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Research article

Animal manure-derived biochars produced via fast pyrolysis for the removal of divalent copper from aqueous media

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A B S T R A C T

Here, we report a pyrolyzed guinea fowl manure-derived biochar (GFM-BC) and cattle manure-derived biochar (CTM-BC) and their use as adsorbent for the removal of divalent copper from aqueous media was evaluated. The BCs physical and chemical properties were characterized by Scanning electron microscopy (SEM), Elemental dispersive x-ray analysis (EDX), Fourier transform infrared microscopy (FTIR) and thermo gravimetric analysis (TGA). The results presented that the BCs obtained higher content were quite effective for Cu (II) removal with maximum capacities of 43.60 and 44.50 mg g^{-1} for GFM-BC and CTM-BC, respectively. From simulation of experimental data with different adsorption isotherms and kinetics models it was found that the adsorption of both BCs was adequately fitted by Freundlich adsorption model and pseudo-second order kinetic model, respectively. Thermodynamic parameters suggested that the adsorption of Cu (II) onto both BCs was feasible, spontaneous and exothermic under evaluated parameters. Thus, the biomass used in this study proved to be effective adsorbents for the removal of Cu (II) from aqueous media.

1. Introduction

Aquatic pollution by trace elements and emerging pollutants originating from textile industries, pharmaceuticals and agrochemicals is predominant in mostly developing countries such as Africa and Asia. Evolving pollutants are a physically varied potentially harmful substances that were earlier unidentified and undetected, and thus unmonitored (Petrie et al., 2015; Sorensen et al., 2015). Mostly, in under developing countries trace elements and aromatic pollutants generally are not satisfactorily delimited. Due to violation of legislation framework and where such legislations obeyed they are either disorganized and/or poorly obligatory. The occurrence of these trace elements in aqueous media, even at a very low level, is highly noticeable ad unwanted (Pourret and Bollinger, 2017). Aromatic pollutants are toxic and have long-standing transport ability and gathered in beings (Pesticide Action Network, 2010). The elimination of such pollutants is challenging in developing countries because progressive water purification methods are cost effective, so not common in developing countries. The bio-sorption for elimination of trace elements is outstanding because huge amounts of biomaterials are easily accessible and lack of advanced water purification techniques for the removal of water contaminants.

Nowadays, different conventional methods such as redox reactions, filtration, chemical precipitation, filtration and ion exchange have been investigated for efficient removal of trace elements (Saleh and Gupta, 2012; Gupta and Nayak, 2012; Ahmed et al., 2017; Chen et al., 2017; Liu et al., 2017). However, all these methods have the limitations of being costly, less sensitive and complex when concentration falls in the range from 1 mg L^{-1} to

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100 mg L^{-1} (Liang et al., 2010). Adsorption is considered to be one of the best methods due to its simplicity, easy operation, feasibility and wide suitability for trace elements removal from aqueous media.

The adsorption technique is also functional for the removal of different types of pollutants such as biological, aromatic and inorganic pollutants. Furthermore, adsorption can also be used for source reduction and retrieval for potable, industrial, and other water purposes. Therefore, researchers have always been in effort to find new adsorbents with better efficiency. An efficient adsorbent is expected to give high removal efficiency, rapid adsorption rate and high selectivity (Gadd, 2009). Different kinds of natural and synthetic adsorbents including activated carbon, metal organic frame works (MOFs) and zeolites etc have been used as an adsorbent for contaminated aqueous media purification. (Gupta et al., 2009; Ali, 2010; Ngah et al., 2011).

Conventional biochar (BC) pyrolyzed at less temperature with high content of carbon entails less investment and are significant of interest in enhancing the adsorption capacity of trace elements from aqueous media. (Mohan et al., 2014). Different types of biomaterials including wood, animal manure, agriculture and sewage sludge have been tested for BC production. Animal manures being rich in organic contents, could be an important candidates for BCs production because of large quantities emanating from livestock and farmyards. Converting manure to BC via pyrolysis can be used for long-term carbon storage. It can also help reduce greenhouse gas emissions from agriculture. In some favorable situations, the development of BC is one of atmospheric carbon sequestration tool, but certainly not a panacea. Recently BCs has also been used for remediation and stabilization of contaminants from aqueous media. A study by Sun et al. (2011) demonstrated that hydrothermal biochar derived from poultry litter and swine solids could adsorb a wide spectrum of polar and non-polar organic contaminants. Additionally, Kumar et al. (2011) demonstrated uranium adsorption using hydrothermally treated switchgrass biochar.

