

Adsorption of Hexavalent Chromium from Aqueous Solution by Pumice: Equilibrium and Kinetic Study

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Abstract—Chromium released into the environment primarily as a result of industrial activity such as leather and electroplating manufacturing process. This heavy metal has caused serious contaminations of water and soils with significant environmental and occupational concerns. Conventional methods of chromium removal are expensive especially for developing countries. This study investigates the use of pumice as a low cost and biosorbent material. Sorption of hexavalent Chromium (Cr (VI)) onto pumice were carried out in batch at room temperatures, with parameters of initial chromium concentrations, and contact time being investigated. Removal of hexavalent chromium increased by increasing contact time, and reduced with increasing initial chromium concentration. Kinetic studies were conducted using the Pseudo-first-order and Pseudo-second-order models, while equilibrium data were fitted using Langmuir and Freundlich isotherm models. Fittings of obtained data onto kinetic models show that the pseudo-second-order kinetic model ($R^2=0.999$) best describes the kinetic sorption of chromium ions onto pumice. Results also showed that Langmuir ($R^2=0.999$) and Freundlich ($R^2=0.999$) model agrees very well with experimental data. The R_L and n values has proved the favorability of hexavalent chromium adsorption onto pumice

Keywords— Adsorption isotherms, pumice, Biosorbent, Hexavalent Chromium.

I. INTRODUCTION

Water is a precious natural resource, vital for life, development and the environment. Water sources have been put under great pressure by population increases in developed and developing countries, through pollution by agricultural, domestic and industrial waste, and by environmental change [14]. Various sources of industrial pollution come from steel industries, chemical industries,

leather industries and electroplating industries. Leather tanning industries are universally recognized as being a noxious industry which produces relatively high volumes of offensive waste both liquid and solid [20]. Chromium is one of the metal ions mainly found in waste from the chrome tanning process and has significant environmental and occupational concerns. Chromium is toxic, corrosive and irritant with when the concentrations values exceed the threshold value. High exposure and ingested levels of chromium may cause stomach upset, ulcers, convulsion, liver or kidney damage, lung cancer or death [10].

Chromium ion (Cr+) mainly occurs in two forms; Trivalent (Cr (III)) and Hexavalent (Cr (VI)). Trivalent chromium is the form of chromium naturally found in the environment and has relatively low toxicity, while, Hexavalent chromium is a carcinogenic and mutagenic agent that can inflict many health problems [5]. According to the World Health Organisation [21], the permissible limit of Cr (VI) is 0.05 mg/L for potable water and 0.1 mg/L for discharge to inland surface water.

Conventional methods of Cr+ removal in wastewater include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, adsorption, electrochemical treatment and membrane technology [16], [17]. Adsorption operations using activated carbon, silica gel, and alumina are widely used in industrial applications of water and wastewater purification. The use of low cost biosorbent including the use of coal, sawdust, hazelnut, rice husks, banana peels and coffee husks have also been studied [2], [11], [13], [19]. Adsorption involves the process where atoms, ions, or molecules from gas, liquid or dissolved solid adhere to a surface either electrostatically by physical adsorption, which produces relatively weak complexes, or chemically by chemisorption which produces strong complexes [3], [12].

The objective of this study was to evaluate the feasibility of pumice for the removal of chromium from aqueous solution using batch studies. The study seeks to investigate the influences of experimental parameters of contact time and initial Cr (VI) concentrations. It also seeks to develop an understanding of controlling reaction pathways and mechanism, as well as quantify the adsorptive capacity of the

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adsorbent. This is done using first and second pseudo kinetic models and Langmuir and Freundlich isotherm models. Results of this study can be utilized in assessing the ability of pumice for chromium heavy metal at the field scale.

II. MATERIALS AND METHODS

A. Preparation of Absorbate

Chromium (VI) stock solution was prepared by dissolving Potassium Dichromate (K_2CrO_4) in distilled water. Chromium samples at required concentrations of 5 mg/l, 10 mg/l, 20 mg/l, 30mg/l, 40 mg/l and 50 mg/l were prepared by appropriate dilution of the stock solution with distilled water.

