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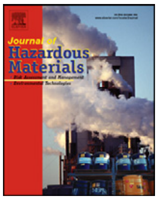

Heterogeneous activation of Oxone by $Co_xFe_{3-x}O_4$ nanocatalysts for degradation of rhodamine B

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HIGHLIGHTS

- $Co_xFe_{3-x}O_4$ magnetic nanoparticle showed high activities in Oxone for degradation of rhodamine B.
- Optimization of operating parameters on the decomposition of rhodamine B was investigated in the $Co_xFe_{3-x}O_4$/Oxone process.
- Reaction mechanism and the stability of $Co_xFe_{3-x}O_4$ NPs was studied.

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ABSTRACT

The removal of Rhodamine B (RhB) by $Co_xFe_{3-x}O_4$ magnetic nanoparticles activated Oxone has been performed in this study. A series of $Co_xFe_{3-x}O_4$ nanoparticles was synthesized using a hydrothermal method. The synthetic $Co_xFe_{3-x}O_4$ nanoparticles were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results showed that they were spinel structures and Co was introduced into their structures. The performances of $Co_xFe_{3-x}O_4$ nanocatalysts on the activation of Oxone for removal of RhB were investigated and we found that the higher cobalt content in the catalyst, the better removal performance was resulted. A series experiments of reaction conditions were also performed, which confirmed that weak acidic, higher temperature, higher dosages of $Co_xFe_{3-x}O_4$ nanocatalyst and Oxone and lower concentration of RhB were favored for the degradation of RhB. The pseudo-first order kinetics was observed to fit the $Co_xFe_{3-x}O_4$/Oxone process. Furthermore, the reaction mechanism was discussed and the scavenging effect was examined by using phenol and tert-butyl alcohol which indicated that sulfate radicals were the dominating reactive species responsible for the degradation process. Finally, the stability of $Co_xFe_{3-x}O_4$ nanocatalyst was studied.

1. Introduction

With rapid development of textile and dye industry, more and more commercially important dyes are discharged into water bodies through different means, which causes severe water pollution, the inhibition of the growth of biota and even irritation to the skin, eyes, gastrointestinal tract and respiratory tract [1,2]. Most of dyes are characterized by complicated constitution and high chemical stability, which render them resistent toward decolorization, biologically degradation and photo-degradation. Rhodamine B (RhB), an important representative of the xanthene dyes, is widely used as a colorant in textiles and food stuffs and is also a well-known tracer fluorescent. Due to its hazardous nature, high toxicity and harmful effects on public health, various treatment techniques of decolorizing and degrading its effluents have been investigated and developed [2], including adsorption [3], biological degradation and filtration processes [4], advanced oxidation processes [5], and so on. Among various advanced oxidation processes, although heterogeneous photocatalysis with UV/solar-irradiated TiO_2/ZnO are the effective process for the degradation of RhB, these traditional UV/solar irradiation sources have a few major drawbacks, such as power instability during long time operation, low photonic efficiency and less life time [6,7].

Over the past years, the promising sulfate radicals-based advanced oxidation processes (SR-AOPs) not only have gained popularity due to their high oxidative capacity and applicability to a wide pH range but have been recognized as the effective and excellent methods for the degradation of hazardous, refractory and non-biodegradable organic pollutants in various types of water [8,9]. Sulfate radicals ($SO_4^{\bullet-}$), with oxidation-reduction potential of +2.6 V vs. NHE [10], can be generated by the combination of Oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) with heating [11,12], ultraviolet [13], microwave [14], ultrasound irradiation [15] or transition metal ions (Fe^{2+}, Co^{2+}, etc.) [16–18]. Even though Oxone can be effectively activated by heat or ultraviolet, transition metal based