This has been attributed to an inherent large surface areas, uniform pores and large volumes, permitting physio-sorption and hydrophobic interaction with pollutants efficiently. All these characteristics make the BCs an efficient adsorbent for trace elements removal from aqueous medium. Biomass production dedicated to the production of biochar raises competition problems with other productions. BC, even from by-products may compete with other uses livestock production, even with the organic matter and humus in the soil. Although activated carbon is ideal for removing contaminants from waste water but it is expensive. However, there is still unknown points regarding remaining contaminates in product. The role of BC in nutrient contribution, water holding capacity and even liming action is limited. BC is powdery, low density, soil incorporation in large quantities and burial seem difficult from a technical point of view.

The purpose of this study, was to observe the (1) removal efficiency of Cu (II) from aqueous media by using the guinea fowl manure- and cattle manure-derived BC, (2) discuss the effect of BCs feed stock materials on the adsorption behavior of Cu (II), (3) to characterize the BCs to associate adsorption characteristics by influential factors (pH, contact time, concentration and temperature), (4) to obtain the distribution coefficient for the adsorption of Cu (II) and (5) to simulate the adsorption data with adsorption kinetics and isotherms. Since the aqueous medium (water) may contain variety of trace elements, their simultaneous removal from aqueous medium is highly advantageous.

2. Methods and materials

2.1. Materials and biochar's production

Raw guinea fowl manure and cattle manure were obtained from the university farmhouse, Peshawar, Pakistan. Both raw manures were separately dried in oven at 70 °C and pyrolyzed at 500 °C shown in Scheme S1†. Initially the furnace temperature was set at 250 °C for 2 h with a heating rate of 2 °C min^{-1} under continuous flow of argon, then the temperature was raised to 500 °C for 3 h with a heating rate of 5 °C min^{-1}. Finally, the pyrolyzed BCs were cooled down to room temperature, crushed and ground to pass a 20–25 μm metal sieving tube and labelled as GFM-BC and CTM-BC, respectively. Further, both the BCs were treated with 70% of HNO_3 then agitated at 160 rpm min^{-1} for 1 h at 30 °C to remove the impurities. After that the BCs were rinsed with double-distilled water until the pH of the elution around 7. The wet BCs were dried at 40 °C for 12 h and stored in desiccator for further use.

2.2. Preparation of solution

All chemicals used in the present study were of analytical purity. Double-distilled water was used throughout the experiments for solution preparation. The stock solution was prepared by dissolving the 3.92 g $CuSO_4 \cdot 5H_2O$ in 1000 mL of distilled water. Working solutions were prepared by diluting the Cu (II) solutions to the required concentrations (2, 4, 8, 15 and 30 mg L^{-1}). To adjust the pH solutions, 0.10 N sodium hydroxide (NaOH) or 0.10 N hydrochloric acid (HCl) solutions were used throughout the experiment. The pH of the solutions were measured using a pH meter in a suspension of 1:10 BC/distilled water after 1 h shaking.

2.3. Characterization

For pyrolysis of BCs a tube furnace (GSL-1100X, Kejing New Mater, Ltd., Hefei, China) was used. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were accomplished using a (SEM, WASINCA X-ACT, 58794, Oxford), Instruments, EDX spectrometer equipped with a field emission scanning electron microscope (FESEM, JSM-6700, JEOL, Japan). Fourier transform infrared (FTIR) spectra were recorded on a (Perkin-Elmer, Varian 7000, USA) spectrometer on KBr pellet samples between 4000 and 400 cm^{-1}, using 8 scans at 4 cm^{-1} resolution. The BCs were submitted to thermogravimetric analysis (TGA), using argon flow in Shimadzu (Kyoto, Japan) analyzer model TA50. The samples were heated from ambient temperature to 1400 °C at a rate of 10 °C min^{-1}. The contents ratio of C, O and Si elements were calculated by a vario (LECO-CHNS932, USA) element analyzer X-ray photo electron spectroscopy (XPS), while the high resolution x-ray photo electron spectroscopy (HR-XPS) were applied with shirley fitting using the VMware Workstation Pro software. The elemental analyses were made in triplicate. The surface analyses were carried out with a volumetric adsorption analyzer (Nova 1000, Quantachrome Instruments). N_2 adsorption-desorption isotherms were measured at 77 K in order to measure surface area by using Brunauer, Emmet and Teller (BET) method (Vaghetti et al., 2003). The pH of BCs were calculated using a pH meter (Mettler Toledo Delta 320) in a suspension of 1:10 BC/distilled water after 1 h shaking. For the detection of Cu (II) concentration in aqueous solution, atomic absorption spectrometer (AAS) model Aanalyst 300 Perkin-Elmer was applied.

2.4. Adsorption studies

The adsorption experiments for evaluation of the ability of GFM-BC and CTM-BC to remove Cu (II) from aqueous media were carried