Research article

NiFe(C$_2$O$_4$)$_x$ as a heterogeneous Fenton catalyst for removal of methyl orange

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ABSTRACT

This paper studies a heterogeneous Fenton catalyst NiFe(C$_2$O$_4$)$_x$, which showed better catalytic activity than Ni(C$_2$O$_4$)$_x$ and better re-usability than Fe(C$_2$O$_4$)$_x$. The methyl orange removal efficiency was 98% in heterogeneous Fenton system using NiFe(C$_2$O$_4$)$_x$. The prepared NiFe(C$_2$O$_4$)$_x$ had a laminated shape and the size was in the range of 2–4 μm, and Ni was doped into catalyst's structure successfully. The NiFe(C$_2$O$_4$)$_x$ had a synergistic effect of catalyst of 24.7 for methyl orange removal, and the dope of Ni significantly reduced the leaching of Fe by 77%. The reaction factors and kinetics were investigated. Under the optimal conditions, 0.4 g/L of catalyst dose and 10 mmol/L of hydrogen peroxide concentration, 98% of methyl orange was removed within 20 min. Analysis showed that hydroxyl radicals and superoxide radicals participated in the reaction. With NiFe(C$_2$O$_4$)$_x$ catalyst, the suitable pH range for heterogeneous Fenton system was wide from 3 to 10. The catalyst showed good efficiency after five times re-use. NiFe(C$_2$O$_4$)$_x$ provided great potential in treatment of refractory wastewater with excellent property.

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1. Introduction

Synthetic dyes are widely used in textile industry, and over 10% dyes is released into wastewater during the dyeing process (Asad et al., 2007). The dyes discharged into wastewater, especially azo dyes, pose threats to the environment and human health (Bafana et al., 2011; Chung & Stevens, 1993). Thus, numerous methods have been studied to remove azo dyes, including coagulation and flocculation, SBR, UASB and biofilm reactor (Sarayu & Sandhya, 2012; Solís et al., 2012; Van der Zee & Villaverde, 2005). However, due to the disadvantages of complex structures and stability of azo dyes molecules, traditional biological treatments were ineffective and physicochemical methods were expensive (Li et al., 2014; Robinson et al., 2001; Sarayu & Sandhya, 2012). Advanced oxidation processes (AOPs) have been considered as promising technologies to decontaminate wastewater effectively and environmental friendly (Kumar & Rao, 2015; Oturan & Aaron, 2014).

Among all AOPs, Fenton reaction can produce free radicals that degrade pollutants with strong non-selective oxidizing ability

(Pignatello et al., 2006), but the low pH condition limits its application (Oturan & Aaron, 2014). In comparison, heterogeneous Fenton reactions have shown good performance in a wide range of pH (Lan et al., 2011), and catalysts can be separated from solution easily. Catalysts can decompose hydrogen peroxide (H$_2$O$_2$) to hydroxyl radical (•OH) like in Fenton reaction, and prevent precipitating of iron hydroxide. The key factors in heterogeneous Fenton system are the suitable catalyst and reaction conditions.

Iron is an effective, cheap and safe element as catalyst. Some researchers have utilized iron materials, including iron oxides (Liu et al., 2013; Shi et al., 2014) and iron organic complexes (Balmer & Sulzberger, 1999, Chen et al., 2011; Naka et al., 2006; Zhang et al., 2009), as heterogeneous Fenton catalysts to remove organic pollutants. Fe(C$_2$O$_4$)$_x$ can catalyze the removal of pollutants in Fenton-like systems; this material is attractive for another reason that iron and iron-based materials are cheap, non-toxic, and commonly found in the aquatic environment (Lan et al., 2011; Lee et al., 2014). However, the suitable pH of Fe(C$_2$O$_4$)$_x$ is still acidic, which limits its application. Under the alkalinity condition of dye wastewater, the removal efficiency would decrease because of the generation of iron oxyhydroxides precipitation (Lee et al., 2014). Some researchers loaded Fe(C$_2$O$_4$)$_x$ complex on supports to form doping catalysts in order to broad the reaction pH (Ayodele et al., 2012;

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Ayodele & Hameed, 2013); and another approach was to mix metal ions to enhance the stability. Fe in iron compounds could be substituted by other divalent cations with similar structure including Ni (Menini et al., 2008). Ni doped into iron organic complexes could prevent iron leaching (Kesavan et al., 1999) due to the similar structure between $Ni(C_2O_4)_x$ and $Fe(C_2O_4)_x$. Thus, nickel was selected and doped into iron-oxalate to enhance the insolubility and stability of $NiFe(C_2O_4)_x$ to prevent iron ions leaching.

This work was to investigate $NiFe(C_2O_4)_x$'s catalytic ability and stability. Methyl orange was selected as the target pollutant. The heterogeneous Fenton system was investigated at various initial pH value, catalyst dosage, H_2O_2 concentration and inorganic anions. The reusability of catalyst was examined to evaluate its applicability and stability.

2. Materials and methods

2.1. Chemicals and materials

Oxalic acid dehydrate ($H_2C_2O_4 \cdot 2H_2O$) and nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) were purchased from Sinopharm Chemical Reagent Co. LTD. Iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and methyl orange ($C_{14}H_{14}N_3SO_3Na$) were purchased from Xilong Chemical Industry Co. LTD. 30% H_2O_2 solution was purchased from Beijing Chemical Works. All chemicals used were analytical grade reagents and were used as received from the supplier. Deionized water was used in all the experiments. NaOH and H_2SO_4 were used for pH adjustments.

