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Sorption of Cr(III) from aqueous media via naturally functionalized microporous biochar: Mechanistic study

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A B S T R A C T

Biochar is a highly efficient and attractive candidate for remediation of heavy metals in aqueous media, due to its immense porosity and surface functionalities. In this study farmyard and poultry manure were converted to biochars. The biochars' pre- and post-characterization was performed through various analytical techniques such as thermogravimetry, X-ray photon spectroscopy, Fourier transform infrared spectroscopy, scanning electron microscopy and energy dispersive spectroscopy. The contemporary batch adsorption work articulates the effect of biochars concentration, H^+ ion concentration, contact time and temperature on sorption efficiency of Cr(III) ions from aqueous media. The sorption kinetics of Cr(III) was sound tailored to the pseudo-second-order equation which confirmed the chemisorption. The sorption isotherms suggested the well-fitting of Freundlich model due to the unfolding of multilayer adsorption. The Cr(III) sorption was assessed as 37.75 and 33.94 mg/g for farmyard manure and poultry manure-derived biochars, respectively. The thermodynamic values designated the spontaneous and exothermic nature of the reaction.

1. Introduction

Heavy metals dissolved in water exert toxic effects on living beings. These deleterious metals are generally present in industrial wastewater and possess a major ecological threat [1–7]. In underdeveloped countries, these toxic metals are not properly removed from the water, and there is no strict legislative implementation of the laws related to environmental quality standards. Consequently, serious environmental and health impacts of these toxic metals in water are common. The presences of these trace metals in water at the very low level are obviously unsolicited [8]. Trivalent chromium (Cr(III)) is essential for metabolism in animals and helps in preventing the diabetes mellitus by maintaining the glucose level in the blood. It controls the concentration of low-density lipoprotein in the human body and decreases the fat levels [9–11]. The Cr(III) ions are present in different food items such as grains, meat, dough and yeast [9]. However, its high concentration in aqueous media is associated with cancer, owing to its frequently occurring +3 oxidation state under normal ecological circumstances. The main sources of Cr(III) in wastewater are the leather, mining and dying industries [12]. Its acute concentration in aqueous media causes several disorders [13].

Multiple techniques have been implemented for the purification of heavy metals from aqueous media such as precipitation, ion exchange, electrodeposition, reverse osmosis and filtration [14–16]. However, all these approaches are expensive, complex and sophisticated. Sorption is one of the unitary operations commonly used for the removal of heavy metals from aqueous media due to its efficiency, simplicity, and cost-effectiveness [17]. The sorption method is also functional for the removal of various organic, inorganic and biological pollutants [18].

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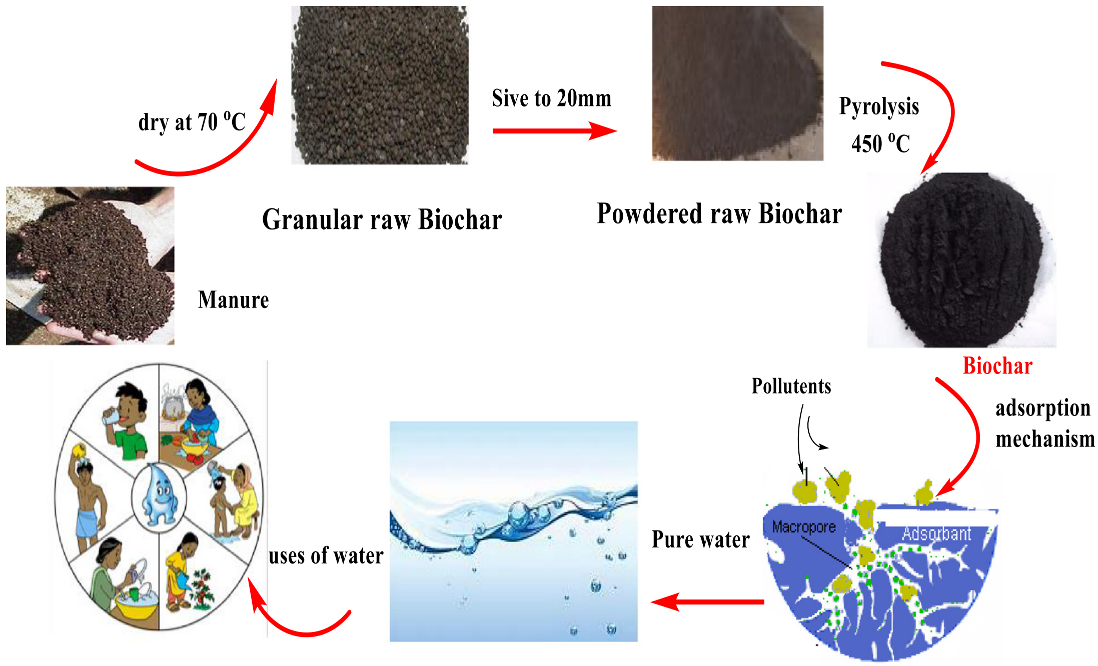

Scheme 1. Schematic illustrations for the preparation of manure derived biochar and its application in aqueous media management.

