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Alkynyl carbon materials as novel and efficient sorbents for the adsorption of mercury(II) from wastewater

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ABSTRACT

For the first time, a series of alkynyl carbon materials (ACMs) were prepared *via* the mechanochemical reaction of CaC_2 with six polyhalogenated precursors, namely CCl_4, C_2Cl_6, C_2Cl_4, C_6Cl_6, C_6Br_6, and $C_{14}H_4Br_{10}$ (ACM-1, ACM-2, ACM-3, ACM-4, ACM-5, and ACM-6, respectively) and used for the adsorptive removal of mercury from aqueous solutions. Based on preliminary investigations, the adsorption of mercury on ACM-5 was studied in depth. Specifically, the effect of pH on mercury adsorptivity, adsorption kinetics, thermodynamics, isotherms, and recyclability was studied. The adsorptivity of mercury on ACMs was found to be closely related to the hydrocarbon precursor, specific surface area of sorbent, and the alkynyl content. ACM-5 showed the best performance and is among the best raw carbonaceous sorbents reported so far, with a Langmuir saturated adsorption capacity of 191.9 mg g^{-1}. The promising mercury adsorption performance mainly arises from the strong Lewis soft acid–soft base interactions between the alkynyl groups and mercury ions. The adsorption isotherms could be satisfactorily correlated with the Langmuir equation. The results show that the ACMs can be used as efficient sorbents for the removal of mercury and may also be useful for the adsorption of other heavy metals.

Introduction

Mercury ion (Hg(II)) pollution in the aquatic ecosystem has caused widespread concern owing to the strong toxicity and bioaccumulation of mercury (Boening, 2000; Fitzgerald and Clarkson, 1991). Considering the serious hazards of mercury to the central nervous system, lungs, kidneys, and chromosomes (Clarkson, 1993; Renzoni et al., 1998), the World Health Organization (WHO) has specified the maximum allowable mercury ion concentration in drinking water as 1 μg/L. However, enormous amounts of mercury are still being emitted into the environment through atmospheric deposition as well as urban and industrial discharges (He et al., 2013; Li et al., 2009; Zhang and Wong, 2007). Therefore, its removal from aquatic systems has become an urgent problem.

For the complete removal of Hg(II) from aquatic ecosystems, numerous techniques such as chemical precipitation, ion exchange, coagulation, reduction, membrane filtration, and adsorption have been explored (Hashim et al., 2011; Plaza et al., 2011; Yu et al., 2008). Among these techniques, adsorption is deemed to be the most practical and economical approach (Fu and Wang, 2011). The identification of efficient sorbents is the key to designing a good adsorption process. In this context, carbon materials (CMs) have received

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considerable attention as sorbents owing to their widespread availability, exceptional water filtration capabilities, and high heavy metal adsorption capabilities (Mohmood et al., 2013; Nasser et al., 2016). In particular, activated carbons (ACs), which are cheap and environmentally benign sorbents, have been extensively used for Hg(II) adsorption (Anirudhan and Sreekumari, 2011; Bailey et al., 1999; Di Natale et al., 2006; Hadi et al., 2015; Kumar, 2006), although their adsorption capabilities are often poorer than task-specific sorbents. Further, the Hg(II) adsorptivity of ACs has been improved by modifying them with Lewis base atoms such as sulfur, oxygen, nitrogen, and halogens (Anbia and Dehghan, 2014; Bhatnagar et al., 2013; Li et al., 2005; Rivera-Utrilla et al., 2011; Yin et al., 2007). Among the modified AC materials, S-modified ACs exhibit superior Hg(II) adsorptivity, owing to the strong affinity between S and Hg(II) as a result of soft base–soft acid interactions (Anbia and Dehghan, 2014; Beck et al., 2000; Bhatnagar et al., 2013; De Canck et al., 2010; Gomez-Serrano et al., 1998). However, the sulfur grafting of ACs has low efficiency, which results in high wastage of energy and resources during the modification process, thereby limiting its commercial use (Bhatnagar et al., 2013; Hsi et al., 2001; Rivera-Utrilla et al., 2011).

