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Adsorption of polyhydroxy fullerene on polyethylenimine-modified montmorillonite

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ABSTRACT

The environmental behaviors and potential ecotoxicity of carbon nanomaterials, such as fullerene and its derivatives, are gaining ever-increasing concerns at present. This work attempts to develop an adsorbent for the effective removal of polyhydroxy fullerene (PHF) from aqueous solution, which was synthesized by modifying montmorillonite (Mt) with a branched polymer polyethylenimine (PEI). The adsorption results showed that the obtained adsorbent (*i.e.*, PEI-Mt) could effectively remove PHF over a wide range of solution pH; both the electrostatic attraction and hydrogen-bond interaction between PHF and PEI-Mt contributed to the strong adsorption. Decreasing solution pH and rising PEI loading amount on Mt could both increase the adsorption amounts of PHF on PEI-Mt. The adsorption isotherms could be well fitted with the Langmuir model, and the calculated maximum adsorption value of PHF on 10%PEI-Mt reached ~213 mg/g, much higher than that on the original Mt (~16 mg/g). The adsorbents after PHF adsorption were further characterized using Fourier transform infrared spectroscopy, X-ray diffraction, and transmission electron microscopy. The results suggested that the adsorbed PHF primarily existed on the outer surfaces of PEI-Mt. This work showed that PEI-Mt can be a potentially efficient adsorbent for the removal of PHF from aqueous solution.

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1. Introduction

Fullerene and its derivatives have gained immense attention so far due to their remarkable properties and potential applications in many areas, including environmental remediation (*e.g.*, adsorbents and catalysts) (Yang *et al.*, 2006; Meng *et al.*, 2012), biomedicine (*e.g.*, antibacterial and antitumor) (Markovic and Trajkovic, 2008; Kwag *et al.*, 2013), and materials science (*e.g.*, sensors, supercapacitors, and hydrogen storage) (Li *et al.*, 2009; Xiong *et al.*, 2012; Rather and De Wael, 2013). With the ever-increasing production and wide applications of fullerene-based carbon nanomaterials, they will inevitably enter into the environment (Colvin, 2003; Klaine *et al.*, 2008). As such, significant concerns have been drawn to their influences on human health and natural environment.

Although fullerene is highly hydrophobic, water-soluble fullerenes, such as aqueous fullerene colloid aggregates (nC_{60}) and polyhydroxy fullerene (PHF), can be conveniently synthesized by ultrasonication, solvent exchange, and chemical modification (Brant *et al.*, 2006; Georgieva *et al.*, 2013). The enhanced water-solubility expands their

applications, but may simultaneously increase their risks to the environment and human health (Klaine *et al.*, 2008). Indeed, the cytotoxicity of water-soluble fullerenes to both bacteria and human cell has been confirmed by many studies (Sayes *et al.*, 2004; Wielgus *et al.*, 2010; An and Jin, 2012). Consequently, proactive research on effective removal of water-soluble fullerenes from aqueous solution is critical to controlling the potential risks and ensuring a sustainable carbon nanomaterials industry.

At present, a number of studies have been conducted to remove nC_{60} from wastewater by various adsorbents, such as biomass (Kiser *et al.*, 2010), activated sludge (Yang *et al.*, 2013), and alum (Wang *et al.*, 2013). In contrast, much less work about the pollution control of PHF has been reported up to now. On the other hand, Prylutskyy *et al.* (2014) indicated that the origin of fullerene solubility in water was probably based on the surface hydroxylation of fullerene molecules; therefore, nC_{60} could be considered as fullerene aggregates with a certain amount of hydroxyls on the outer surfaces. Furthermore, when exposed to the environment, fullerenes and nC_{60} could be transformed into PHF by many factors (*e.g.*, long-term mixing, ultraviolet radiation, and interaction with microbes and oxidants) (Hwang and Li, 2010; Qu *et al.*, 2010; Chae *et al.*, 2014). Hence, being regarded as the main products of fullerenes in the environment, PHF need large concerns in terms of their pollution control.

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Table 1
Meanings of the abbreviations for the samples.

Abbreviation	Meaning
PHF	Polyhydroxy fullerene
PEI	Polyethylenimine
Mt	Montmorillonite
2%PEI-Mt	2%PEI-modified Mt
10%PEI-Mt	10%PEI-modified Mt
Mt-PHF	Mt after the adsorption of PHF ($C_0 = 400$ mg/L)
2%PEI-Mt-PHF	2%PEI-Mt after the adsorption of PHF ($C_0 = 400$ mg/L)
10%PEI-Mt-PHF	10%PEI-Mt after the adsorption of PHF ($C_0 = 400$ mg/L)

With 2D nano-sized structure, high cation exchange capacity, and large specific surface area, montmorillonite (Mt) as a low-cost and environmental-friendly adsorbent for cationic contaminants (e.g., cationic dyes and heavy metal cations) has been widely applied in environmental remediation (Bergaya and Lagaly, 2013; Yuan et al., 2013; Zhu et al., 2016). However, owing to the negatively charged layers, raw Mt exhibits a poor affinity toward anionic contaminants (Zhu et al., 2016). A number of studies indicated that Mt could be easily modified by cationic modifiers to synthesize various adsorbents, such as the cationic surfactant modified Mt for organic contaminants (Roberts et al., 2006; Zhu et al., 2011), and the hydroxymetal polycations modified Mt for oxyanions (Zhou et al., 2010; Ma et al., 2015). As an important type of modifiers for Mt, the cationic polymers have received broad attentions because of their large charge/mass ratio (Yue et al., 2007; Zhu et al., 2010). In this regard, cationic polymers could readily saturate the CEC of Mt and change the surface charge of Mt from negative into positive. As a result, the modified Mt could provide adsorption sites for anionic contaminants (Kang et al., 2009; Li et al., 2011). Given that PHF generally exhibit negative surface charges in water (Brant et al., 2007), one could propose that cationic polymers-modified Mt may be an efficient adsorbent for PHF.

