Research article

Degradation of aniline by heterogeneous Fenton's reaction using a Ni-Fe oxalate complex catalyst

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A B S T R A C T

A Ni-Fe oxalate complex catalyst was synthesized and characterized by means of Brunauer–Emmet–Teller (BET) method, scanning electron microscope (SEM) and X-ray photo-electron spectroscopy (XPS). The catalyst showed good catalytic activity for aniline degradation by heterogeneous Fenton's reaction, in which the synergetic index was 9.3. The effects of reaction temperature, catalyst dosage, hydrogen peroxide concentration and initial pH were investigated. Under the optimum conditions (T = 293 K, catalyst dosage = 0.2 g/L, H_2O_2 concentration = 4 mmol/L and initial pH = 5.4), 100% aniline could be removed within 35 min, and approximately 88% deamination efficiency was achieved in 60 min. The aniline degradation process followed the pseudo-first-order kinetic (k = 0.177 min^{-1}) with activation energy (E_a) of 49.4 kJ mol^{-1}. Aniline could be removed in a broad initial pH (3–8) due to the excellent pH-tolerance property of the catalyst. The detected ammonium ion indicated that deamination occurred during aniline degradation. It was proposed that deamination synchronized with aniline removal, and aniline was attacked by free radicals to generate benzoquinonimine and phenol. This system is promising for the removal of aniline from water.

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1. Introduction

Aniline, a key precursor and intermediate in many industries, has been frequently found in the environment (Chen and Huang, 2015a; Jiang et al., 2016). Aniline and its derivatives are highly toxic to human health and the environment (Brillas and Casado, 2002). Thus it is listed in the blacklist of priority-controlled pollutants in China, and the maximum permissible concentration in wastewater is 1 mg/L (Liu et al., 2015). Aniline containing wastewater can be treated by biodegradation (Pati et al., 2012; Wang et al., 2007) and adsorption (Yang et al., 2011). However, the biological degradation of aniline is ineffective due to its toxicity, and the disadvantages of high cost and poor adsorbent reproducibility limit the application for adsorbents. Therefore, it is necessary to search for a new treatment method to remove aniline in aqueous systems.

Advanced oxidation processes (AOPs) have been considered as a promising treatment for aniline degradation (Chen and Huang, 2015b; Chu et al., 2007; Oturan and Aaron, 2014). Among AOPs,

Fenton's reaction has attracted great attention due to its advantages of low capital cost, easy operation, and high efficiency (Anotai et al., 2006; Masomboon et al., 2009). Usually, iron species catalyze the decomposition of H_2O_2 to produce free radicals including hydroxyl free radical (•OH). These produced free radicals have strong non-selective oxidizing ability, and can degrade aniline easily in an aqueous system. But Fenton's reaction requires strong acidic environment (pH = 2.0–4.0), which significantly limits its application. Besides, the large amount of ferric sludge produced during the Fenton process also causes other environmental problems. To overcome these disadvantages of classic Fenton's reaction, various catalysts have been introduced to form a heterogeneous Fenton system to promote the generation of free radicals.

Iron-based materials, including iron oxides (Liu et al., 2013; Shi et al., 2014) and iron organic complexes (Naka et al., 2006; Zhang et al., 2009), have been investigated to remove organic pollutants in heterogeneous Fenton's reaction. Iron-oxalate was found effective in heterogeneous Fenton's reaction to remove chlorophenol (Lan et al., 2011; Lee et al., 2014). In addition, because of the good insolubility and stability, nickel-oxalate was used as a catalyst and showed good catalytic effect in the ozonation of 2-ethoxy ethyl acetate (Amutha et al., 2014). Nickel doped into iron-oxalate

complex not only had good catalytic effect in heterogeneous Fenton systems, but also prevented iron leaching (Kesavan et al., 1999) due to the similar structure of iron-oxalate and nickel-oxalate.

Therefore, we prepared a Ni-Fe oxalate complex catalyst for heterogeneous Fenton's reaction for aniline degradation. This paper examined the feasibility of aniline degradation using this new catalyst and investigated the effects of operational parameters like temperature, catalyst dosage, H_2O_2 concentration, and initial pH. Synergistic index of catalyst and H_2O_2 was calculated to evaluate the catalytic efficiency. The concentration of ammonia nitrogen was measured and by-products were determined to investigate the possible aniline degradation pathways.

2. Materials and methods

2.1. Chemicals and materials

In this study, all chemicals used were of analytical grade without further purification. Oxalic acid dehydrate and nickel chloride hexahydrate were obtained from Sinopharm Chemical Reagent Co. LTD. Iron (II) sulfate heptahydrate and aniline were obtained from Xilong Chemical Industry Co. LTD. Hydrogen peroxide was obtained from Beijing Chemical Works. Deionized water was used in all experiments.

2.2. Preparation of Ni-Fe oxalate complex

Ni-Fe oxalate complex was prepared by the co-precipitation method assisted with ultrasound. $NiCl_2 \cdot 6H_2O$ (0.48 g) and $FeSO_4 \cdot 7H_2O$ (2.23 g) were dissolved in 50.0 mL of deionized water, and so was $H_2C_2O_4 \cdot 2H_2O$ (1.26 g). The obtained solution was sonicated for 60 min in an ultrasonic generator (SB-800DT, Ningbo Scientz Biotechnology Co Ltd, 40 kHz, 800 W) at 25 °C. After ultrasonic irradiation, $H_2C_2O_4$ solution was slowly added into the Fe-Ni mixed solution drop by drop, and the solution was then stirred vigorously for 60 min. After that, the suspension was sonicated for another 5 min, and then the Ni-Fe oxalate complex was separated by centrifugation at 5000 rpm for 10 min. Later on, it was washed several times with deionized water, and then dried at 100 °C in an air-circulating oven. Finally, the yellow Ni-Fe oxalate complex was stored in a drying vessel.