Considering the difficulties in grafting soft bases onto CMs, we have developed a facile approach for introducing alkynyl groups onto CMs *via* a one-step carbon synthesis process, forming a new type of alkynyl carbon material (ACM). The ACMs are expected to exhibit strong Hg(II) adsorption arising from the strong interactions between the alkynyl group and Hg(II) (soft base–soft acid complexation), as manifested by the excellent catalysis of $HgCl_2$ in the hydrochlorination of acetylene (Hutchings, 1985). With this in mind, six ACMs were synthesized by reacting CaC_2 with a specific polyhalogenated hydrocarbon (PHHC) in a planetary ball mill at ambient temperature. The Hg(II) adsorptivity of different ACMs was compared, and the effect of pH, adsorption kinetics, adsorption isotherms, and recyclability were studied.

1. Experimental

1.1. Materials and reagents

Calcium carbide (75%–80%) was purchased from Alfa Aesar Chemical Company (China) and ground into 100 mesh particles before use. Elemental mercury (99.9999%) was kindly supplied by the Ministry of Environment Protection of China. Carbon tetrachloride (AR), hexachloroethane (AR), tetrachloroethylene (AR), nitric acid (65%–68%), and hydrochloric acid (36%–38%) were obtained from Beijing Chemical Works (China). Hexachlorobenzene (AR), hexabromobenzene (AR), decabromodiphenylethane (AR), and potassium hydroxide (GR) were procured from Aladdin Industrial Corporation (China). Ultrapure water produced with a CP-500S water purification system (CANPURE, China) was used for all the experiments, unless specifically mentioned otherwise.

A stock solution of Hg(II) (100 mg/L) was prepared by the nitrolysis of specific amounts of elemental mercury, followed by dilution with water. It was stored in darkness, and the working solutions were prepared immediately before use by diluting the stock solution.

1.2. Synthesis and characterization of ACMs

A planetary ball mill (QXQM-2, Tianchuang, China) was used for the mechanochemical synthesis of the ACMs. To a stainless-steel pot (250 mL) containing 250 g of stainless-steel balls of four different diameters (15, 12, 10, and 8 mm), CaC_2 and PHHC were added in a specific mass ratio and the pot was sealed air-tight. Ball milling was conducted at room temperature and at a specific rotation speed under vacuum. The resulting solid mixture was treated with dilute nitric acid and washed three times with pure water. The ACMs were then obtained by vacuum drying at 100°C for 5 hr. The yield of the ACMs and the carbon content were determined by elemental analysis (VarioELcube, Germany). The experimental conditions used, the ACM yields, and the results of elemental analysis are shown in Table 1.

1.3. Hg(II) adsorption by ACMs

All the adsorption experiments were conducted in 100 mL conical flasks at specific temperatures. To the conical flask, 25 mg of sorbent and 50 g of 50 mg/L Hg(II) solution were added and stirred magnetically at 200 r/min for 3 hr. The liquid samples were withdrawn using a syringe with a 0.22 μm membrane filtration head, and the Hg(II) concentrations were measured by a spectrophotometric method using rhodamine-6G in a LabTech UV–vis spectrophotometer at 575 nm (Ramakrishna et al., 1976). The Hg(II) standard curve is shown in Appendix A Fig. S1. The equilibrium adsorbed capacity of the sorbents was calculated using the following equation:

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

where, q_e (mg/g) is the equilibrium adsorption capacity of the sorbent; C_0 (mg/L) and C_e (mg/L) are the Hg(II) concentrations at initial and equilibrium states, respectively; V (L) is the solution volume, and W (g) is the mass of sorbent. All the samples were analyzed thrice and the average values are reported. As shown in Appendix A Tables S2–S6, the average absolute relative deviation (AARD) and the root mean square deviation (RMSD) values of the experimental data are within 3.3% and 3.5%, respectively. Based on the initial experimental results, ACM-5 was chosen as the sorbent for the subsequent experiments.

1.4. Effect of solution pH

The effect of solution pH on Hg(II) adsorption was studied for the ACM-5 sorbent in the pH range of 1.0–8.0. The pH values were adjusted using 0.1 mol/L HNO_3 and 0.1 mol/L NaOH solutions. A pH meter from Rex Electric Chemical (ID-2) was used for the pH measurements. The pH meter was calibrated using standard buffer solutions with pH values of 4.00, 6.86 and 9.18.

1.5. Adsorption kinetics and activation energy

The kinetics of Hg(II) adsorption on ACM-5 was studied at 20, 40, and 60°C, at a pH of 5.8. Pseudo-first and second-order

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