B. Preparation of Pumice adsorbent

Pumice used in the study was obtained from Nakuru, Kenya. Natural pumice was rinsed with distilled water several times until the effluent turbidity was lower than 0.1 NTU. The pumice was then dried in an oven at 100°C for 24h. Finally the raw sample was crushed to powder, and then sieved to particle size fraction of 20 mesh size (0.841mm)

C. Analysis

The concentrations of Cr (VI) in the solutions before and after adsorption were determined by Perkin –Elmer 3100 Atomic adsorption spectrometer (Buck 210VGP/220 Graphite furnace, East Norwalk, USA) at 357.9 nm and a slit width of 1 nm using an air–acetylene flame. The pH of the solution was determined using Hanna HI 98129 pH meter, Woonsocket, Rhode Island, USA.

D. Adsorption experiment

Batch adsorption experiments were performed by contacting 1g of pumice, with a range of different concentrations of Cr (VI) solution from 5-50 mg/L. Agitation contact time was kept for 3 hrs with a constant agitation speed of 150 rpm at room temperature. A pH value of between 4.0 and 5.0 were maintained throughout the experiment by adding 0.1 N NaOH or HNO_3 before each experiment. Finally the mixture was filtered using a Whatman filter paper No.597 (45mm) and the filtrate analyzed to evaluate the amount of Cr (VI) adsorbed. The Cr (VI) concentration retained in the adsorbent phase was calculated using equation 1:

$$q_e = \frac{V(C_i - C_e)}{W} \quad (1)$$

where, q_e is the Cr+ adsorbed (mgg^{-1}), C_i and C_e are the initial and final concentration (mgL^{-1}) Cr (VI) solution respectively; V is the volume (L) and W is the dry weight of biosorbent.

a. Effect of time

To evaluate the effect of time, 3g of pumice was contacted with 300ml stock chromium solution of concentration 20

mg/L and 50mg/L at natural solution pH of 4.45 and at room temperature. The solution was then stirred at a speed of 150rpm for a specified time (0 to 200 min). 20 ml samples the solution was taken at 1, 5, 10, 15, 20, 30, 60, 90, and 180 minutes. The samples were then filtered and the filtrate was analyzed to evaluate the amount of Cr (VI) adsorbed.

b. Effect of initial concentration

Evaluation of the effect of initial hexavalent chromium concentration was investigated in the range of 5, 10-50 mg/l at pH values between 4.0-5.0. The contact time was kept at 3hrs with adsorbent doses of 0.1g/L and at room temperatures. The solution was then filtered and filtrate analysed for Cr (VI).

III. RESULTS AND DISCUSSION

A. Effect of Contact time

The effects of the contact time on Cr (VI) sorption was investigated with six Cr (VI) concentration sets (5-50mg/l). The Percentage removal of Cr (VI) was observed to be rapid in the initially and thereafter the rate of Cr (VI) removal becomes relatively constant (Fig 1.). This is probably due to the availability of large number of active binding sites initially in the pumice adsorbent and consequently large numbers of Cr (VI) ions. The adsorption equilibrium of chromium ions by pumice and charcoal was attained within 2hr after which there were no significant increases in the chromium uptake (Figure 5.1). The equilibrium time was observed at 90 min. At equilibrium the uptake of chromium ions was a 2.9 mg/g (57.3%) and 1.4 mg/g (70.6%) of chromium at concentrations of 50 and 20 mg/L respectively. The equilibrium time for pumice was found to be similar to studies conducted using powder pumice [18], however the removal rates recorded were lower than those recorded in previous studies [18],[23].

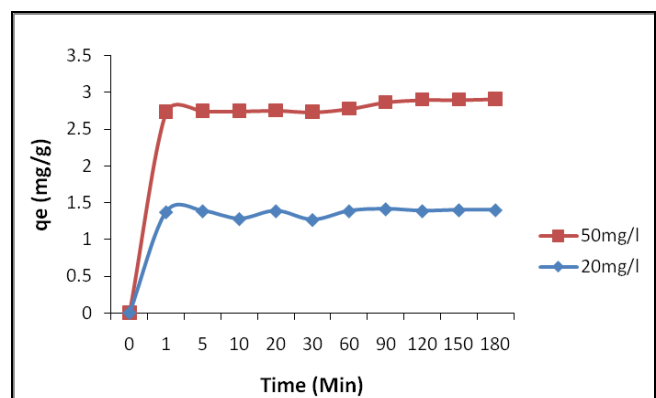


Fig.1: Effect of contact time on Cr+ removal on pumice at 20 and 50 mg/l concentrations

B. Effect of Initial Concentration

The effect of initial concentration on removal of Cr (VI) on the adsorption efficiency by pumice was investigated as shown in Fig. 2.