2.3. Characterization of the catalyst

The specific surface area, porosity and average pore size of samples were measured by BET with a 3H-2000PS2 (BeiShiDe Instrument-S&T Co., Ltd) analysis instrument. Surface morphology of samples was investigated using a ZEISS MERLIN Compact SEM analyzer at different scales and magnifications. The X-ray photoelectron spectra (XPS) were measured on a Thermo Fisher ESCALAB 250Xi spectrometer equipped with XR6 mononchromated X-ray source.

2.4. Experimental procedures

All experiments for aniline degradation were carried out in 150 mL glass beakers. In all cases, the desired catalyst dosage and H_2O_2 concentration were introduced into 100 mL of 20 mg/L aniline solution at the beginning of the reaction, and the mixed solution was stirring under constant temperature. At set intervals, 1.5 mL of sample was analyzed after immediately filtering through a 0.22 μm membrane filter. The solution's initial pH (ranging from 3 to 8) was adjusted with sodium hydroxide and sulfuric acid.

The concentration of aniline was analyzed by using a high performance liquid chromatography (HPLC, Hitachi Primaide 1210 Aotu Sampler) equipped with a UV detection wavelength of 280 nm, and a StableBond-C18 reversed phase column (5 μm, 4.6 mm × 250 mm.) was used for separation. Elution conditions: mobile phase was composed of 60/40 v/v acetonitrile and deionized water; flow rate was 1 mL/min; 10 μL of sample was injected into HPLC. In this way, the peak of 280 nm was associated with the benzene ring, but intermediate products which had benzene rings also contributed to the absorbance. Thus, the aniline concentration measured by this method is higher than the actual, and removal efficiency calculated is lower than actual. The concentration of NH_4^+-N was measured according to the national standard method HJ 535-2009.

3. Results and discussions

3.1. Characterization of Ni-Fe oxalate complex catalyst

The obtained Ni-Fe oxalate complex catalyst had a specific surface area of approximately 0.81 m^2/g based on the BET analysis, and the pore volume and pore diameter were 0.0205 mL/g and 101.27 nm, respectively. N_2 adsorption-desorption isotherm curve of Ni-Fe oxalate complex was shown in Fig. 1(a). As shown in Fig. 1(a), the curve belonged to the Type III isotherm type according to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature, which indicated that weak absorption took place in the macrospore structure. The morphology of the catalyst particles was scanned by SEM and results are shown in Fig. 1(b). The catalyst had a laminated shape, and the size of particles was in the range of 2–4 μm.

The composition of this catalyst was analyzed by X-ray photoelectron spectroscopy in order to identify the chemical states of Fe and Ni. The XPS survey spectrum for the catalyst was displayed in Fig. 1 (c). The peaks of Ni2p, Fe2p, O1s and C1s were shown in this figure, which demonstrated the existence of Ni, Fe, O and C in this catalyst, and the binding energy of 284.5 eV C1s peak was the calibration reference. As shown in Fig. 1 (d), the binding energy of Fe 2p3/2 photoelectron could be fitted into two contributions at 706.4 and 710.2 eV, and the binding energy of Fe 2p1/2 photoelectron could be fitted into two contributions at 719.8.7 and 724.0 eV. The peaks at 710.2 and 724.0 eV were assigned to Fe (II), while peaks at 706.4 and 719.8 eV indicated the existence of Fe^0 because of decomposition of Ni-Fe oxalate (Weng et al., 2014; Zhou et al., 2010). Fig. 1 (e) shows the peaks of Ni 2p3/2 located at binding energies of 852.4 and 856.5 eV, and the peaks of Ni 2p1/2 located at binding energies of 869.9 and 876.0 eV. The existence of two peaks at 855.8 and 852.3 eV were corresponding to Ni (II) and Ni^0 (Fang et al., 2011; Galtayries and Grimblot, 1999). It indicated that nickel had been mixed into ferrous oxalate structure, and the Fe^0 and Ni^0 ion on the catalyst surface might promote the catalytic activity of the Ni-Fe oxalate complex.

3.2. Feasibility study

A series of experiments were carried out to evaluate the feasibility of aniline degradation by heterogeneous Fenton's reaction with Ni-Fe oxalate complex catalyst. Fig. 2 showed that the aniline removal efficiency was 2.2% and 2.8% in 30 min by hydrogen peroxide and catalyst alone respectively, while 100% removal was achieved in the heterogeneous Fenton system. The low aniline removal efficiency by catalyst alone indicated the low absorption capacity of Ni-Fe oxalate complex catalyst.

The removal of aniline followed the pseudo-first-order kinetic in general. The rate constants in the H_2O_2, catalyst, and heterogeneous Fenton systems were 0.018, 0.001, and 0.146 min^{-1}, respectively. Clearly, the high rate constant of aniline degradation in the