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activation is the most viable for field application owing to avoiding high requirement of energy and decreasing the complexity and the costs of the process. The formation of $SO_4^{\bullet -}$ activated by the transition metal ions may be expressed as following reactions (M represents Fe^{2+}, Co^{2+}, etc.) [10,19,20]:

$$M_{surf}{}^{n+} + HSO_5{}^{-} \rightarrow M_{surf}{}^{(n+1)+} + SO_4{}^{\bullet -} + OH^{-} \quad (1)$$

$$M_{surf}{}^{(n+1)+} + HSO_5{}^{-} \rightarrow M_{surf}{}^{n+} + SO_5{}^{\bullet -} + H^{+} \quad (2)$$

$$SO_4{}^{\bullet -} + H_2O \rightarrow SO_4{}^{2-} + H^{+} + {}^{\bullet}OH \quad (3)$$

Although a series of experimental evidences have proved that Oxone/Co^{2+} can effectively degrade organic pollutants [19,21,22], the potential health hazards caused by the dissolved Co^{2+} in water render such a homogeneous Oxone/Co^{2+} system with limited use. Therefore, a heterogeneous activated system on Co(□)-based catalysts is highly demanded and has been given great attention. Zhang et al. [23] reported that cobalt oxide catalysts loaded on various oxides (such as MgO, Al_2O_3, SBA-15) were used to degrade organic dyes via a sulfate radical approach. It was found that the performance of the Co/MgO catalyst was better than both homogeneous cobalt ions and heterogeneous Co_3O_4 catalyst. Shukla et al. [24] investigated cobalt exchanged zeolites for heterogeneous catalytic oxidation of phenol in the presence of peroxymonosulphate and demonstrated that cobalt ion was bonded strongly in ZSM-5 framework making it quite stable performance in the reaction. However, these methods fail to recover or recycle the catalyst in a simple and efficient way.

Recently, Fe_3O_4 magnetic nanoparticles (MNPs) as a popular catalyst material have been of particular interest because of their peroxidase-like activity and separation properties [25]. Zhang et al. [26] demonstrated that Fe_3O_4 MNPs exhibited good stability and reusability during the process of eliminating phenolic and aniline compounds in the presence of H_2O_2. However, the catalytic ability of Fe_3O_4 MNPs is generally not strong and catalytic degradation rate of target substances is generally not high. Recent studies demonstrated that the introduction of Co, Mn, Ti and Cr into $Fe_{3-x}M_xO_4$ remarkably improved catalytic activity of the resulting magnetite in heterogeneous Fenton reaction while Ni inhibited the reaction [27]. Now, Fe_3O_4 has been applied to the oxidation process of $Fe_3O_4/S_2O_8{}^{2-}$ for the removal of sulfamonomethoxine owing to the similar structure of O—O bond contained in H_2O_2 and $S_2O_8{}^{2-}$ [28].

It is reported that the coupling of Fe_3O_4 NPs with a suitable amount of cobalt ions (i.e. $Co_xFe_{3-x}O_4$) might be the efficient way to attain efficient nanoscale catalyst for activating Oxone. Yang et al. have investigated the application of iron-cobalt mixed oxide nanocatalysts synthesized via thermal oxidation on the activation of peroxymonosulfate for removing 2,4-DCP and concluded that $CoFe_2O_4$ possessed suppressed Co leaching properties due to strong Fe–Co interaction and was easy to recover due to its unique ferromagnetic nature [29]. Cobalt ferrite is not only a hard magnetic material with high cubic magnetocrystalline anisotropy but a promising, efficient and environmental benign catalyst owing to its enhanced catalytic activity and convenient magnetic separation [30].

To date, few studies have reported the development of a novel approach of using $Co_xFe_{3-x}O_4$ nanocatalyst as a heterogeneous activator of Oxone for the removal of RhB in aqueous solution. The purposes of this study were: (1) to evaluate the performances of $Co_xFe_{3-x}O_4$ nanocatalysts prepared by hydrothermal method on the activation of Oxone in aqueous solution; (2) to investigate the effects of various operating parameters on the removal of RhB; (3) to discuss the reaction mechanism and determine the dominating reactive species; (4) to study the stability of $Co_xFe_{3-x}O_4$ nanocatalysts.