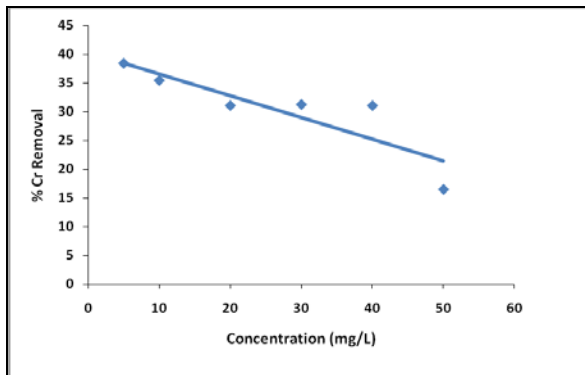


Fig 2: Effect of Initial concentration on Cr (VI) removal by pumice (adsorbent: 10g/l, agitation: 180min)

It was observed that the percentage removal of Cr (VI) decreased with the increase in initial Cr (VI) concentration. At initial concentrations of 5 mg/l the maximum Cr (VI) removal efficiency was found to be 38.5 %, while at levels of 50 mg/l the removal efficiency was at 16.5%. Hence the removal of chromium is observed to be dependent on the initial concentration of chromium present in the solution.

C. Adsorption Kinetic study

The kinetics of Cr (VI) ions adsorption process onto pumice was analyzed using pseudo-first-order and pseudo-second-order kinetic models.

Pseudo-first-order model

The pseudo-first-order kinetic model can be expressed linearly as [8]:

$$\text{Log}(q_e - q_t) = \text{Log}q_e - K_1 \frac{t}{2.303} \tag{2}$$

Where q_e and q_t are the amounts of Cr (VI) Ions adsorbed (mg/g) at equilibrium and at time t (min), respectively and K_1 the rate constant of pseudo-first-order adsorption (min^{-1}). Linear lines were obtained by plotting $\log(q_e - q_t)$ against t as shown in Fig 3. The linear plot of the experimental data and the calculate parameters were summarized in Table 1. It was observed that the experimental data is not well fitted to the pseudo- first-order kinetic equation. Although the values of R^2 at 50 mg/l are high ($R^2=0.921$), the values at 20 mg/l are low ($R^2=0.208$). They is also a significant difference between the calculated and experimental q_e values These results hence concludes that the adsorption process of Cr (VI) onto pumice is not a first-order reaction.

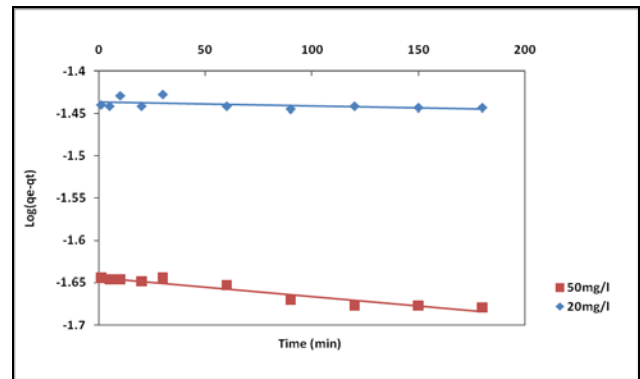


Fig. 3 Linear plot of Pseudo-first-order equations of Cr (VI) adsorption onto pumice at 20 and 50 mg/l concentrations

Table 1: Parameters of the pseudo-first-order kinetics

Parameter	First –order Kinetic Model			
	K_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	$q_{e,Exp}$ (mg/g)
Initial Cr+ Conc.				
50 (mg/L)	0.0005	0.023	0.921	0.028
20 (mg/L)	0.0001	0.037	0.208	0.011

Pseudo- Second-order model

The pseudo-second-order equation can be represented in the linear form as [6]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

Where, K_2 is the rate constant of pseudo-second-order adsorption (g/mg min).The second order rate constants were used o calculate the initial adsorption rate, h (mg/g min), given the equation:

$$h = K_2 q_e^2 \tag{4}$$

The equilibrium adsorption capacity q_e and the second-order rate constant K_2 were calculated from the slope and intercept of the plot of t/q_t against t as shown in Fig. 4. The calculate parameters for the data of second-order-kinetic model were summarized in Table 2. Results indicated a good fit ($R^2=0.999$) of the experimental data with the second-order kinetic equation. The linear plots also show a good agreement between the experimental ($q_{e,exp}$) and calculated ($q_{e,cal}$) values. This finding indicates that the adsorption of Cr (VI) onto pumice follows the pseudo-second-order kinetic model. Results also shows that as the initial Cr (VI) concentration increases, adsorption capacity at equilibrium (q_e), initial sorption rate (h) and the adsorption rate (K)also increased.

