



Ozone degradation of 1-naphthol on multiwalled carbon nanotubes/iron oxides and recycling of the adsorbent



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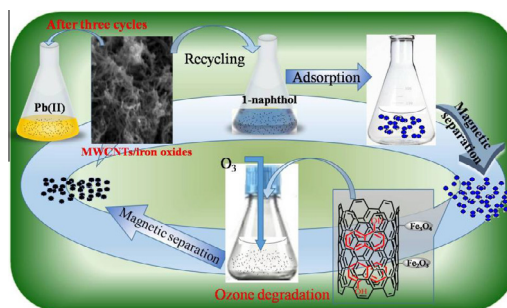
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HIGHLIGHTS

- Ozone degradation of 1-naphthol on MWCNTs/iron oxides.
- MWCNTs/iron oxide adsorption for metal ions was enhanced after degradation of adsorbed naphthol.
- The pre-concentration of PAHs on MWCNTs/iron oxides prior to ozone degradation is a novel method.

GRAPHICAL ABSTRACT



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ABSTRACT

This work investigated the pre-concentration of 1-naphthol on multiwalled carbon nanotubes (MWCNTs)/iron oxides followed by ozone degradation as a post processing method for degrading 1-naphthol, while recycling the MWCNTs/iron oxides. Ozone degradation kinetics for 1-naphthol on MWCNTs/iron oxides and in solution indicated that the ozone degradation of 1-naphthol was faster on MWCNTs/iron oxides than in solution. The main degradation intermediates were identified by Gas Chromatograph Mass Spectrometer (GC–MS), and the possible pathways of 1-naphthol ozone degradation on the MWCNTs/iron oxides were demonstrated by combining GS–MS with a High Performance Liquid Chromatography. The adsorption capacity of the MWCNTs/iron oxides for heavy metal ions was greatly enhanced after ozone degradation of the adsorbed 1-naphthol, which resulted from the introduction of oxygen-containing groups during the ozone degradation process and was important for recycling adsorbents. Our results indicated that the ozone degradation of 1-naphthol on MWCNTs/iron oxides is a post processing method of adsorption, and this method could degrade the adsorbed 1-naphthol and allow for adsorbent recycling. The pre-concentration of polycyclic aromatic hydrocarbons on MWCNTs/iron oxides prior to ozone degradation is a novel method for industrial wastewater treatment.

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1. Introduction

A great deal of concern has been given to the environmental fate and behavior of polycyclic aromatic hydrocarbons (PAHs)

due to their carcinogenic potential [1]. PAHs are mainly produced from petroleum products, dyestuffs, pharmaceuticals and agro-chemical industries [2,3]. Most PAHs are poorly biodegradable. Many studies have focused on finding appropriate treatment methods, such as bioremediation, chemical oxidation processes and adsorption to carbon nanotubes (CNTs), for water contaminated with PAHs [4–7]. Among these techniques, the ozone-based oxidation process for PAH degradation is effective [8–13]. The ozonation of 1-naphthol was studied by Bernatek and Frensen as

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early as 1962 [14]. In 1995, Chen and Larson studied the reaction of ozone and 1-naphthol, and they thought that the degradation products of 1- and 2-naphthol could be easily isolated and identified [15].

Ozone is a chemical oxidant that is widely used in wastewater and in drinking water treatment. Ozonation can transform PAHs into oxygenated intermediates that are more soluble and more biodegradable than parent compounds [16]. Ozonation is widely used for disinfection, taste and odor control, color removal, and for the oxidation of micro-pollutants [17]. Generally, ozone treatment involves the direct injection of ozone gas into an aqueous solution. However, the ultimate efficiency of ozone degradation for oxidizing pollutants largely depends on the oxidant concentrations (ozone and the ·OH radical produced during the decay of ozone) and on the second-order rate constants for the reaction of ozone with the available pollutants [18]. When faced with a large volume of polluted water, the efficiency of ozonation is not high due to poor mass transfer. Thus degradation is not completed and the use of ozone is not cost-effective. Much work has been done in the last decade to improve ozone mass transfer efficiency.

Adsorption is another widely used technique for eliminating of PAHs from polluted water due to its low cost and easy operation. Various materials, such as polymer resin, natural materials and carbon-based materials, have been used for these processes [19–21]. One important finding from these studies was that CNTs were potentially superior adsorbents for removing PAHs. In addition, researchers have proposed that the direct adsorption of PAHs to the carbon-based nanomaterial surface is driven by π - π electron-donor-acceptor (EDA) interactions [22,23].

Although the adsorption of PAHs on CNTs can remove most of PAHs from solutions, the post processing remains a problem. Strong EDA interactions result in difficulties regarding the desorption of PAHs from CNTs in aqueous solutions. The most common post processing methods are thermal and catalytic incineration. Thermal oxidation typically requires temperatures between 750 and 1150 °C and catalytic oxidation requires temperatures between 200 and 500 °C [24]. These methods require a great deal of energy and resources and limit how the superior adsorbents can be recycled. Some studies have shown that activated carbon and multi-walled CNTs (MWCNTs) are efficient ozonation catalysts [25–27].

