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Enhanced removal of acetaminophen from synthetic wastewater using multi-walled carbon nanotubes (MWCNTs) chemically modified with NaOH, HNO_3/H_2SO_4, ozone, and/or chitosan

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ABSTRACT

This study investigates the technical feasibility of MWCNTs for acetaminophen (Ace) removal from synthetic wastewater in batch mode. To improve their removal performance, the surface of the MWCNTs was chemically modified with NaOH, HNO_3/H_2SO_4, ozone and/or chitosan. The effects of pertinent parameters such as reaction time, dose, pH, and agitation speed on the Ace removal were evaluated. Their removal performance on Ace was compared to those of previous studies. The adsorption mechanisms of Ace removal by the MWCNTs are also presented. It is evident from this study that after chemical modification on its surface, the treated nano-adsorbent significantly enhanced Ace removal from wastewater. Among all types of those adsorbents, the ozone-treated MWCNT stands out for the highest Ace removal (95%) under the same initial Ace concentration of 10 mg/L. Their adsorption capacities, applicable to the Freundlich isotherm model, are listed as: ozone-treated MWCNT (250 mg/g) > chitosan-coated MWCNT (205 mg/g) > acid-treated MWCNT (160 mg/g) > NaOH-treated MWCNT (130 mg/g) > as-received MWCNT (90 mg/g). Although the ozone-treated MWCNT has the most outstanding performance in Ace removal, its treated effluent still could not meet the required effluent limit of less than 0.2 mg/L set by China's legislation. This suggests that further treatment using biological processes needs to be carried out to complement Ace removal from the wastewater samples.

1. Introduction

In recent years, pharmaceuticals and personal care products (PPCPs), which are not easily biodegradable and possess serious threats to public health, have been identified as one of emerging contaminants [1–2]. Compared to persistent organic pollutants (POPs) such as pesticides, pollutants from PPCPs category are distinguished by their high polarity and low volatility [3].

Among the various PPCPs, acetaminophen (Ace) has been identified as one of the most widely used drugs for fever and headache [4]. The drug is toxic when it is overdosed, as it causes acute liver and kidney failure [5]. The pollutant is often found in the municipal sewage effluents with varying concentrations from 0.1 to 10 mg/L. After conventional treatment using biological processes, the Ace, however, is still detected in sewage treatment plants and surface water [6]. Therefore, there is a growing concern regarding its implications on the aquatic environment, since biological processes alone cannot remove the pollutant effectively from contaminated water [7].

Among various physico-chemical treatments [8], adsorption may be technically feasible and cost-effective to remove this pollutant. Basically, it is a mass transfer process where a substance is transferred from a liquid phase to the surface of adsorbent and becomes bound by physico-chemical interactions [9]. Over the past years, granular activated carbon (GAC) in bulk form has been widely used to eliminate pollutants such as heavy metals [10–13]. Considering that nano-sized materials have properties different from their corresponding bulk forms, it is necessary to explore the applicability of carbon nanotubes (CNT) for Ace removal.

Due to its unique characteristics such as small size, uniform pore distribution, reactivity and large surface area per mass ratio [14], CNT represents one of the most promising functional nanomaterials for water treatment applications. It is a sheet of graphite rolled into a tubular structure, of which its building block consisting of carbon atoms [14]. Based on the hybridized carbon atom layers and diameter range, CNT is classified either as single-walled carbon nanotube (SWCNTs) or as MWCNTs. In this study, MWCNTs were tested, as they are more cost-effective than that of the formers [15].

Although the MWCNTs have been widely used for the removal of inorganic pollutants like heavy metals [16–18], to the best of our knowledge, their applications for treatment of wastewater laden with organic

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pollutants have been rarely reported in the literature. A preliminary study has been conducted by Tao et al. [19] on Ace removal using graphene/TiO_2 nanotubes. However, their study did not provide any information on their surface modification to improve their removal performance.

In this study, oxidative pretreatments using oxidizing agents such as nitric/sulfuric acid or ozone were used to modify the surface of the MWCNTs. This method could attach oxygenated complexes such as carboxyl, lactone, phenol, and ketone on their surface [20–22] and increase their surface charge density, making them become more hydrophilic to attract adsorbate in aqueous solutions through columbic forces [23]. While oxidative pretreatment may enlarge its surface area, alkaline pretreatment of the MWCNT could increase the concentration of oxygenated complex on their surface for enhancing adsorption process [24–25].

The laboratory study reported in this article investigates the technical feasibility of MWCNTs for Ace removal from synthetic wastewater in batch modes. Due to its potential adsorbability on MWCNT, Ace was used as a model compound of PPCPs. To improve its removal performance, the surface of MWCNT was chemically modified with NaOH, HNO_3/H_2SO_4, chitosan and/or ozone. The effects of parameters such as contact time, dose, pH, and agitation speed on Ace removal were evaluated. Their Ace removal performance is compared to those of previous studies. The adsorption mechanisms of Ace removal by the MWCNT are also presented.

