**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 optimised 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 hours. 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.

Keywords: Adsorption, Bone char, Reaction kinetics, Equilibrium concentration, Isotherms

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+} , Cr(OH)_2^+ , Cr(OH)_3^0 and Cr(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, 5, 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 degrade into harmless end products like organic pollutants, which are biodegradable [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, 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 heterogenous 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 color 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, California, 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 analyzer (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 analyze adsorption capacity, adsorption reaction kinetics, and equilibrium isotherm.

About 2.8269 g of potassium dichromate ($K_2Cr_2O_7$) 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 15.8M HNO_3 or 1M 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 to 24 h and 1 mL sample was collected in each day from day 2 - 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 analyzed to measure the Cr(VI) concentrations using a graphite furnace equipped atomic absorption spectrophotometer (GF-AAS) with an air-acetylene flame and chromium hollow cathode lamp at a slit of 2 nm and wavelength of 357.9 nm. Prior to sample analysis, the GF-AAS instrument was calibrated regularly.

All batch tests were performed in duplicate, and average values were used in the plots presented here. The experimental blanks were run in parallel. All working solutions were prepared freshly prior to use in the batch tests. The glassware were presoaked in 5% HNO_3 solution overnight and then washed with tap water, rinsed three times with deionized water and dried in air before use.

2.3 Effects of operating parameters and equilibrium studies

The optimum pH was determined by using solution pHs of 1, 2 to 9 with bone char dosage of 2 g/50 mL solution. Subsequently, different bone char dosages of 0.5, 1, 2 and 3 g in 50 mL Cr(VI) solutions were used to identify the optimum bone char dosage at the predetermined optimum pH. The initial Cr(VI) concentration was kept at 10 mg/L to investigate optimum pH and bone char dosage. The initial Cr(VI) concentrations of 5, 10, 20, 50 to 800 mg/L [27] were evaluated with 2 g of optimum bone char dosage in 50 mL solution at optimum pH to determine the Langmuir and Freundlich isotherms properly.

The Cr(VI) concentrations at equilibrium (C_e) and at any particular time (C_t) were evaluated for different initial Cr(VI) concentrations (C_0) of 5, 10, 20, 50 to 800 mg/L by maintaining the pH and bone char dosage constant at the optimum value. These concentrations (C_0 , C_e , C_t) were employed to calculate the adsorption capacity of bone char at any particular time (q_t) and at equilibrium (q_e) according to the mass balance Equations (1) and (2) shown below, respectively [1]. Afterward, these adsorption capacities (q_e , q_t) were used to determine the equilibrium adsorption isotherms and the kinetics model plots.

$$q_t = \left(\frac{C_0 - C_t}{m} \right) V \quad \text{Eq. (1)}$$

$$q_e = \left(\frac{C_0 - C_e}{m} \right) V \quad \text{Eq. (2)}$$

where C_0 is the initial Cr(VI) concentration in mg/L, C_t is the Cr(VI) concentration at a particular time in solution in mg/L, C_e is the equilibrium Cr(VI) concentration in mg/L, V is the volume of the solution in liter (L), and m is the dry mass of bone char in gram (g).

2.4 Determination of *adsorption isotherms (Langmuir and Freundlich)*

The Langmuir and Freundlich models are expressed linearly in Equations (3) and (4), respectively to evaluate the *adsorption isotherms* of Cr(VI) onto bone char [28, 29].

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad \text{Eq. (3)}$$

$$\log(q_e) = \frac{1}{n} \log(C_e) + \log(K_F) \quad \text{Eq. (4)}$$

where C_e denotes the equilibrium Cr(VI) concentration in mg/L, q_e represents the equilibrium *adsorption capacity* of bone char in mg/g, q_m is the maximum *adsorbed amount* of Cr(VI) per mass of bone char in mg/g, K_L is the Langmuir equilibrium *adsorption constant* (L/mg) *related to the free energy of adsorption* [30], K_F is the Freundlich constant [(mg/g)(L/mg)^{1/n}] *related to the strength of the adsorptive bond* [30], and $1/n$ is the *adsorption intensity factor* or *surface heterogeneity* (unit less).

