolved oxygen, and iron hydroxides were also involved in the reaction. Therefore, the DNT removal by iron–carbon micro-electrolysis followed pseudo-first-order reaction at room temperature. The kinetic equation was:

$$C_t = C_0\, e^{-kt} = 200 \times e^{-0.00203t} \tag{8}$$

4. Conclusions

The factors influenced the iron–carbon micro-electrolysis system for treating DNT-containing wastewater were investigated. The appropriate conditions for treating DNT-containing wastewater are as follows: an initial value of pH 3, an iron dosage of 10 g/L, a mass ratio of iron–carbon of 1, and a Na_2SO_4 concentration of 200 mg/L. Under these process conditions, the removal efficiency of DNT reached 55.98%. The study on the reduction kinetics of DNT indicated that the removal of DNT by iron–carbon micro-electrolysis followed a pseudo-first-order reaction at room temperature.

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