2. Materials and methods

2.1. Materials

With their outer diameters of 8 nm, lengths of about 10 nm, and purity of 98%, the MWCNT samples were supplied by Chengdu Chemicals (Chengdu, China). Other chemicals such as NaOH, HNO_3, H_2SO_4, obtained from Sigma Aldrich (China), were of analytical grade. Acetaminophen, provided by Acros (New Jersey, USA), was used as a source of synthetic wastewater. Its characteristics are presented in Table 1. The pH of Ace solution, adjusted by 0.1 M NaOH or 0.1 M H_2SO_4, was measured using a pHmeter (model Mettler FE 20, Switzerland). All of the standard solutions were freshly prepared from a stock solution using deionized water.

2.2. Surface modification of MWCNT samples

2.2.1. Alkali pretreatment of MWCNT with NaOH

To remove any remaining impurities during their production, the MWCNT samples were repeatedly washed with deionized water. Afterwards, they were soaked in 0.1 M NaOH solution with a volume ratio of 1:7 for 24 h at 150 rpm of agitation speed. The same samples were then thoroughly washed with deionized water until their solution pH became neutral. Subsequently, the samples were dried in an oven overnight at 100 °C and stored in a desiccator. The samples were referred as 'NaOH-treated MWCNT'.

2.2.2. Oxidation of MWCNT with HNO_3/H_2SO_4

About 10 g of MWCNT samples were immersed in a mixture of 0.1 M HNO_3/H_2SO_4 solution with a volume ratio of 1:3. After undergoing ultrasonic treatment for 4 h at 60 °C, they were cooled and their supernatants were drained. The samples were repeatedly washed with deionized water until their solution pH was stable. Finally, the samples were dried in an oven for 24 h at 100 °C and stored in a desiccator for further studies. They were labeled as 'acid-treated MWCNT'.

2.2.3. Coating MWCNT with chitosan

Approximately 10 g of chitosan flakes (90% deacetylated) were immersed with 0.1 L of 1% (v/v) CH_3COOH and mechanically agitated using a rotary shaker at 150 rpm for 24 h to form a homogenized gel. Then, about 0.1 g of the sample (after oxidation with HNO_3/H_2SO_4) was dipped into 0.5 L of chitosan-acetic acid solution and the suspension was magnetically stirred for 24 h. Afterwards, the gel-coated MWCNTs was repeatedly washed with 1% (v/v) CH_3COOH to remove any remaining chitosan in the solution. They were dried in an oven overnight and labeled as 'chitosan-coated MWCNT'.

2.2.4. Ozonation of MWCNT

Ozonation of the samples was carried out by an ozone generator (model WH-X-10, Nanjing, China) using ambient air as the feeding gas. In a closed system, the samples were continuously treated with gaseous ozone at an inflow concentration of 6 mg/L and a flow rate of 1.8 L/min (a mass rate of 10.8 mg/min) for 12 h. After ozonation, the samples were thoroughly washed with deionized water and dried in an oven overnight at 100 °C. The samples were called as 'ozone-treated MWCNT'.

2.3. Characterization of MWCNT

To detect changes in their morphologies before and after pretreatment, characterization methods were employed. Firstly, their morphologies were analyzed using a scanning electron microscope (SEM) model Zeiss Sigma (Germany), which operated at 15 kV. Fourier transform infrared (FTIR) spectroscopic measurements (model IS50 Thermo, USA) were also undertaken to identify certain vibrations of chemical bond in the samples. Their chemical structures were analyzed using an X-ray power diffraction (XRD) model Rigaku Ultima IV (Japan), which operated at 40 kV and 30 mA. A range of diffraction angles (2θ) from 10° to 80° at a scanning speed of 10°/min were applied.

2.4. Batch adsorption experiments

Batch experiments were conducted at ambient temperature under optimized dose, pH, agitation speed and reaction time. Subsequent tests were undertaken with only optimized parameters. After attaining equilibrium, the samples were periodically collected and filtered using a 0.22 μm nylon filter. All of the tests were carried out in triplicate and their relative standard errors were less than 5%. When the relative error exceeded this criterion, the data were disregarded and the forth experiment would be conducted until the relative error fell within an acceptable range.

2.5. Regeneration of MWCNT

Before undertaking regeneration experiments, the spent MWCNTs were separated from synthetic wastewater by filtration. The samples were then thoroughly washed with deionized water and ultrasonically treated for 10 min. Afterwards, the same samples were dried at 100 °C

Table 1
Properties of acetaminophen.
Source: [19].

	Molecular formula	Molecular weight (g/mol)	λ_{max} (nm)	Molecular structure
Acetaminophen	$C_8H_9NO_2$	151.16	243