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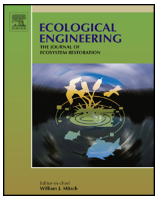

Short communication

Adsorption of Cd by peanut husks and peanut husk biochar from aqueous solutions

Qiming Cheng[a], Qing Huang[a,*], Sardar Khan[a,b,**], Yingjie Liu[a], Zhenni Liao[a], Gang Li[a], Yong Sik Ok[c]

[a] Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
[b] Department of Environmental Science, University of Peshawar, Peshawar 25120, Pakistan
[c] Korea Biochar Research Center, Kangwon National University, Chuncheon 200-701, South Korea

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ABSTRACT

This study was conducted to investigate the best absorbent for cadmium (Cd) present in aqueous solutions. Among the selected absorbents ($n = 22$), peanut husk biochar (PHB) was the best absorbent for Cd and its adsorption reached to equilibrium within 12 h. In this study, the optimum conditions observed for Cd adsorption were pH 5.0, an initial Cd concentration of 200 mg L^{-1}, a PHB dosage of 40 g L^{-1}, and room temperature. The Cd removal efficiency of the tested biochar reached to 99.9% at these optimum conditions. EDX analysis confirmed that Cd was adsorbed onto PHB more than onto PHs. It is concluded that PHB can be used as a good remediating material for removal of Cd from contaminated environmental matrixes.

1. Introduction

Cadmium (Cd) is a non-essential heavy metal and highly toxic to all living organisms including plants, animals, and human beings. The enrichment of Cd in the environmental matrixes occurs through natural processes and anthropogenic activities (Khan et al., 2010; Liu et al., 2013; Luo et al., 2011). Cd enters into humans and other living organisms through contaminated water and the food chain and can cause irreversible damage.

Traditional methods used for removal of Cd from contaminated water have several disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge or other waste products that require disposal and further treatment (Sud et al., 2008; Bilal et al., 2013; Won et al., 2014; Moubarik and Grimi, 2015). Efforts are being made to develop efficient and innovative methods of wastewater treatment. While developing new methods, economic feasibility and environmentally friendly concepts are of great importance.

Biomass-based high-performance adsorbent techniques are being developed for the treatment of wastewater containing Cd and have become a hot research topic due to their easy availability and presence in wide economic range of low cost (Sud et al., 2008; Coelho et al., 2014; Sun et al., 2014; Weng et al., 2014; Ammari, 2014; Šćiban et al., 2011; Vafakhah et al., 2014). These techniques are quick, easy to use, and have high adsorption capacity for toxic heavy metals, especially when these toxins are present at low concentrations in wastewater (Bilal et al., 2013).

However new, economical, locally available, environmentally friendly and highly effective Cd sorbents are still needed. Comparatively, peanut husks (PHs) are a very cheap material produced in agriculture and oil extracting industries. China produces peanut husks at the rate of 3.14 million tons per year with a constant annual increase (Zhang et al., 2008; Wang et al., 2010a). PHs and their derived biochar (PHB) can be used as biomass-based adsorption materials for the treatment of wastewater containing heavy metals. In recent years, different researchers have applied different biomass and biochar materials for removal of toxic metals present in environmental matrixes (Sud et al., 2008; Purkayastha et al., 2014; Khan et al., 2015; Waqas et al., 2015). However, long term application of these adsorbents for treatment of wastewater and their mechanisms needs further investigations.

In this study a total of 22 kinds of materials were tested to find the best candidate for Cd removal from aqueous media. The

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* Corresponding author. Tel.: +86 92 6190559; fax: +86 592 6190977.
** Corresponding author at: Department of Environmental Science, University of Peshawar, Peshawar 25120, Pakistan. Tel.: +92 91 9216742; fax: +92 91 9218401.
E-mail addresses: qhuang@iue.ac.cn, qh425806@163.com (Q. Huang), khan2008@yahoo.com (S. Khan).

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performance of PH and PHB was compared with other materials. The effects of various operating parameters such as initial pH, Cd concentrations, different sorbent dosages, and contact time were monitored and the optimal experimental conditions were determined. Characterization of PHs and PHB were studied using different techniques such as BET, FT-IR, SEM, and CNS and CHNS—O—Cl; the kinetic data were used to understand the adsorption mechanism.

2. Methods and materials

2.1. Biomasses and preparation of biochars

Pyrolyzed biochars were prepared from several feedstocks ($n = 22$) including mushroom waste, Wolffia, lemna, rice materials (straw, stubble, husk, and root), water hyacinth materials (stems, leaves, and roots), legume straw, oil-tea camellia seed cake, and peanut husks were collected from Xiamen, China. Further detail is given in Supporting Information (SI).

2.2. Experimental designs

Initially, screening experiments were conducted to test different materials for Cd removal. The detailed information is given in SI. Adsorption experiments for PHs and PHB with different pH levels (from 1 to 6 units) were conducted for the removal of Cd from the aqueous solution. Similarly, experiments for different adsorption times (from 10 to 5760 min) at room temperature were also conducted at room temperature. For more information, see SI. In order to find the adsorption equilibrium, PHs and PHB (0.2 g each) were added into 50 mL of $Cd(NO_3)_2$ solution (pH 5.0) with different initial Cd concentrations (from 10 to 800 mg L^{-1} each in triplicates). The flasks were shaken at room temperature at 200 rpm for 24 h. In order to determine the optimum biochar dosage, different dosages (from 0.1 to 5.0 g each in triplicates) were added into 50 mL of $Cd(NO_3)_2$ solution (pH 5.0) with an initial Cd concentration of 200 mg L^{-1}. The flasks were shaken at 200 rpm for 24 h at room temperature.

