Polyethylenimine modified biochar adsorbent for hexavalent chromium removal from the aqueous solution

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HIGHLIGHTS

- A PEI modified biochar with abundant amino groups was prepared for Cr removal.
- The adsorption performance of biochar for Cr removal has been significantly improved.
- The maximum adsorption capacity of PEI-alkali-biochar for Cr is about 435.7 mg/g.
- Adsorption–desorption studies reveal the modified biochar has a good stability.
- PEI modified biochar has a good potential as a suitable material for Cr(VI) removal.

ARTICLE INFO

ABSTRACT

A chemical modified biochar with abundant amino groups for heavy metal removal was prepared using polyethylenimine (PEI) as a modification reagent, and used as an adsorbent for the removal of Cr(VI) from aqueous solution. The biochars before and after modification were characterized by Fourier transformed infrared spectroscopy, X-ray photoelectron spectroscopy etc. The adsorption of Cr(VI) by the modified biochar was obeyed pseudo-second-order kinetic model and Langmuir adsorption isotherm model. Its maximum adsorption capacity was 435.7 mg/g, which was much higher than that of pristine biochar (23.09 mg/g). Results also indicated that the removal of Cr(VI) by the PEI modified biochar depended on solution pH, and a low pH value was favorable for the Cr(VI) removal. The results herein revealed that the PEI modified biochar had a good potential as a suitable material for sorption and detoxification of Cr(VI) from aqueous solution.

1. Introduction

Water pollution by heavy metals has become a serious issue in the present scenario, affecting all living creatures, household, recreation, fishing, transportation, and other commercial activities (Ali, 2012; Fu and Wang, 2011), due to their high toxicity and carcinogenicity. Most chromium exists in the environment as Cr(VI) and Cr(III). Compared with Cr(III), Cr(VI) is a highly toxic heavy metal, which is able to cause carcinogenesis, mutation to humans and animals, thus has been designated as one of the top-priority toxic pollutants by the U.S. EPA. The toxicity limits (LD_{50}) in the rat are 3250 mg Cr/kg for Cr(III) and 57 mg Cr/kg for Cr(VI), respectively (Katz and Salem, 1993). Besides, Cr(III) is susceptible to precipitation in soil strata while Cr(VI) is mobile and always leached out by ground water. Cr(VI) is widely used in industries like leather tanning, furnace cooling, plating, rinse waters, wood preservation,

etc. Thus, removal of Cr(VI) is more prior from wastewater or soil to avoid Cr pollution.

Several methods for Cr(VI) removal from wastewater have been investigated, including chemical precipitation, ultrafiltration, ion exchange, adsorption, reverse osmosis, and electrodialysis etc. Compared to other methods, adsorption is one of the most popular and cost-efficient method, and can be used for recovering Cr(VI) at a low content (Volesky, 2007). Various adsorbents, including bark, clay, seaweed, saltbush, activated carbon, resin, and mesoporous silica, have been used to remove heavy metals (Fu and Wang, 2011; Sawalha et al., 2006). Among them, carbonaceous materials, such as granular activated carbon, fullerene and graphene, because of the high stability, large surface area and pore volume, and broad pore size distribution, have been regarded as the promising absorbents, and widely used in pollutants removal (Chandra et al., 2010; Zhao et al., 2011a,b). Biochar, as a by-product of fast thermochemical decomposition of lignocellulosic biomass (Liu et al., 2011; Manya, 2012; Muradov et al., 2010), plays a great potential in the remediation, revegetation and restoration of contaminated

soils (Beesley et al., 2011; Freddo et al., 2012). Due to the high specific area and various of functional groups (e.g., amino, carboxyl, and hydroxyl groups) (Liu et al., 2011), biochar also can be used as a low cost adsorbent for organic pollutants and heavy metal removal from water (Mohan et al., 2007). However, the adsorption capacities of the raw biochar for heavy metals are not very high since the contents of the surface functional groups are still insufficient for heavy metal removal. Therefore, surface modification of carbon materials with more functional groups to enhance their capacity and selectivity for heavy metal removal have been attracted more and more attentions in recent years (Rivera-Utrilla et al., 2011).

Several methods, such as acid and alkali modification, oxidation, and chemical graft, have been used to improve their functional group contents and thus enhance their adsorption performance (Li et al., 2010; Liu et al., 2012). Polyethylenimine (PEI), containing large number of primary and secondary amine groups on the line type macromolecular chains, exhibits strong adsorption ability for heavy metals. Furthermore, it is charged over a wide pH range. Therefore, PEI can bind with heavy metal ions through complexation or electrostatic interaction (Pang et al., 2011a,b). It can provide plenty of functional groups for heavy metals (such as Cr) adsorption when PEI is modified to the adsorbent surface, thus enhance their sorption capability.

Thus, in this study, the biochar obtained from a pilot-scale industry was modified by PEI, and used for the Cr(VI) removal. The effects of pH, contact time, and initial concentration of Cr(VI) on the removal of Cr(VI) from the aqueous solution by the modified biochar were investigated. The mechanism between Cr(VI) and the functional groups on the surface of the PEI modified biochar was discussed. This work will provided an alternately low cost adsorbent for detoxification of Cr(VI).