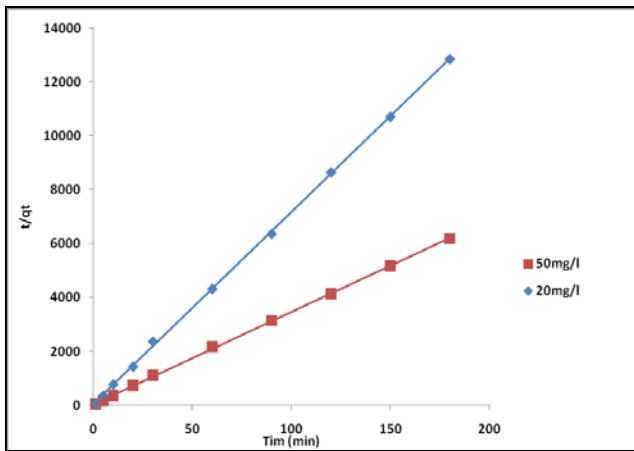


Fig. 4 Linear plot of Pseudo-Second-order equation for Cr (VI) adsorption onto pumice at 20 and 50 mg/l concentrations

Table 2: Parameters of the pseudo-second-order kinetics

Parameter	Second-order Kinetic Model				
Initial Cr+ Conc.	K ₂ (mg min)	q _{e,cal} (mg/g)	h	R ²	q _{e,Exp} (mg/g)
50 (mg/L)	30.978	0.029	0.026	0.999	0.028
20 (mg/L)	91.411	0.014	0.018	0.999	0.011

D. Adsorption Isotherms

To describe the experimental data, the most widely accepted adsorption models, Langmuir and Freundlich isotherms, were used.

Langmuir Isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. The model assumes maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The linear form of Langmuir isotherm model is described as [9]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{5}$$

Where C_e is the equilibrium concentration in liquid phase (mg/L), q_e is the equilibrium amount of adsorbate (mg/g), q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir constant (L/mg) related to the energy of adsorption [1].

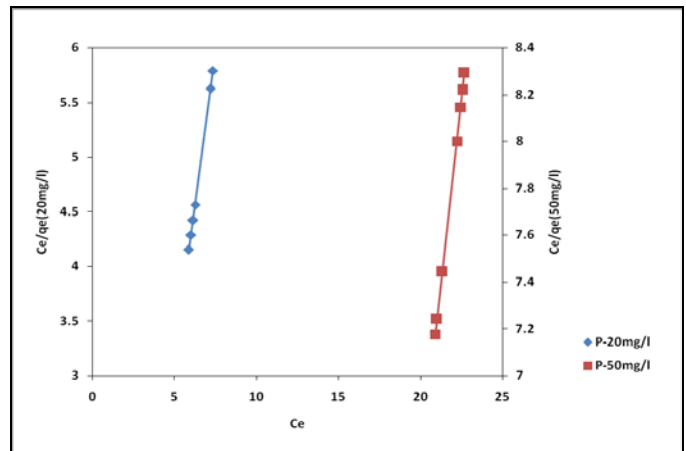


Fig.5 Langmuir Isotherm of Cr (VI) adsorption onto pumice at 20 and 50 mg/l concentrations

The slope and intercept of plots of C_e/q_e versus K_L (Fig.5) were used to calculate q_m and K_L and the Langmuir isotherm parameters are summarized in Table. 3.

Table 3: Parameters of the Langmuir

Parameter	Langmuir isotherm			
Initial Cr+ Conc.	q _m	K _L	R _L	R ²
50 (mg/L)	1.592	0.105	0.003	0.999
20 (mg/L)	0.890	0.456	0.020	0.999

The maximum monolayer adsorption capacity, q_m were found to be 1.592 and 0.890 mg/g for 20 and 50mg/L Cr (VI) concentrations respectively. The correlation Coefficients (R² = 0.999) clearly suggest that the adsorption of Cr (VI) onto pumice follows the Langmuir isotherm.