2.2. Synthesis

The $NiFe(C_2O_4)_x$ was prepared by a novel co-precipitation method assisted with ultrasound. Due to the mechanical effect of ultrasonic waves, the dispersion of solution could be enhanced and the aggregation of precipitate could be avoided. 2 mmol $NiCl_2 \cdot 6H_2O$ was added to 50 mL water containing 10 mmol $H_2C_2O_4 \cdot 2H_2O$, and sonicated for 60 min in an ultrasonic bath (SB-800DT, Ningbo Scientz Biotechnology Co Ltd, 40 kHz, 400 W). Similarly, adding 8 mmol $FeSO_4 \cdot 7H_2O$ into 50 mL water containing 10 mmol $H_2C_2O_4 \cdot 2H_2O$ and then sonicated. These two solutions were then slowly mixed under stirring for 60 min, then sonicated for 60 min again, and centrifuged at 5000 rpm for 10 min to separate the products. The settled products were washed 4–5 times using deionized water, then dried at 50 °C for 12 h in the vacuum drier (DZF-6020, Shanghai Yiheng Instruments Co Ltd). Finally, the yellow $NiFe(C_2O_4)_x$ was obtained. $Fe(C_2O_4)_x$ and $Ni(C_2O_4)_x$ were prepared by the same method without mixing two solutions.

2.3. Characterization

The characteristics of $NiFe(C_2O_4)_x$ were detected by Brunauer–Emmet–Teller (BET) method, scanning electron microscope (SEM) and X-ray diffraction (XRD). The structural features and mineralogy of samples were analyzed by XRD. The catalyst was scanned on the Bruker D8 Advance X-ray diffractometer at 2θ from 10° to 90°. Surface morphology was investigated by a ZEISS MERLIN Compact SEM analyzer at different scales and magnifications. The specific surface area, porosity and average pore size were measured by nitrogen adsorption/desorption isotherms with a 3H-2000PS2 instrument (BeiShiDe Instrument-S&T Co., Ltd).

2.4. Removal tests and analytical methods

All experiments were carried out in 150 mL glass beakers. The catalyst and H_2O_2 were added into 100 mL of 20 mg/L methyl orange solution at the beginning of experiment. The solution's initial pH was adjusted with NaOH or H_2SO_4 to the desired value. The amount of $NiFe(C_2O_4)_x$ was 1 g/L at first. The solution was under continuous stirring at room temperature. 2 mL of sample was withdrawn regularly from the reactor and filtrated to remove the suspended solids, and then was used to determine methyl orange concentration using Beijing Pu Xi TU-1900 UV–vis spectrophotometer at detection wavelength of 464 nm. The concentration of leached iron was determined using Hitachi Z-2000 Atomic Absorption Spectrophotometer (AAS) with maximum absorbance wavelength of iron obtained at 248.3 nm. The experimental range was selected based on other heterogeneous Fenton studies (Pignatello et al., 2006; Zhao et al., 2014).

All data reported were the average of two or three parallel experiments.

3. Results and discussions

3.1. Characterization of $NiFe(C_2O_4)_x$ catalyst

The morphology of $NiFe(C_2O_4)_x$ particles was scanned by SEM, and results are shown in Fig. 1(a). Clearly, the obtained $NiFe(C_2O_4)_x$ had rectangle shape, and the particles were with uniform size in the range of 2–4 μm. N_2 adsorption-desorption isotherm curve of $NiFe(C_2O_4)_x$ was shown in Fig. 1(b). According to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature, the curve belonged to the Type III isotherm type, which indicated that weak absorption took place in the macrospore structure. The specific surface area, porosity and average pore size of $NiFe(C_2O_4)_x$ were measured using BET method. For the $NiFe(C_2O_4)_x$, the specific surface area was 45.2061 m^2/g, the total pore volume was 0.1898 mL/g and the average pore size was 16.79 nm. XRD patterns of the catalyst particles are shown in Fig. 1(c). The peaks of catalyst particle were at 18.47°, 22.96°, 29.18°, 34.64° 42.97°, 45.96° and 49.41° as the labels of (1), (2), (3), (4), (5), (6) and (7) respectively. The main diffraction peak of catalyst particle was at 18.47°, which was between those of $Ni(C_2O_4)_x$ and $Fe(C_2O_4)_x$, indicating that the phase constitution of catalyst was similar to them. Besides, there was no diffraction peak of $Ni(C_2O_4)_x$ or $Fe(C_2O_4)_x$ in X-ray diffraction test. Clearly, iron and nickel precipitated together during synthesis process, and the catalyst was $NiFe(C_2O_4)_x$ instead of compound of $Fe(C_2O_4)_x$ and $Ni(C_2O_4)_x$.

3.2. Methyl orange removal process

3.2.1. Catalytic performance of $NiFe(C_2O_4)_x$

The catalytic performance of $NiFe(C_2O_4)_x$ was evaluated by the removal efficiency of methyl orange in the heterogeneous Fenton system. As shown in Fig. 2, methyl orange was hardly removed by hydrogen peroxide. The fact that only 4.05% of methyl orange was removed by $NiFe(C_2O_4)_x$ alone indicated that the catalyst had little absorption. The methyl orange removal was only 7.9% in heterogeneous Fenton system using $Ni(C_2O_4)_x$. 98% and 100% of methyl orange was removed by using $NiFe(C_2O_4)_x$ and $Fe(C_2O_4)_x$ respectively.

The experimental data were best fitted into pseudo-zero-order kinetic model. The rate constants (k) of H_2O_2, catalyst and heterogeneous Fenton systems were 0.04, 0.118 and 3.9 min^{-1} respectively. To evaluate the catalytic property of $NiFe(C_2O_4)_x$, synergistic index was calculated. Synergistic index is defined as the ratio of rate constants for heterogeneous Fenton system to the sum of catalyst and H_2O_2 alone, expressed as in Eqn (1),

$$\text{Synergistic index} = k_{sy}/(k_{H2O2} + k_{cat}) \qquad (1)$$