The Langmuir isotherm indicates that the *free energy of adsorption is independent on the surface coverage of adsorption sites and the solid surface saturation occurs by a monolayer coverage of adsorbate at high C_e values and a linear relationship at low C_e values* [8]. To effectively evaluate the Langmuir isotherm, the values of $1/q_e$ were plotted against $1/C_e$ and the values of K_L and q_m were calculated using the slope and intercept of the best fit line, respectively. Furthermore, the values of $\log q_e$ and $\log C_e$ were plotted to evaluate the Freundlich isotherm parameters of $1/n$ and K_F . The Freundlich constant, K_F represents the *quantity of adsorbed metal ions for a unit equilibrium concentration (i.e. $C_e=1$)* [31]. The regression coefficients (R^2) values were used to evaluate the fit of the Langmuir and Freundlich isotherms to the experimental data. The isotherm that had R^2 value nearest to 1.0 was selected as the operating *adsorption isotherm* and used for

the adsorption of Cr(VI) onto bone char. For Langmuir sorption, R_L , a dimensionless separation factor was used to describe the type of isotherm and was expressed in Equation (5) [32].

$$R_L = 1/(1+K_L C_0) \quad (5)$$

where C_0 (mg/L) and K_L (L/mg) are initial metal concentration and Langmuir constant, respectively. Thus, the value of R_L identifies whether the adsorption process is favourable or unfavourable. The process is irreversible for $R_L = 0$, favourable for $R_L < 1$, linear for $R_L = 1$ and unfavourable for $R_L > 1$ [8].

2.5 Determination of sorption reaction kinetics (First and Second order)

The pseudo first-order (Equation 6) and second-order kinetics (Equation 7) shown below were used to describe the adsorption reaction kinetics of Cr(VI) onto bone char [33, 34].

$$\log(q_e - q_t) = -\frac{K_1}{2.303} t + \log q_e \quad \text{Eq. (6)}$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{K_2 \cdot q_e^2} \quad \text{Eq. (7)}$$

where q_e and q_t represent the adsorption capacities (mg/g) of bone char at equilibrium and at a particular time t (h), respectively. The first-order and second-order kinetic rate constants are denoted by K_1 (h^{-1}) and K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$).

The pseudo first order kinetic model was established by plotting the value of $\log(q_e - q_t)$ vs time (t) to determine the values of K_1 , q_e , and R^2 . However, the values of t/q_t were plotted against time (t) in order to establish the pseudo second order kinetic model and to calculate the values of K_2 , q_e , and R^2 . The regression coefficients (R^2) of the first and second order kinetic model were compared to check which of the models is suitable for Cr(VI) adsorption onto bone char. The

deviation of equilibrium adsorption capacity (q_e) obtained from the models, and the experimentally obtained value was also calculated.

2.6 Statistical Analysis

Independent two-sample t- test was performed at a 95% confidence interval between the replicate values obtained during the tests to determine whether or not the replicate values were significantly different. To verify the optimum pH values, bone char dosage, and initial Cr(VI) concentration for maximum percentage removal of Cr(VI), a one-way ANOVA test was conducted at a 95% confidence interval. In addition, the one-way ANOVA test was also performed to identify the effects of initial Cr(VI) concentration on the adsorption capacity of bone char. A Tukey Honestly Significant Difference (HSD) test was performed for multiple comparisons when the ANOVA test showed significant differences (p value < 0.05).

3. Results and discussions

3.1 Textural properties of bone char

After reducing the particle size between 53 and 250 μm , the surface area (BET), pore volume, and average pore diameter were found to be 105 m^2/g , 0.05253 cm^3/g and 1.999 nm, respectively. The surface area of the particles did not increase significantly. The pore volume was observed to decrease from 0.225 cm^3/g to 0.05253 cm^3/g , which is over 75% due to size reduction as expected.

3.2 Effect of solution pH

The Cr(VI) removal efficiencies were observed to decrease consistently with increase in pH from 1- 9. The removal efficiencies were observed to increase slightly with time at all pH values as shown in Fig. 2A. At a pH of 1, the Cr(VI) removal efficiency was about 85 % after 0.5 h of adsorption reaction, and increased to 98 % after 2 h. The removal efficiencies were about 60 %, 45 %, 43%, 35 %, and 32 % at pHs of 2, 3, 5, 7, and 9, respectively, after 2 h of reaction. Since the highest removal efficiency was obtained at the lowest pH of 1 by using bone char sample, the optimum pH was considered to be 1. Dahbi et al [35] have also recommended the same optimum pH. At low pH values, the dominant species of Cr(VI) in solution is HCrO_4^- . This is converted to CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions as the pH increases. The adsorption free energy change for HCrO_4^- is lower than those of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions. Therefore, HCrO_4^- is more easily adsorbed than CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ at lower pH values [36]. Moreover, bone char has been reported to exhibit positively charged surface species due to surface group protonation at low pH values, thus leading to the binding of anionic species of Cr(VI) by an electrostatic attraction between the bone chars and Cr(VI) anions [37, 38] and also resulted in a final pH increase. Since Ca^{2+} might dissociate from the bone surface at lower pH, metal ions could be exchanged easily in the site of Ca^{2+} [39]. The exchangeable metal ion could be Cr(III) because Cr(VI) could be reduced to Cr(III) at pH below 3.0 (Fig.1). At higher pH values, OH^- and Cr(VI) species (CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$) compete for the same adsorption site on the bone char, resulting in a lower removal of Cr(VI) [23, 40]. In addition, surface OH^- ions of bone char increase with an increase in pH, resulting in a more Coulombic repulsion of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ species [10, 41]. Thus, Cr(VI) removal efficiency is higher at lower pHs as compared to that of higher pHs.

