Chemosphere 164 (2016) 32–40

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Adsorption of arsenic, phosphorus and chromium by bismuth impregnated biochar: Adsorption mechanism and depleted adsorbent utilization

Ningyuan Zhu [a, b], Tingmei Yan [a, *], Jun Qiao [a], Honglei Cao [a, b]

[a] *Institute of Soil Science, Chinese Academy of Sciences, No. 71 East Beijing Road, Nanjing 210008, China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*

HIGHLIGHTS

- Bismuth activated carbons derived from wheat straw were fabricated.
- Bismuth particles grown within biochar matrix.
- BiBC500 showed high adsorption capacity to arsenic, phosphorus and chromium.
- Adsorption mechanisms of arsenic, phosphorous and chromium were illustrated.
- Phosphate depleted material could photodegrade dye pollutant.

ARTICLE INFO

Article history:
Received 20 April 2016
Received in revised form
25 July 2016
Accepted 7 August 2016

Handling Editor: X. Cao

Keywords:
Bismuth
Activated carbon
Adsorption mechanism
Depleted adsorbents

ABSTRACT

Bismuth impregnated biochar were synthesized to deal with wastewater pollution. Nitrogen adsorption-desorption isotherms, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to determine the characteristics of adsorbents and explore the main adsorption mechanism. Results showed that bismuth particle was carried successfully within the biochar matrix, making contributions to creating micropore and boost specific surface area. The loaded bismuth, served as the adsorption site, rather than the specific surface area played an important role in arsenic and phosphorus adsorption. Batch adsorption experiments demonstrated a fit Langmuir model for arsenic (As) and phosphorus (P) and a suitable Freundlich model for chromium (Cr). Thermodynamic parameters depicted the endothermic nature and the spontaneous process for phosphate and arsenic adsorption. Besides, this contaminant-loaded carbon adsorbent was further applied for the removal of methylene blue from aqueous solution.

1. Introduction

The continuous growth of population, increasing reinforcement of agricultural activities and rapid development of urbanization and industrialization worsen water quality of our water resources which is the most essential component for life (Ali, 2012). The excessive input of phosphorus in surface water worsened eutrophication and algae blooms as well as deteriorated the quality of the groundwater severely. Heavy metals, especially the chromium and arsenic, are more problematic and threatening to ecological environment and human beings because of their high toxicity, non-biodegradation and accumulation through food chain. Thus, the World Health Organization recommended that the maximum permissible limit for arsenic should be 10 $\mu g\ L^{-1}$ while the maximum limit for chromium be 0.05 mg L^{-1} in drinking water (Liu et al., 2008; Tang et al., 2014; Wang et al., 2010).

Therefore, it is very imperative to deal with contaminated wastewater prior to its discharge into soil and water environment. Many researchers have explored various methods such as chemical precipitation, gravity separation, solvent extraction, reverse osmosis, ion-exchange, electrocoagulation and electrodialysis, flotation and adsorption for removing phosphate or heavy mental irons from sewage system (Hua et al., 2012). For instance, Afkhami et al. synthesized DNPH (nano-alumina modified with 2,4-

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* Corresponding author.
E-mail address: tmyan@issas.ac.cn (T. Yan).

http://dx.doi.org/10.1016/j.chemosphere.2016.08.036
0045-6535/

dinitrophenylhydrazine) with a satisfying adsorption capacity toward Pb (II), Cr (III) and Cd (II) ions in a multiple-metal solution, indicating that DNPH is a promising adsorbent for heavy mental treatment (Afkhami et al., 2010). Nevertheless, few researches developed effective, efficient, economical and eco-friendly materials or methods for reduction of arsenic, phosphate and chromium pollutant which are more difficult to be removed because of their anion form (Alemayehu et al., 2011; Onnby et al., 2014). In addition, the removal efficiency of As (III) is much lower than As (V) for adsorption process was unable to act on the uncharged form of As (III) especially at environmentally relevant pH (Sun et al., 2013). But, arsenite is more toxic, soluble, and mobile than arsenate.

Fortunately, metal salt, metal oxides and hydrous metal oxides such as granular ferric hydroxide (Banerjee et al., 2008), TiO_2 (Liu et al., 2008), akaganeite (Lazaridis et al., 2005), and $Na_2SO_3/FeSO_4$ (Pan et al., 2014) have been well explored for arsenic, phosphorus or chromium treatment. Adsorption is recognized as one of the most available option because of its low cost and high efficiency. However, handling and disposal of the waste sludge is still a cumbersome problem limiting their actual industrial application. Furthermore, there is still lack of economical way to transform more agricultural residues like straw resources to valuable and green by-product whether in production sites or in factory for their high-fibre content and low-protein quality. After harvest season, farmers burn crop stalk in great quantities, causing serious environmental problems such as haze which may pose a serious threat to public health.

Biochar, originated from biomass pyrolysis under oxygen-limited environment can be used as soil amendment to increase soil fertility, double or triple plant yields, fix carbon and cut greenhouse gas emissions in a vast scale. Besides, the chemical modified biochar also adsorb contaminants either by electrostatically attractive forces or by ligand exchange mechanism without the adverse waste sludge production (Loganathan et al., 2013; Marris, 2006). Thus, application of the adsorption methods with biochar based adsorbent is a promising way for arsenic, phosphate and chromium treatment. Herein, to enhance the adsorption ability of biochar and probe into the rational straw utilization of straw resources, bismuth oxide and wheat straw were explored to prepare a cost-effective but high efficiency material for wastewater treatment for the first time. The specific objectives of this work were to: (1) prepare and characterize Bi_2O_3 impregnated biochar composites, (2) test its sorption capacities for As (III), P and Cr (VI), and (3) investigate the possible mechanisms involved in the As (III), P and Cr (VI) adsorption.