2.3. Cd analyses and characterization PHs and PHB

The concentrations of Cd were measured using inductively coupled plasma-mass spectrometer (ICP-MS: Agilent Technologies, 7500 CX, USA). The initial pH and EC of PHs and PHB were determined at a ratio of 1:10 w/v in DDW. The specific surface areas and porous textures of PHs and PHB were measured by nitrogen adsorption at 77 K using a surface area and porosimetry system (ASAP 2020M+C, USA). The surface characteristics of PHs and PHB were analyzed using field emission-scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan).

Elemental analysis was performed using a CNS and CHNS-O-Cl analyzer (Vario MAX, Germany). The elemental analyses of PHs and PHB before and after adsorption of Cd were carried out by an energy-dispersive X-ray spectrometry (EDX, Genesis XM2, USA) detector with an SEM (Hitachi S-4800). Similarly, samples were screened for functional groups using Fourier Transform Infrared Spectroscopy (FTIR) (Nicolet iS 10 model, Thermo Scientific, USA) following the KBr tablet method, which was equipped with a TGS/PE detector and silicon beam splitter with 1 cm^{-1} resolution. Infrared spectra were obtained in the range of 400–4000 cm^{-1}. For data analyses such as the efficiency (E) of PH and PHB materials for Cd removal and two sorption isotherms (Langmuir and Freundlich models) were used, see the SI.

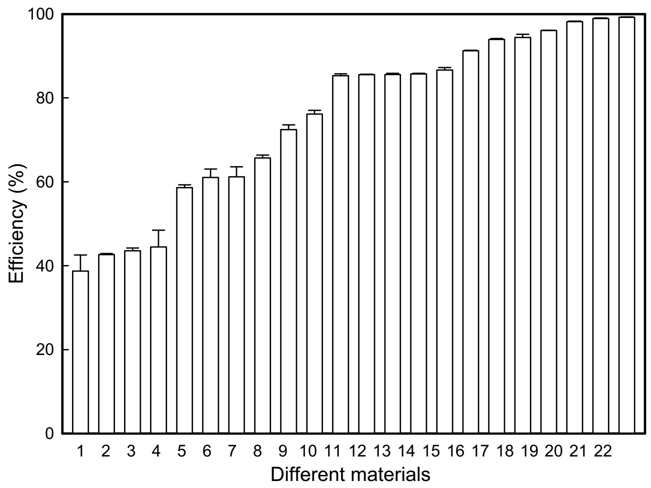

Fig. 1. Effects (%) of different adsorbents on removal of Cd. The number 1–22 represent materials used i.e, (1) powder of mushroom waste, (2) powder of rice straw, (3) powder of oil-tea camellia seed cake waster, (4) Imported activated carbon (AC-1), (5) powder of Lavenda oil extraction residue, (6) powder of rice stubble, (7) powder of rice husk, (8) powder of rice root, (9) powder of PHs, (10) powder of water hyacinth stem, (11) powder of Wolffia, (12) powder of Lemna, (13) powder of water hyacinth leave, (14) powder of water hyacinth root, (15) powder of soybean straw, (16) mushroom waste biochar, (17) water hyacinth root biochar, (18) soybean straw biochar, (19) rice straw biochar, (20) oil-tea camellia seed cake biochar, (21) Domestic activated carbon (AC-2), (22) PHB.

3. Results and discussion

3.1. Characterization and best sorbent selection

The major characteristics of PHs and PHB materials are given in Table S1, while Fig. 1 summarizes the efficiencies of different materials for sorption of Cd from aqueous solution. Among the biomasses, the lowest efficiency (38.7%) was observed for mushroom waste, while the highest (86.6%) was observed for soybean straw. PHB showed significantly ($P = 0.001$) higher efficiency (99.2%) for the sorption of Cd as compared to the other kinds of biochars tested in this research.

Furthermore, results indicated that the Cd sorption capacity of the PHB was higher than the PHs (Fig. 1), indicating that there is need for biochar preparation from PHs to use as an adsorbent for Cd from aqueous solution. The results obtained in this study are consistent with those reported in earlier papers (Table S2), but different research groups had been tested the biochar at different pH levels.

3.2. Effect of pH on Cd adsorption

In this study, the pH ranged from 1-2 units was shown no significant effect on the sorption of Cd by PHB, but the higher pH 3-4 units has shown rapid sorption of Cd (Fig. 2A). However, further increases in pH (5–8) did not affect the sorption of Cd. This equilibrium pH value changed according to the biochar material tested and ranged from 4 to 5, as reported in previous studies (Sun et al., 2014). It means that Cd sorption reaction is adaptable to a wide range of pH and is dependent on the biochar characteristics determined by the temperature range of pyrolysis and feedstock materials. PH contains many compounds such as lignin, cellulose, pentosan, organic acids, and tannins that can bind metals (Ding et al., 2012). PHB contains different active functional groups (—COOH and —OH) on its surface (Ahmad et al., 2014; Khan et al., 2015) (Table S3 and Fig. S1). According to earlier studies, at low pH high concentration of H^+ is present in the reaction system which protonates the functional groups on the biochar surface (Elaigwu et al., 2014)