The one-way ANOVA test results show that the percentage Cr(VI) removal was significantly different for various pH values used in the experiment. Therefore, Tukey HSD test, as shown in Table 2, was performed for multiple comparisons among various pHs. The percentage Cr(VI) removal was significantly different between pH values except between 3 and 5, and 7 and 9. Since the percentage removal of Cr(VI) is maximum at pH 1 as shown in Fig. 2A, and also Tukey HSD test indicates that the Cr(VI) removal at pH 1 is significantly different than that of other pH values, then pH 1 can be considered as the optimum pH.

3.3 Effect of bone char dosages

As expected, the increase in bone char dosage from 0.5 - 3 g resulted in sharp increases in removal efficiencies of Cr(VI) as shown in Fig. 2B. The highest percentage of Cr(VI) removal was observed for the highest studied bone char dosage of 3 g. About 95 % Cr(VI) removal was occurred within the first 0.5 h, and this increased to 100 % in about 1.5 h for bone char dosage of 3 g. For bone char dosage of 2 g, about 100% Cr(VI) removal was also observed after 2h. For the same 2 h of experimental adsorption reaction, the removal efficiencies were about 60% and 66% for bone char dosages of 0.5 g and 1 g, respectively. Since the removal efficiencies were similar (100 %) for bone char dosages of 2 g and 3 g after 2 h, bone-char dosage of 2 g was considered to be the optimum value for purposes of our studies. Another previous study has also recommended similar optimum value of bone char dosage for Cr(VI) adsorption [35].

The one-way ANOVA test results show that the percentage Cr(VI) removal was significantly different for various bone char dosages used in the experiment. By using Tukey HSD test, it was observed that the percentage Cr(VI) removal is significantly different by using bone char

dosages of 0.5g and 2g (HSD = 41.25>11.1), 0.5 g and 3g (HSD = 45.5>11.1), 1g and 2g (HSD = 31>11.1), 1g and 3g (HSD = 35.25>11.1). There is no significant Cr(VI) removal difference between 2g and 3g of bone char dosage. Therefore, bone char dosage of 2 g can be considered as an optimum dosage.

3.4 Effects of initial Cr(VI) concentration

At optimum pH and bone char dosage, Cr(VI) removal efficiency generally decreased with increase in initial Cr(VI) concentration as shown in Fig. 2C. The removal efficiencies also increased with time at all initial Cr(VI) concentrations. For an initial Cr(VI) concentration of 5 mg/L, the Cr(VI) removal efficiency was around 94% after 0.5 h, and this increased to the highest value of about 100 % after 2 h. Similar trends were observed for all the other initial Cr(VI) concentrations studied. The removal efficiencies reached maximum values of about 98%, 95%, 88%, 85%, 82%, 71% and 22% for initial Cr(VI) concentrations of 10, 20, 50, 70, 90, 100 and 800 mg/L, respectively, in 2 h (all data are not presented in Fig. 2C). Since the removal efficiencies were almost similar for both the initial Cr(VI) concentration of 5 and 10 mg/L after 2 h of adsorption reaction, 10 mg/L of Cr(VI) was considered to be the optimum initial concentration in the present study. Another study has also reported similar optimum value for initial chromium concentration [35].

The one-way ANOVA test also shows that the percentage of Cr(VI) removal was significantly different when initial Cr(VI) concentrations were varied from 5 mg/L to 800 mg/L. Therefore, Tukey HSD test was performed and found that the percentages of Cr(VI) removal were significantly different between 5 mg/L and 50 mg/L, 5 mg/L and 70 mg/L, 5 mg/L and 90 mg/L,

5 mg/L and 100 mg/L and so on. Eventhough there were not significant differences in percentages of Cr(VI) removal between 5 mg/L and 10 mg/L, 5 mg/L and 20 mg/L, the optimum initial Cr(VI) concentration was considered to be 10 mg/L because the percentages of Cr(VI) removal were similar (100%) at initial Cr(VI) concentration of 5 and 10 mg/L and 95% at 20 mg/L after 2 h as shown in Fig. 2C.