Based on the previous results, MWCNTs are high efficient adsorbents [28–34]. Here, MWCNTs/iron oxides were prepared to serve as easily separated and recyclable super adsorbents. Ozone degradation was used as a post processing method to remove the adsorbed 1-naphthol from the MWCNTs/iron oxides. 1-Naphthol was selected as a model for PAHs. The ozone and ·OH will react with many different functional groups and result in a large number of products [35,36]. Qualitative and quantitative analyses of the major degradation intermediates were analyzed to understand the main reaction mechanisms using a Gas Chromatograph Mass Spectrometer (GC-MS) and High Performance Liquid Chromatography (HPLC). The potential of recycling ozone treated magnetic MWCNTs/iron oxides was investigated. After the ozone degradation of adsorbed 1-naphthol, the MWCNTs/iron oxides were re-used for removing heavy metal ions.

2. Materials and methods

2.1. Chemicals

MWCNTs (outer diameters 10–15 nm) were purchased from Shenzhen Nanotech Co., China. The analytical pure 1-naphthol reagent was purchased from the Sinopharm Chemical Reagent Corporation (China) and no significant impurities were detected using HPLC analysis. The main degradation intermediates, such

as phthalic acid, phthalic anhydride, 1,4-naphthoquinone and 2-hydroxynaphthalene-1,4-dione were obtained from Sinopharm with purities of more than 99%. All other chemicals were of analytical purity and were used without further purification. Stock solutions were prepared with Milli-Q water.

2.2. Preparation and characterization of the MWCNTs/iron oxides

The MWCNTs/iron oxides were prepared using a chemical coprecipitation reaction between the ferrous and ferric ions and the MWCNTs. Briefly, 0.4 g of the MWCNTs was dispersed in 250.0 mL of Milli-Q water. The solution containing 8.95 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 5.25 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added dropwise to the MWCNT suspension at room temperature. A 30% ammonia solution was added until a pH value of 10.0 was achieved. Next, the solution temperature was increased to 90 °C. After rapidly stirring for 4 h, the solution was cooled to room temperature. The solution was filtered and washed with Milli-Q water and ethanol several times before drying in vacuum [28].

The magnetic composites before and after ozone exposure were characterized by scanning electron microscopy (SEM) (JEOL JSM-6700, Tokyo, Japan), powder X-ray diffraction (XRD), Fourier transformed infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The XRD patterns were measured using an X'Pert PRO diffractometer with Cu K α radiation ($\lambda = 0.154$ nm). In addition, the FTIR spectra were measured using a Nicolet 8700 FTIR spectrometer (Thermo Scientific Instrument Co., USA), and the XPS measurements were conducted using a VG Scientific ESCALAB Mark II spectrometer.

2.3. Preconcentration and ozone degradation of 1-naphthol

Preconcentration of the 1-naphthol was conducted by mixing 100.0 mL of the 1-naphthol solution (120.0 mg L^{-1}) with 0.1 g of the MWCNTs/iron oxides. Next, the mixture was adjusted to pH 7.0 by adding negligible volumes (0–10 μL) of 0.1 M HNO_3 or NaOH. After the mixture was shaken for 2 days in the dark at 293 K to achieve adsorption equilibrium, the solid and liquid phases were separated using magnetic separation methods. This supernatant was labeled as supernatant (I) and was used to measure the solid adsorption capacity. The concentration of 1-naphthol in supernatant (I) after adsorption equilibrium was determined using HPLC. The amount of 1-naphthol that was adsorbed on the solid was calculated as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where C_0 (mg L^{-1}) is the initial concentration of 1-naphthol in the suspension; C_e (mg L^{-1}) is the equilibrium concentration of 1-naphthol in the supernatant solution after separation; V (mL) is the volume of the solution; m (g) is the mass of the solid and q_e (mg g^{-1}) is the amount of 1-naphthol that was adsorbed per weight of solid after equilibrium.

The adsorbed 1-naphthol on the MWCNTs/iron oxides that was magnetically separated was mixed with 100 mL of Milli-Q water in a 200 mL of glass tubular reactor in the dark. Gaseous ozone was bubbled to the reactor from the top side through a Teflon tube that extended to the bottom of reactor. The reactor contents were continuously stirred to ensure that the gaseous ozone was dispersed homogeneously in the solution. Ozone was generated from the ambient air using a discharged ozone generator (Saige SGF-YW5g, China). A gas flow rate of 50 mL min^{-1} was used and was regulated by a mass flow controller, producing $0.029 \text{ mg min}^{-1}$ of ozone. Constant inlet ozone concentration in liquid phase (50 mg L^{-1}). The ozone gas was slowly bubbled (diffused) over time into the supernatant solution at the natural pH (around

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