2. Experimental

2.1. Chemicals and materials

The commercially available dye Rhodamine B (Formular: $C_{28}H_{31}ClN_2O_3$, Formular weight: 479.02) and Oxone (Formular: $KHSO_4 \cdot K_2SO_4 \cdot KHSO_5$, Formular weight: 614.7) were purchased from Shanghai Chemical Reagent Company, China. All the other chemicals were of analytical grade and were provided from Tianjin, China, including $FeCl_3 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, NaAc, ethylene glycol, methanol, ethanol, phenol and tert-butyl alcohol (TBA). The water used in all experiments was purified by a Milli-Q system.

2.2. Preparation and characterization of $Co_xFe_{3-x}O_4$

The $Co_xFe_{3-x}O_4$ NPs were synthesized by the hydrothermal method. A typical experiment for preparing $Co_xFe_{3-x}O_4$ NPs was as follows: desired amounts of $FeCl_3 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ based on stoichiometric Fe/Co ratio were mixed in 30 mL ethylene glycol, followed by adding 2.461 g NaAc with stirring for 30 min at room temperature. Then the resulting mixture was transferred to a Teflon-lined stainless steel autoclave and heated to 200 °C for 10 h under autogenous pressure. After cooling, the resultant product was washed several times with de-ionized water and ethanol, centrifuged and dried in a vacuum oven at 50 °C. The different nominal compositions of $Co_xFe_{3-x}O_4$ NPs were referred as $x = 0$, $x = 0.2$, $x = 0.5$ and $x = 0.75$, respectively.

A black powder was obtained and characterized by the following techniques. The crystallographic structure and the mineralogy of $Co_xFe_{3-x}O_4$ were investigated by a D8-Advance X-ray diffraction (XRD) system. The sample was scanned at 2θ from 5° to 80°. The morphology and size distribution of $Co_xFe_{3-x}O_4$ were examined by transmission electron microscope (TEM, JEM1400).

2.3. Procedures and analysis

The degradation experiments were performed in 250 ml closed batch reactors. Prior to each experiment, a known volume of RhB solution were transferred into the reactors and then appropriate amounts of Oxone and $Co_xFe_{3-x}O_4$ NPs were added to achieve the predefined molar ratios of contaminant, oxidant and catalyst. The solution pH was adjusted using a known quantity of 0.1 mmol/L sulfuric acid and/or 0.1 mmol/L sodium hydroxide and determined at room temperature using a S-25 pH-meter. The initial volume of the reaction solution was fixed at 100 mL and the reaction was initiated under vigorous stirring. At given time intervals, 4 mL samples were drawn out and were mixed immediately with excess methanol, which was a well-known quenching agent for sulfate radicals and hydroxyl radicals and was used to prevent further reaction. Then the samples were centrifuged at 8000 rpm for several minutes with an TGL-16C centrifugal (Shanghai, China) to remove the catalyst. The concentrations of the remnant dye were determined by monitoring decrease in absorbance at the maximum wavelength (554 nm) with UV–vis spectroscopy. All the experiments were carried out in duplicate in order to minimize the errors.

For chemical oxygen demand (COD) measurement, sodium nitrite was chosen as the quencher and the analytic method of COD was based on 5220D [31], which was adjusted with potassium hydrogen phthalate standard solution. The closed reflux colorimetric method was used to determine COD values. Test solution (2 mL) was pipetted into the dichromate, mercury sulphate, silver sulfate reagent and digested at 150 °C for 2 h in an Aqualytic AL 32 COD reactor. COD concentration was measured colorimetrically at $\lambda = 420$ nm using an Aqualytic PC compact COD vario photometer.

For the recycle runs of RhB degradation, the used catalyst was collected by centrifugation, washed with deionized water and