3.5 Evaluations of the *adsorption capacities*

The *adsorption capacity* (q_t) was found to increase with an increase in the initial Cr(VI) concentrations from 5 to 800 mg/L until it reached equilibrium value (q_e) as shown in Fig. 3. The lowest *adsorption capacity* of 0.13 mg/g was found after 3 h for the lowest studied initial Cr(VI) concentration of 5 mg/L. However, the highest *adsorption capacity* of 4.8 mg/g was obtained after 5 h for the highest studied initial Cr(VI) concentration of 800 mg/L. The *adsorption capacities* reached constant equilibrium values of 0.25, 0.5, 1.25, 1.75, 2.5 and 3.62 mg/g for initial Cr(VI) concentrations of 10, 20, 50, 70, 100 and 500 mg/L, respectively. Equilibrium time was not dependent on the initial Cr(VI) concentration. In general, a more efficient utilization of the *adsorption capacity* of the *adsorbent* is expected at a higher initial Cr(VI) concentration due to the greater driving force from concentration gradient [42]. Normally, a higher initial concentration leads to higher collisions between the *adsorbent* and Cr(VI) species, resulting in a driving force that is able to overcome all mass transfer resistances between the solid and aqueous phases [43].

The one-way ANOVA test also shows that the percentage of Cr(VI) removal was significantly different when initial Cr(VI) concentrations were varied from 5 mg/L to 800 mg/L. Therefore,

Tukey HSD test was performed and by multiple comparison, it was concluded that Cr(VI) adsorption capacity onto bone char is maximum at 800 mg/L of initial Cr(VI) concentration as shown in Fig. 3.

3.6 Evaluations of the adsorption isotherms (Langmuir and Freundlich)

The adsorption isotherm of Cr(VI) onto bone char was evaluated using the plots of Langmuir and Freundlich models as shown in Figs. 4A and 4B. These two models are the most common isotherms used to describe solid-liquid adsorption systems. The isotherm coefficients for these two models are presented in Table 3. Since, the maximum adsorption capacity (q_m) obtained from the experimental result and Langmuir model was not similar, the deviation of q_m value obtained from the experimental result to Langmuir model was 43 %. The value of R_L (0.27), the essential characteristics of Langmuir dimensionless separation factor or equilibrium parameter, indicates the favourable adsorption process of Cr(VI) to the adsorbate [44].

Based on the alignment of the experimental data with the model lines in Figs. 4A and 4B, together with the regression coefficient (R^2), it is clear that the adsorption data of Cr(VI) onto bone char fit the Langmuir model better with an R^2 of 0.9871, as compared to the Freundlich model ($R^2 = 0.9745$). The suitability of Langmuir model can be interpreted to mean that the adsorption of Cr(VI) took place on a homogeneous monolayer surface of bone char, and that Cr(VI) species did not interact with each other during the adsorption process [23]. Table 4 represents the values of q_m from Langmuir isotherm obtained by using other adsorbents for removing Cr(VI) reported in other studies [10, 45,46] . Value of 'n' obtained from Freundlich

isotherm was 1.8, which indicates a good adsorption potential of Cr(VI) to the bone char [39, 47].

3.7 Evaluation of the adsorption kinetic model

To better understand the adsorption behavior of Cr(VI) onto bone char, the kinetic sorption data were tested based on the pseudo first-order kinetic model as shown in Fig. 5A and the pseudo second-order kinetic model as shown in Fig. 5B for the initial Cr(VI) concentration of 10 mg/L. The plot line of the pseudo first-order kinetic model is not well aligned with the experimental data, showing an R^2 value of 0.9191. However, the pseudo second-order kinetic model shows a good linear correlation with an R^2 value of 1, and with excellent agreement between the theoretical model line and the experimental data line. The adsorption of Cr(VI) onto bone char can therefore be described in terms of second order kinetics [48, 49]. Since the experimental data follow the pseudo second-order kinetic model, the uptake of Cr(VI) onto bone char could take place through chemisorption by generating new chemical species on the bone char surface [23]. Moreover, the pseudo second-order kinetic model indicate that the adsorption reaction of Cr(VI) on bone char depend upon the concentration of Cr(VI) in solution and the amount of bone char needed to adsorb the maximum Cr(VI) ions from solution at equilibrium. The kinetic parameters and correlation coefficients of the two models tested are summarized in Table 5. The deviation of the experimentally obtained equilibrium adsorption capacities from the value estimated from the pseudo first-order model was 47.3%. However, no deviation was observed for the second-order kinetic model because the experimental value of the equilibrium adsorption capacity (q_e) was similar to the value calculated from the second order kinetic model.

