

Adsorption isotherm and kinetic studies of hexavalent chromium removal from aqueous solution onto bone char



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ABSTRACT

The adsorption of hexavalent chromium [Cr(VI)] onto bone char was optimized as a function of pH, initial Cr(VI) concentration, and bone char dosage using aqueous solution in batch tests. The initial Cr(VI) concentrations were varied between 5 and 800 mg/L to investigate equilibrium, kinetics, and the adsorption isotherms. About 100% of Cr(VI) was removed at initial pH of 1.0 with initial Cr(VI) concentration of 10 mg/L, using 2 g of bone char after 2 h. The maximum adsorption capacity of the bone char was 4.8 mg/g for an initial Cr(VI) concentration of 800 mg/L. The adsorption kinetics of Cr(VI) onto bone char followed a second order kinetic model. The adsorption isotherm followed the Langmuir model for Cr(VI) adsorption. In general, bone char demonstrated promising results as an effective adsorbent for removal of Cr(VI) from the aqueous solution. The results from this study could be useful in designing a filtration unit with bone char as the adsorbent in a full-scale water and wastewater treatment plant for the removal of Cr(VI) from contaminated water.

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1. Introduction

Chromium is considered as the 21st most abundant element in the world with a concentration of about 122 mg/L in the aqueous solution [1]. As a key contaminant in surface water and groundwater, chromium is generated from various industrial activities including electroplating, tannery, automobile, pigments, paper and pulp, fertilizer, textile, steel, and metal finishing industries [1,2]. Trivalent (Cr(III)) and hexavalent chromium (Cr(VI)) are the two major oxidation states of chromium that are detected in industrial effluents. Depending on the variation of redox potential (Eh)-pH, the change of chromium species is shown in Fig. 1. According to Fig. 1, Cr(III) is the most stable state thermodynamically under the reducing condition. Cr(VI) remains stable under likely oxidizing condition. Cr(III) predominates at pH below 3.0. The hydrolysis of aqueous Cr(III) tends to convert trivalent chromium into hydroxy species at pH above 3.5. The hydroxy species includes CrOH^{2+} , $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^0$ and $\text{Cr}(\text{OH})_4^-$ [3]. Cr(VI) is more toxic compared to the Cr(III) species and has severe adverse impacts from simple skin irritation to lung carcinoma [4–6]. The US Environmental Protection Agency (EPA)

recommended that the maximum allowable limit for Cr(VI) should be 0.1 mg/L for discharge into inland surface waters, and 0.05 mg/L in potable water [7].

Metal ions cannot be degraded into harmless end products like organic pollutants, which are bio-degradable [8]. In view of its toxic nature, suitable treatment methods for Cr(VI) removal from industrial wastewater and groundwater resources are being developed and applied. The common treatment methods include precipitation [9,10], ion exchange [11,12], membrane separation (i.e. ultrafiltration and reverse osmosis) [13,14], reduction and electrochemical reduction [15]. However, most of the above mentioned treatment technologies have limitations which include the generation of toxic sludge, high operation and maintenance expenditure, high energy requirements, long treatment times, and poor removal efficiencies [1,15].

Adsorption processes have been shown to be effective and low-cost techniques for the removal of a variety of metal ions, including chromium from aqueous solutions. The significant benefits of adsorption processes include effective and economical contaminant removal, recovery and recycling of adsorbed metals from adsorbent, low sludge production, simple process and high removal efficiencies [1,16,17]. As an effective and economical adsorbent, activated carbon has been widely employed for wastewater treatment [17]. In addition, other low cost adsorbents have also been reported for Cr(VI) removal from wastewater,

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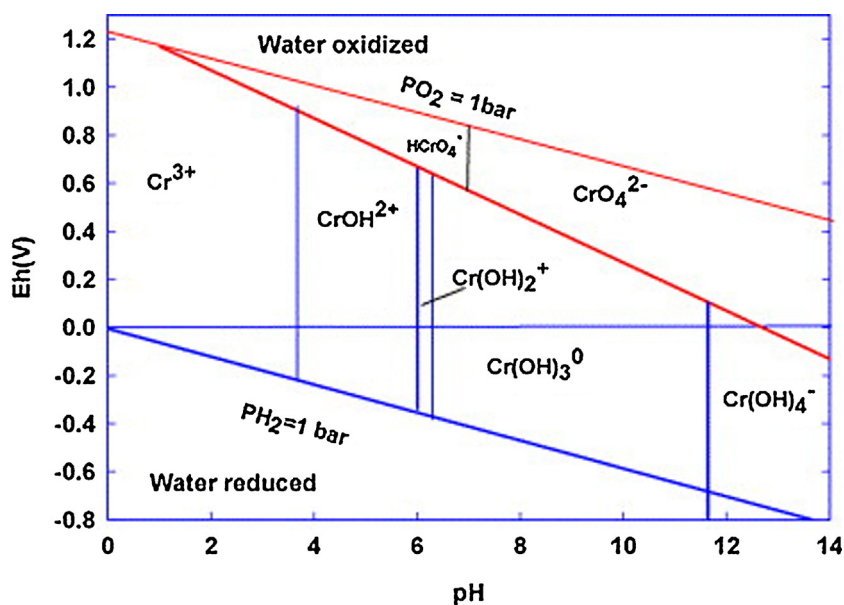