The separation factor was calculated as the following equation:

$$R_L = \frac{1}{1 + K_L C_i} \tag{6}$$

Where, K_L is the Langmuir constant (L/mg) and C_i is the initial concentration of metal ions (mg/L). The values of R_L are listed as shown in Table 4.

Table.4 R value based on isotherm

R Value	Type of Isotherm
R=0	Irreversible
0 < R < 1	Favorable
R= 1	Linear
R > 1	Unfavorable

The calculated Values of R_L was found to be 0.020 and 0.003 for initial concentrations of Cr (VI) of 20mg/L and

50mg/L respectively (Table 3). This confirms that Cr (VI) adsorption onto pumice is favorable [17].

Freundlich isotherm

The Freundlich isotherm is an empirical model that is based on adsorption on heterogenous surface and is an indicator of the extent of heterogeneity of the adsorbent surface. The linear form of Freundlich isotherm is expressed as [4]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

Where, q_e represents the amount of adsorbed Cr (VI) per gram of adsorbent at the equilibrium (mg/g), C_e is the equilibrium solution concentration (mg/L), and K_f and n are Freundlich constants, which represent adsorption capacity (mg/g) and adsorption intensity, respectively.

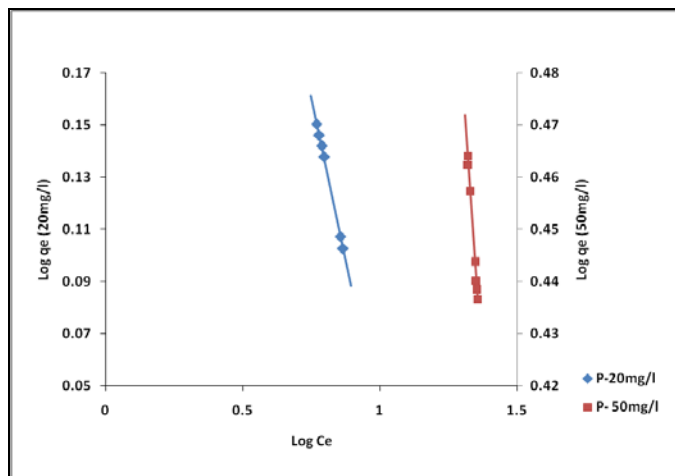


Fig.6 Freundlich Isotherm of Cr (VI) adsorption onto pumice at 20 and 50 mg/l concentrations

Freundlich equilibrium constants were determined from the plot of $\log q_e$ against $\log C_e$ (Fig.6) and the calculated parameters shown in Table 5. Based on the correlation coefficients values ($R^2 = 0.999$), the Freundlich isotherm model fitted well with the experimental data. The Freundlich constants K_f were found to be 3.404 and 30.409 for concentrations of 20 and 50 mg/L. The type of isotherm is described by the n value, which indicates the degree of nonlinearity between solution concentration and adsorption. High value of n indicates a strong bond between the adsorbent and the adsorbate [22] and if $n > 1$, this indicates a favorable sorption process [6],[7]. The observed n values were higher than 1.0, indicating the physical biosorption of Cr (VI) onto pumice and that its is a favourable process.

Table 5: Parameters of the Freundlich isotherm

Parameter	Freundlich Isotherm		
Initial Cr+ Conc.	K_f	n	R^2
50 (mg/L)	30.409	1.297	0.999
20 (mg/L)	3.404	2.016	0.999

IV. CONCLUSION

The present batch studies investigations on the use of pumice to adsorb Cr (VI) from aqueous solutions in batch mode studies the adsorption was dependent on initial metals ion concentration, and agitation time. Cr (VI) uptake equilibrium was attained within 2 hours, and pumice was observed to be able to adsorb 2.9 mg/g and 1.4 mg/g of chromium at concentrations of 50 and 20 mg/L respectively. Cr (VI) adsorption onto pumice was also observed to decrease as the initial concentrations of Cr (VI) increased. The adsorption Cr (VI) onto pumice follows a pseudo- second-order kinetics and shows good fits with both the Langmuir ($R^2 > 0.999$, $q_m > 0.890$) and Freundlich ($R^2 > 0.999$) isotherm models. This study can conclude that pumice provides a low cost favorable option from Cr (VI) removal in aqueous solution.

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