Herein, polyethylenimine (PEI), a water-soluble cationic polymer with a large number of amino groups and high charge density (Fig. S1) (Zhang et al., 2014), was selected to modify Mt. The adsorption capacities of Mt and the PEI-modified Mt (PEI-Mt) toward PHF were investigated, and the potential adsorption mechanisms were further elucidated through X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). Our results indicated that PEI-Mt exhibited high affinity toward PHF, with the maximum adsorption amount of ~213 mg/g. As such, PEI-Mt could be used as a promising adsorbent toward PHF.

2. Materials and methods

2.1. Materials

The sodium-exchanged Mt used in this work was prepared by dispersing the calcium-rich Mt (CEC was 110.5 mmol/100 g, purity >95%, Inner Mongolia, China) in a 0.5 mol/L solution of NaCl, followed by stirring for 24 h at 80 °C (repeated 3 times). The obtained suspension was centrifuged and washed repeatedly with distilled water until AgNO_3 test confirmed no chloride in the supernatant. After being dried at 60 °C, the sodium-exchanged Mt was collected for the follow-up experiments. For brevity, Mt was used to denote the sodium-exchanged Mt in the following text. The cationic polymer, branched PEI (molecular mass = 10,000, 99%), was supplied by Shanghai Aladdin Bio-Chem Technology Co., Ltd. PHF was purchased from Suzhou Dade Carbon Nanotechnology Co., Ltd.

2.2. Synthesis of adsorbents

PEI-Mt was prepared as follows: a desired amount of PEI was dissolved into distilled water under stirring for 10 min, followed by adding 10 g of Mt. The mixture was vigorously stirred for 12 h at room temperature, and then the resulting OMTs were collected by centrifugation, washed with distilled water (3 times), and freeze-dried for 24 h. The added amounts of PEI were 2% and 10% of the weight of Mt, and the corresponding OMTs were denoted as 2%PEI-Mt and 10%PEI-Mt, respectively. For clarity, the meanings of all the abbreviations for the samples are listed in Table 1.

2.3. Adsorption experiments

In order to determine the adsorption equilibration time, the adsorption kinetics experiments were conducted with the adsorption time ranged from 10 min to 24 h. In detail, 0.1 g of the adsorbents (i.e., Mt and 2%PEI-Mt) were added into 20 mL of the PHF solution with the concentration of 200 mg/L. The suspension were steadily agitated in an incubator shaker at 200 rpm and 25 °C. Subsequently, the influences of pH on the adsorption of PHF on PEI-Mt were investigated. In this case, the pH was initially adjusted using 0.1 M NaOH or 0.1 M HCl, and the initial concentration of PHF for 2%PEI-Mt and 10%PEI-Mt were 200 and 800 mg/L, respectively. Besides, batch adsorption experiments were conducted to evaluate the adsorption capacities of the raw Mt and PEI-Mt toward PHF from aqueous solutions. Specifically, 0.1 g of the adsorbents were mixed with 20 mL of PHF solutions containing different

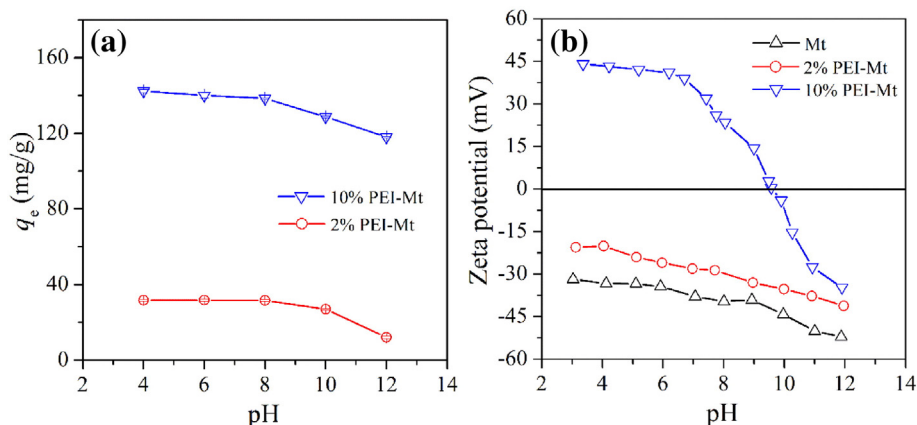


Fig. 1. Effects of pH on the adsorption capacities of 2%PEI-Mt and 10%PEI-Mt toward PHF(a). Zeta potential of Mt, 2%PEI-Mt, and 10%PEI-Mt as a function of solution pH(b).

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