Research is advancing in search of low-cost sorbents for removing heavy metal ions from aqueous media [19]. In general, absorbent can be assumed as "low cost" if it requires little processing cost and abundant in nature.

Carbonaceous materials are the most commonly employed sorbents for toxic metals removal from aqueous media because of well-developed pore size structures and high surface area that leads to high sorption efficiency. Various types of the reported low-cost sorbents include peat moss, moss, tannin-rich materials, and cotton. Recently, biochar (a carbonaceous material obtained from pyrolysis of organic matter) has gained attraction in the field of sorption studies. Animal-derived biochar such as farmyard manure and poultry manure have been studied to investigate their effectiveness in binding heavy metal ions [18,19]. Compared to activated carbon, biochar presents the good ability for the removal of toxic metals from aqueous media. This enhanced performance of biochar might be ascribed to the presence of carboxyl, hydroxyl and amino groups that can bind the metal ions [2,20]. This makes biochar an efficient sorbent for the removal of a wide range of anions and cations [21,22].

Converting animal manure into biochar is a useful and economical strategy for combating environmental hazards such as greenhouse gas emission and leaching of pollutants associated with manure. It is also important to determine the interaction of biochar with the pollutant, so that the long-term binding and/or releasing of the pollutant from biochar material should be assessed. In the present work, batch sorption tests were conducted to examine the sorption capability of manure-derived biochar for the removal of Cr(III) from aqueous media. The biochars were well characterized by advanced analytical techniques such as scanning electron microscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy and X-ray photon spectroscopy to explore the mechanisms underlying Cr(III) sorption onto biochars.

The specific objectives of this study were to (i) assess the uptake capacity of biochars derived from poultry manure and farmyard manure for removal of Cr(III) from aqueous media, (ii) evaluate the effects of temperature, pH, exchange period and concentration on the sorption of Cr(III) by the biochar, and (iii) simulate the sorption data with sorption isotherms, kinetics, and thermodynamics.

2. Materials and methods

2.1. Manure-derived biochar production

Farmyard and poultry manure were collected from the PMAS-Arid Agriculture university farmhouse, Rawalpindi, Pakistan and used for the preparation of biochar. It was washed with deionized water to remove the surface impurities and dried at 70 °C in an oven for 24 h, crushed with mortar to obtain small pieces. The samples were separately pyrolyzed in a furnace tube under a limited supply of oxygen at 450 °C presented in Scheme 1. The pyrolyzing conditions were the same as mentioned in our previously reported study. Primarily the temperature was adjusted at 250 °C for 2 h at 2 °C min^{-1} under argon, formerly temperature was elevated to 450 °C for 3 h at 5 °C min^{-1} [53]. Finally, the biochars produced from farmyard manure and poultry manure were cooled at room temperature, crushed, ground and sieved through 25 μm mesh and labeled as BC-FM and BC-PM, respectively. The impurities of the biochar (such as ash) were removed by treating them with 0.1 M HNO_3 and agitating at 180 rpm for 40 min at 35 °C. The deionized water was used until the pH of elution was around 7. The wet biochar was oven dried at 80 °C overnight and stored in airtight bottles for future use.

2.2. Preparation of stock solution

All the chemicals used in this study were of analytical grade. Chromium chloride ($CrCl_3$) was used to prepare a 1000 mg/L stock solution. The stock solution was prepared by dissolving 3.054 g of $CrCI_3$ salt in 1000 mL of deionized water. Then, further required concentrations of 2, 4, 8, 15 and 30 mg/L were prepared in 250 mL flask. To adjust the pH, 0.1 mol/L NaOH and 0.1 mol/L HCl were used. The pH of the solutions was measured using a digital pH meter, in a suspension of 1:10 ratio of sorbent and deionized water.

2.3. Biochar characterization

The variation in the functional groups was observed by FTIR spectroscopy (BRUKER Ettlingen, Germany). Thermal