



Research paper

Calcined Mg/Al layered double hydroxides as efficient adsorbents for polyhydroxy fullerenes



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ABSTRACT

The environmental behaviors and pollution control of engineered nanomaterials are drawing increasing interests nowadays. This work showed that the calcined layered double hydroxides (LDH), i.e., layered double oxides (LDO), could effectively adsorb polyhydroxy fullerenes (PHF) from aqueous solution. The maximum adsorption capacity of LDO reached ~476 mg/g, much higher than that on LDH (~47 mg/g) and activated carbon (~28 mg/g). All of the three equilibrium adsorption isotherms could be well fitted with the Langmuir equation. The high adsorption capacity of PHF on LDO can be attributed to the enhanced accessibility to the adsorption sites for PHF during structural reconstruction of LDO. In addition, the rehydrated LDH, with a net positive surface charge, has high affinity for negatively charged PHF through an electrostatic interaction. Cl^- , CO_3^{2-} , and SO_4^{2-} could slightly enhance the adsorption of the PHF on LDO, while HPO_4^{2-} showed an evident inhibiting effect in the whole concentration range of PHF. The adsorbents before and after the adsorption of PHF were characterized by XRD, FT-IR, and TG. The obtained results indicated that the adsorbed PHF could not intercalate into the interlayer spaces of the reconstructed LDH, but could effectively compete with CO_3^{2-} during the adsorption process.

1. Introduction

Carbon-based nanomaterials such as fullerenes, carbon nanotubes, graphene, and graphitic carbon nitride have received increasing interest nowadays because of their unique physicochemical properties and potential applications in a wide range of fields (Jordá-Beneyto et al., 2007; Mauter and Elimelech, 2008; Dai et al., 2012; Jiang et al., 2012; Cha et al., 2013). As most of the engineered carbon nanomaterials will eventually end up in the environment (Nowack and Bucheli, 2007), their potential adverse effects on human health and environment require serious attentions. In this case, their environmental behaviors and toxicity to organisms have been investigated by a number of studies (Sayes et al., 2004; Jia et al., 2005; Perez et al., 2009; Turco et al., 2011; Song et al., 2012; Fortner et al., 2012; Zhu et al., 2013).

Among the various carbon nanomaterials, fullerenes and their derivatives as a family of carbon nanomaterials have potential applications in a wide range of areas, e.g., as biomedicine (Djordjevic and

Bogdanovic, 2008; Markovic and Trajkovic, 2008), catalyst (Niu et al., 2011), adsorbents for contaminants (Cheng et al., 2004), hydrogen storage (Yoon et al., 2007), nanofillers for nano-composites (Jung et al., 2010), and antioxidant in cosmetics (Gharbi et al., 2005), etc. As such, the research enthusiasm on this family of carbon nanomaterials is ever increasing, leading to a 'fullerene fever'. As the polyhydroxy fullerenes (i.e., PHF) have high solubility in bulk water while retaining most of the physicochemical properties of fullerenes, it can be conveniently applied in aqueous environment (Djordjevic and Bogdanovic, 2008; Niu et al., 2011; Georgieva et al., 2013). In addition, PHF have been identified as the main products during the exposure of fullerenes to the environment. Many factors such as UV light irradiation, interaction with oxidants (such as hydroxyl radicals) (Lee et al., 2010; Qu et al., 2010; Wu et al., 2014), and interaction with microbes (Chae et al., 2014), can transform fullerenes into PHF.

However, many researchers found that PHF presented cytotoxicity to both bacteria and human cell (Sayes et al., 2004; Isakovic et al.,

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2006; Yamawaki and Iwai, 2006). For example, Isakovic et al. (2006) found that PHF could cause cell membrane damage, lipid peroxidation, and necrotic cell death due to a direct generating of reactive oxygen species. Yamawaki and Iwai (2006) found that PHF represented potential risk for cardiovascular diseases, including atherosclerosis and ischemic heart disease. As such, much attention should be paid to the pollution control of PHF in aqueous solution. As both fullerenes and PHF are relatively resistant to biodegradation and chemical attack because of their sp² hybridized carbon-carbon bonds and toxicity for bacteria (Heyman, 1991; Perez et al., 2009; Avanasi et al., 2014), therefore, adsorption may be a relatively suitable approach for the removal of PHF from aqueous solution, in which choosing proper adsorbents is of critical importance.

With nano-sized layered structure, some clays, such as layered double hydroxides (LDH) and montmorillonite, generally have large surface area, charged layers, and exchangeable ions between the layers (Cavani et al., 1991; He et al., 2010; Zhu et al., 2016). As such, they can effectively adsorb some ions from water through an ion-exchange process (Fortner et al., 2012; Chen et al., 2016). Chen et al. (2016) found that cationic polyethylenimine-modified montmorillonite had high efficiency for the removal of PHF from aqueous solution. Given that PHF are generally negatively charged (Georgieva et al., 2013), LDH, also known as anionic clays, may be good adsorbents for PHF. LDH consist of brucite-like hydroxide sheets, where partial substitution of trivalent for divalent cations results in a positive sheet charge compensated by anions within interlayer spaces (Cavani et al., 1991). One of the interesting characteristics of LDH is that their calcined products, also known as LDO, can rehydrate and recover to LDH in aqueous environment. Previous studies showed that LDO may be more effective adsorbents than LDH in the adsorption of anions from water, as the adsorption of contaminants simultaneously happens with the rehydrating of LDH. In this case, the interlayer spaces (i.e., the adsorption sites) of the rehydrated LDH can be better accessed by contaminants (Zhu et al., 2005; Lv et al., 2008; Crepaldi et al., 2002).