2. Methods

2.1. Chemicals

PEI (molecular weight of 25,000) used in this study was purchased from Sigma–Aldrich Company. The pristine biochar, supplied by Anhui Yineng Bioenergy Co. Ltd., Hefei, China, was derived from rice-husk by fast pyrolysis at 723–773 K. Other reagents used in this work were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Shanghai, China.

2.2. Surface modification of biochar by PEI

Before modification, the biochar was treated by acid or alkali. The acid or alkali solution (200 mL of 70% HNO_3 or 3 mol/L KOH) was added to 20 g of pristine biochar in a flask, and agitated at 160 rpm for 1 h at room temperature to remove the impurities of the biochar. After that, the biochar was rinsed with deionized water until the pH of the elution was around 7.0. The wet biochar was dried at 353 K for 12 h and then stored in desiccator before use, which was defined as acid–biochar or alkali–biochar, respectively.

The modification of biochar by PEI was performed according to previous study (Park et al., 2012; Sun et al., 2011). The acid or alkali treated biochar was added to 100 mL 10% (w/v) PEI/methanol solution, and agitated at 160 rpm and 303 K for 24 h. Then the biochar was immediately transferred to a 200 mL 1% (w/v) glutaraldehyde solution for cross-linking. The solution was agitated at 160 rpm and 303 K for 30 min. After that, the modified biochar was washed with deionized water and defined as PEI–acid–biochar or PEI–alkali–biochar.

2.3. Characterization of the biochar

The functional groups of biochars before and after modification were measured by a Fourier transform infrared (FTIR) spectroscopy (Nicolet Magana-IR 750 spectrometer) in the wavenumber range of 400–4000 cm^{-1}. The surface states of the biochar were characterized by X-ray photoelectron spectroscopy (XPS) by using VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum chambers. The zeta potentials of the biochar at various pH values were measured using a ZETASIZER 3000 HSA system.

2.4. Adsorption experiments

The adsorption performance of the modified biochar was evaluated in the batch adsorption of Cr(VI) at room temperature. Generally, 1 g/L of biochar was mixed with Cr(VI) solution in a flask. Then the mixture was shaken in a thermostatic shaker at 160 rpm for 24 h. Afterwards, the suspension was filtered with a syringe filter of 0.22 μm, and the concentrations of Cr(VI) in the filtrate were determined. The concentration of Cr(VI) in the filtrate was measured colorimetrically using a UV–Vis spectrophotometer (UV-754, Shanghai, China) at a maximum wavelength of 540 nm after complexation with 1,5-diphenylcarbazide (Chen et al., 2011). The solution pH was adjusted by adding small quantities of concentrated H_2SO_4 or NaOH solution. The equilibrium adsorption isotherm experiment was conducted by varying the initial Cr(VI) concentrations were in the range of 10–1000 mg/L.

In order to assess the practical utility of the adsorbent, adsorption–desorption experiments were conducted. Modified biochar with adsorbed Cr(VI) was treated by 1 M NaOH for 1 h. Afterwards, the desorbed biochar was rinsed, and dosed to Cr(VI) solution (100 mg/L, 100 mL) in a flask again and shaken at 160 rpm in a thermostatic shaker at 303 K for 24 h. The adsorption–desorption process was repeated six cycles.

The removal efficiency of Cr(V) was measured using following relation

$$\text{Removal efficiency } (\%) = \left(\frac{C_0 - C_e}{C_0}\right) * 100 \quad (1)$$

where C_0 and C_e (mg/L) are the Cr(VI) concentrations at initial and at equilibrium.

3. Results and discussion

3.1. Characterization of the biochars before and after modification

The changes in the functional groups of biochars before and after modification were analyzed by FTIR spectroscopy. The IR spectra of PEI, the pristine and PEI modified biochars are given in Fig. S1. The functional groups of the modified biochar are much more abundant than those of pristine biochar. The peaks of PEI spectrum at 2934, 2810 and 1559 cm^{-1} were attributed to –CH stretching vibration in –CH and –CH_2 and N–H stretching vibration in amide bond, respectively. The predominant peak at 3436 cm^{-1} in the spectrum of pristine biochar was assigned to –OH stretching vibration. No obvious peak between 3000 cm^{-1} and 2000 cm^{-1} could be found in the spectrum of pristine biochar. Compared with the spectrum of pristine biochar, more peaks occurred in the spectra of PEI modified biochar. The peaks of O–H stretching vibration and N–H stretching vibration were shifted to 3398 cm^{-1} and enhanced significantly. The appearance of new peaks at 2930 and 2849 cm^{-1} in the spectrum were attributed to C–H stretching vibration in –CH and –CH_2 The new strong peak at 1653 cm^{-1} in the spectrum of PEI–alkali–biochar was attributed to the stretching of C=N or C=O bonds. The peaks at 1439 and 1379 cm^{-1} were