Fig. 1. Variation of chromium species depending of Eh–pH change [50].

including maple saw dust [18], bentonite and expanded perlite [19], *Nymphaea rubra* [20], *Pseudomonas aeruginosa* and *Bacillus subtilis* [21], and *Mucor racemosus* [22].

However, bone char has only been rarely investigated as an adsorbent for metal removal from aqueous systems [10,23]. Thus, a significant knowledge gap exists for the possible use of this low-cost biomass derived material as a possible economically viable adsorbent to remove metal from aqueous systems. Bone char is a heterogeneous adsorbent [24], which is produced from the destructive distillation of dried, crushed cattle bones. Typically, it has been utilized in the sugar industry for the removal of colour by sorption. The bones from cattle, goat, sheep, chicken etc. are accumulating day by day as waste materials and require proper solid waste management. The utilization of this bone for the synthesis of bone char, which can be used as an adsorbent to remove contaminants from the wastewater, can provide a better solution for the waste management [25]. Therefore, the main objective of the present study was to evaluate the performance of bone char, a waste product, generated from calcination of cattle bone for the removal of Cr(VI) from aqueous systems. The secondary objectives were to optimize the operational parameters, including pH, adsorbent dose, initial Cr(VI) concentration and contact time for the maximum Cr(VI) removal from the wastewater, and to also perform equilibrium and kinetics studies for Cr(VI) removal.

2. Experimental

2.1. Preparation and characterization of bone char

The bone char used in this study was purchased from anthracite filter media (AFM), Culver City, CA, USA and the composition was provided by the company as shown in Table 1. It is a carbonaceous granular solid material prepared by calcining cattle bones at 450 °C. The bone-char was crushed and sieved to get the particle sizes between 53 and 250 μm to increase its surface area because increased surface area might promote high adsorption of Cr(VI) onto the bone char [26]. The surface area and pore volume of the reduced particle size of bone char were determined using a NOVA 1200 surface area analyser (Quantachrome Instruments, version

2.0, Boynton Beach, FL) with the Bruanuer–Emmett–Teller (BET) nitrogen adsorption method at 77 K of temperature.

2.2. Adsorption procedure

The optimum pH, bone char dosage, and initial Cr(VI) concentration were determined by batch adsorption studies. The optimum parameters were then used to analyse adsorption capacity, adsorption reaction kinetics, and equilibrium isotherm.

About 2.8269 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) salt (Sigma–Aldrich LTD, USA) was dissolved in deionized water to prepare the stock solution of 1000 mg/L of Cr(VI). The stock solution of Cr(VI) was subsequently diluted using deionized water to the required working concentration prior to use in the batch tests. The pH of the solution was varied by using either about 15.8 M HNO_3 or 1 M NaOH. The Cr(VI) and bone char mixture was placed on a platform shaker (New Brunswick Scientific, model: Innova 2300) at 150 rpm at room temperature during the tests. Typically, about 2 g of bone char was added to a 50 mL solution of 10 mg/L concentration of Cr(VI).

About 1 mL sample was collected using separate syringes at 0.5, 1, 2–24 h and 1 mL sample was collected in each day from day 2 to 6 from the same testing solution. The collected samples were then filtered through 0.45 μm syringe filter (Sterlitech, Kent, WA, USA). Filtered samples were stored in glass bottles and preserved, when necessary, in the refrigerator at 4 °C with sample pH below 2 to avoid the degradation of Cr(VI) concentration. The samples were then analysed to measure the Cr(VI) concentrations using a graphite furnace equipped atomic absorption spectrophotometer (GF–AAS) with an air–acetylene flame and chromium hollow

Table 1
Chemical and physical properties of the original bone char sample.

Chemical properties		Physical properties	
Compounds	Limits (%)	Compounds	Limits
Hydroxyapatite	70–76	Total surface area	100 m^2/g
Carbon content	9–11	Pore volume	0.225 cm^3/g
Calcium carbonate	7–9	Particle size	250–480 μm
Calcium sulfate	0.1–0.2	–	–

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