This work examined the adsorption capacity of PHF on LDH and LDO. As activated carbon has been widely used as adsorbent for various contaminants because of its high specific surface area, high adsorption capacity, and low-selectivity for pollutants (Faria et al., 2004; Nakagawa et al., 2004), the adsorption of PHF on a commercial activated carbon was compared as well. In addition, the structures of LDO after PHF adsorption were characterized by XRD, FT-IR, and TG.

2. Experimental

2.1. Materials

PHF were obtained from Suzhou Dade Carbon Nanotechnology Co., Ltd. Activated carbon was purchased from Taishan City Guangdong Overseas Reagent Plastic Co., Ltd. All reagents were used as received. All labware were washed by ultra-pure water (> 18 MΩ/cm) before the experiments.

2.2. Preparation of LDH and LDO

A co-precipitation method following Reichle (Reichle, 1986) with some modifications was used to prepare Mg/Al-CO₃-LDH. Briefly, 3.5 mol NaOH and 0.943 mol Na₂CO₃ were dissolved in 1000 mL deionized water to which 700 mL mixed solution containing 0.5 mol Al(NO₃)₃·9H₂O and 1.0 mol Mg(NO₃)₂·6H₂O (Mg: Al molar ratio = 2:1) was added at a rate of 1.0 mL/min under vigorous stirring. The resulting slurry was aged at 80 °C for 24 h while stirring. After cooling to room temperature, the slurry was centrifuged and washed using deionized water at least eight times to remove free ions. Then the material was dried at 80 °C over night, ground and passed through a 100-mesh sieve. Part of the resulting material was calcined at 500 °C for 3 h to obtain LDO. The LDH sample and LDO sample were then placed in a

CaO desiccator.

2.3. Adsorption experiments

The adsorption kinetics of the contaminants were conducted with the reaction time in the range of 5 min to 48 h to determine the equilibration time. In particular, 0.02 g LDO, LDH, or activated carbon were dispersed in 0.02 L of PHF solutions with the concentrations at 250, 25, and 25 mg/L, respectively. Different concentrations of PHF were used because these adsorbents have different adsorption capacity. The mixture was stirred at 200 rpm and 25 °C in a shaking table. After adsorption, the suspensions were centrifuged at 4200 rpm for 15 min.

Equilibrium adsorption experiments were carried out to determine the adsorption capacity of PHF on LDO, LDH, and activated carbon. Equilibrium studies were conducted in 0.05 L Teflon tubes by mixing 0.02 L of PHF solution with 0.02 g LDO, LDH, or activated carbon. The mixture was stirred at 200 rpm and 25 °C in a shaking table for 12, 12, and 24 h (equilibration time was selected according to the adsorption kinetic curve results), respectively. The suspensions were centrifuged at 4200 rpm for 15 min.

Cl⁻, SO₄²⁻, or H₂PO₄⁻ was selected to study the effect of co-existing anions on PHF adsorption by LDO. The experiment was conducted in the solution containing 800 mg/L (~7 mM) PHF, at which the adsorption amount of PHF on LDO has almost reached maximum. Specifically, 0.02 g LDO was dispersed in 0.02 L of solution containing both PHF and a co-existing anion (Cl⁻, SO₄²⁻, or H₂PO₄⁻), with the concentration of ~7 mM for PHF and 0.14 M for the co-existing anion, respectively. After shaking of the adsorbent mixtures at 25 °C for 12 h, the supernatants were separated by centrifugation at 4200 rpm for 15 min.

The concentration of PHF was measured spectrophotometrically by monitoring the absorbance at 230 nm (maximum absorption wavelength was confirmed by the full wave scanning) using a UV-Vis (759S, Shanghai JingHua Instrument Co. Ltd., China) (Krishna et al., 2006). The full wave scanning also showed that Cl⁻, SO₄²⁻, and H₂PO₄⁻ had no noticeable absorption at 230 nm. All batch experiments were carried out in triplicate and the error bars were displayed in the figures.

2.4. Characterization

In order to investigate the adsorption mechanism of PHF on LDO and the structure of LDO/PHF compound, the LDO before and after adsorbed PHF were characterized by XRD, FT-IR, and TG. PHF and LDO/PHF compound are denoted as PHF and LDO-PHF, respectively. In addition, according to the adsorption capacity of PHF, the adsorption products with 175, 348, and 476 mg/g PHF are herein referred to as LDO-PHF175, LDO-PHF348, and LDO-PHF476, respectively. For clarity, the meanings of all the abbreviations are summarized (Table 1).

XRD patterns were obtained using a Bruker D8 ADVANCE X-ray diffractometer (Karlsruhe, German), operating at 40 kV and 40 mA with CuKα radiation. The patterns were recorded over the 2θ range of 3–80° at a scanning speed of 1°/min. FT-IR spectra of KBr pellets in the range

Table 1
Meanings of the abbreviations for the samples.

Abbreviation	Meaning
LDH	Layered double hydroxides
LDO	Layered double oxides
PHF	Polyhydroxy fullerenes
LDO-PHF	LDO after PHF adsorption
LDO-PHF175	LDO after 175 mg/g PHF adsorption
LDO-PHF348	LDO after 348 mg/g PHF adsorption
LDO-PHF476	LDO after 476 mg/g PHF adsorption
R-LDH	Rehydrated LDH
LDH/PHF	The mixture of LDH and PHF

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