4. Conclusions

In this study, bone char was used to adsorb Cr(VI) from the aqueous solution. The optimum value of pH, bone char dosage, and initial Cr(VI) concentration were found to be 1, 2 g/L, and 10 mg/L, respectively for the highest adsorption level of Cr(VI) onto bone char. The maximum adsorption capacity of 4.8 mg/g was obtained after 5 h of adsorption at initial Cr(VI) concentration of 800 mg/L. The Langmuir model showed a good fit for Cr(VI) adsorption onto the bone char with a regression coefficient (R^2) of 0.9871. Kinetic analysis of the Cr(VI) adsorption on bone char showed good alignment with a second order reaction model ($R^2 = 1$). The results obtained in this study suggest that bone char has the potential to be an economical and efficient adsorbent for Cr(VI) removal from water and wastewater resources. Therefore, a filtration unit incorporating bone char as adsorbent can be operated based on the optimum conditions, adsorption isotherm and kinetic model obtained in this study in a full-scale water and wastewater treatment plant for the removal of Cr(VI) from the contaminated waters.

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519 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	-	-

520

521 Table 2: Tukey HSD test of Cr(VI) removal at various pH

pH values	mean difference in % Cr(VI) removal	HSD value	Comments
1 and 2	31.75	6.09	Significant difference
1 and 3	49.5	6.09	Significant difference
1 and 5	51.5	6.09	Significant difference
1 and 7	59.25	6.09	Significant difference
1 and 9	61.75	6.09	Significant difference
2 and 3	17.75	6.09	Significant difference
2 and 5	19.75	6.09	Significant difference
2 and 7	27.5	6.09	Significant difference
2 and 9	30	6.09	Significant difference
3 and 5	2	6.09	not Significant difference
3 and 7	9.75	6.09	Significant difference
3 and 9	12.25	6.09	Significant difference
5 and 7	7.75	6.09	Significant difference
5 and 9	10.25	6.09	Significant difference
7 and 9	2.5	6.09	not Significant difference

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523 Table 3: Coefficients of Langmuir and Freundlich model

Langmuir model			Experimental	Deviation	Freundlich model		
R ²	K _L	q _m	q _m	q _m	R ²	K _F	1/n
-	(L/mg)	(mg/g)	(mg/g)	%	-	(mg/g). (L/mg) ^{1/n}	-
0.9871	0.0023	8.4	4.8	43%	0.9745	0.138	0.5589

524

Table 4: The adsorptive capacities of various adsorbents for Cr(VI)

Adsorbent	q_m (mg/g)	pH	Reference
Bone char	8.41	1	Present study
Oak bark wood char	4.62	2	Mohan et al., 2011
Powdered activated carbon	0.03	2	Rao et al., 2002
Coconut tree sawdust derived activated carbon	3.5	3	Selvi et al., 2001

Table 5: Coefficients of the first and second order kinetic model

First order kinetic model			Second order kinetic model		
R^2	K_1	q_e	R^2	K_2	q_e
-	(h^{-1})	(mg/g)	-	($g \cdot mg^{-1} \cdot h^{-1}$)	(mg/g)
0.9191	1.813	0.1317	1	219	0.25

Figure Captions

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

Fig. 2: Removal efficiencies of Cr(VI) onto bone char as sorbent with (a) different pHs at initial Cr(VI) concentration of 10 mg/L, bone-char of 2 g; (b) different dosages of bone-char at pH of 1, initial Cr(VI) concentration of 10 mg/L and c) different initial Cr(VI) concentration: pH of 1 and 2 g bone-char

Fig. 3: Sorption capacities of bone-char with time for different initial Cr(VI) concentrations: pH of 1, bone-char of 2 g.

Fig. 4: Plots of a) Langmuir and b) Freundlich isotherms for Cr(VI) sorption onto bone char. pH: 1; bone char: 2 g. The solid line is experimental data and dashed line is the linearized Langmuir model.

544 Fig. 5: Plots of a) First-order kinetic model and b) second-order kinetic models for Cr(VI)
545 sorption onto bone char at optimum initial concentration of 10 mg/L. pH: 1; amount of bone
546 char: 2 g.
547

Figure 1

(a)

(b)

(c)

Figure 2

Figure 3

(a)

(b)

Figure 4

(a)

(b)

Figure 5