2. Materials and methods

2.1. Preparation of adsorbents

Bismuth oxide solution (Bi-solution) was prepared by adding 10 mmol Bi_2O_3 to 20 ml hydrochloric acid (0.12 mol) and then diluted to 100 ml with distilled water. A stock solution of 3000 mg L^{-1} KH_2PO_4, 200 mg L^{-1} sodium arsenite and 200 mg L^{-1} potassium dichromate were prepared in a volumetric flask and diluted to the required concentrations (60–1800 mg L^{-1}). Bi_2O_3, KH_2PO_4, $NaAsO_2$, $K_2Cr_2O_7$ and other reagents used in this work were all at analytical grade.

Wheat straw (WS) was obtained from Wuxi city, Jiangsu province, China. It was milled and sized into particle with diameters between 0.60 and 0.80 mm. Bismuth oxide activated carbon (BiBC) and control biochar (CBC) were produced as follow: 10 g WS was mixed with 100 ml Bi-solution and hydrochloric acid (0.12 mol) respectively, stirred vigorously at 80 °C for 3 h, exposed to ultrasonic treatment to get the targeted particles as small as possible and then dried at 105 °C. The biochar precursors were then heated to setting temperature (400, 500 and 600 °C) and finally maintained for 60 min in a furnace with the heating rate of 10 °C min^{-1} under nitrogen flow. Finally, the biochar materials were washed with 0.01 M $NaHCO_3$ solution and distilled water for three times. Activated carbons were labelled as BiBC400, BiBC500 and BiBC600 while the control labelled as CBC400, CBC500 and CBC600.

2.2. Characterization of adsorbents

Porosity and surface characteristics were measured by N_2 (0.162 nm^2) adsorption using a NOVA-2000E (Quantachrome, USA) surface area analyzer. Brunauer-Emmertt-Teller (BET) surface area and average pore diameter of the BiBCs and CBCs were determined by multipoint BET analysis of adsorption data points with relative pressures of 0.05–0.3. Surface functional groups were detected by Fourier transform infrared spectroscopy (FTIR) (Nicolet IS10, Thermo Electron Co, USA) at a spectral range of 4000 cm^{-1} to 400 cm^{-1} with a resolution of 8 cm^{-1}. X-ray diffraction (XRD) patterns of the synthesized biochars were measured by a Siemens D-501 diffractometer with Ni filter and graphite monochromator. Furthermore, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to further investigate the adsorption mechanism and determine its surficial morphology characteristics.

2.3. Adsorption experiments

Adsorption experiments were used to reveal the adsorption potential of different biochar samples. Effect of pH on phosphorus, arsenic and chromium adsorption was investigated in a conical flask containing 0.1 g adsorbent and 50 ml of 50 mg L^{-1} adsorbate (phosphate, sodium arsenite and potassium dichromate). The pH level was adjusted at the range of 2–10 with hydrochloric acid and sodium hydroxide. To evaluate the stability of the BiBC during those three adsorbates adsorption process, the desorbed bismuth concentration from aqueous solution was also analyzed.

Adsorption dosage experiments were executed by adding 0.01, 0.05, 0.1, 0.25, 0.5, and 1 g sorbent in a conical flask with 50 mL solution under the optimum pH value at initial 50 mg L^{-1} concentration of phosphate, sodium arsenite or potassium dichromate. The mixture was agitated at 150 rpm in an orbital shaker (SHA-C) at 25 °C for 2 h and then placed for 24 h to reach the equilibrium condition.

Adsorption kinetics experiments were conducted as follows: 0.1 g bismuth oxide activated carbon was added in 50 mL phosphate, arsenic or chromium solution with initial concentration of 300, 10, and 20 mg L^{-1} under the optimum pH level, respectively. The sorption amount of phosphorus, arsenic and chromium were investigated at different time intervals (0, 0.5, 1, 2, 5, 10, 30, 60, and 120 min). The mixture was agitated at 200 rpm in an orbital shaker (SHA-C) at 25 °C for 24 h to reach the equilibrium condition.

Adsorption isotherm experiments were conducted as follows: 0.1 g adsorbent was mixed with 50 ml adsorbate solution with concentration ranging from 60 to 1800 mg L^{-1} for phosphate and concentration ranging from 5 to 200 mg L^{-1} for potassium dichromate or sodium arsenite under the optimum pH value in the centrifuge tube respectively. All the vessels above were shaken at 150 rpm in the oscillator for 2 h and then placed in the water bath under constant temperature (15, 25 and 45 °C) for 24 h to reach equilibrium.

Besides, adsorbate saturated materials were prepared by mixing 4 g adsorbent with 2 L 500 mg L^{-1} phosphate or 100 mg L^{-1} sodium arsenite/potassium dichromate solution under the optimum pH value and then named as BiPBC500, BiAsBC500 and BiCrBC500