Adsorption of Chromium (VI) from Aqueous Solution by Acacia Tree (*Acacia tortilis*) Charcoal

Cecilia. W. Muriuki [1*], Urbanus. N. Mutwiwa[1*], Patrick. G. Home[1*] and Fidelis. N. Kilonzo[2*]

[1]*Department of Biomechanical and Environmental Engineering, Jomo Kenyatta University of Agriculture and Technology,*
P.O Box 62000-00200 Nairobi, Kenya

[2]*Department of Water & Environmental Engineering, Kenyatta University*
P.O Box 43844-00100 Nairobi, Kenya

*Corresponding Author - E-mail: ceciliamuriuki@jkuat.ac.ke

Abstract: The adsorption of chromium (VI) ions from aqueous solution by charcoal from acacia (*Acacia tortilis)* tree were studied in a batch adsorption system. Various parameters such as the effect of initial chromium concentrations, pH, and contact time on Cr (VI) removal were investigated. The removal of Cr (VI) ions was observed to increase with contact time, and reduced with increasing initial chromium concentration. The optimum pH for chromium (VI) removal was attained between pH 5.0 and 6.0. Simulation kinetic models results showed that the pseudo-second–order kinetic model ($R^2>0.983$) best describes the kinetic sorption of Cr (VI) ions onto the acacia charcoal. Moreover, the Langmuir and Freundlich models agreed very well with experimental data with a regression coefficient of 0.999 and 0.998, respectively. Desorption studies using nitric acid (HNO_3) indicated high capability of chromium regeneration with desorption of higher than 92% being observed. Use of acacia tree charcoal for adsorption of Cr (VI) ions in this study exhibited high potentials for chromium ions removal from aqueous solution. These results suggest that acacia tree charcoal can be employed as an efficient adsorption for Cr (VI) removal in contaminated waters and can be utilized for recovery of chromium. Results from this study can be utilized in assessing the effectiveness of acacia tree charcoal for Chromium heavy metal at the field scale.

Keywords- adsorption isotherms, Chromium (VI), natural charcoal.

1. Introduction

Chromium is a naturally occurring element found in rock, soil, and groundwater. Chromium ion 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. Hexavalent chromium is a carcinogenic and mutagenic agent that can cause many health problems [18]. There are three dissolved chromium (VI) species that occur in water: chromic acid (H_2CrO_4), bichromate ion ($HCrO_4$), and chromate ion (CrO_4). The concentration of anionic species depends on solution pH and chromium concentration, which in turn affect its toxicity and bioavailability [13].

Chromium ion is released into the environment primarily as a result of industrial activity such steel manufacturing, electroplating processes, leather and textile manufacturing, and other chromium applications in the industry. Reference [34] shows that chromium has caused serious contaminations of water and soils with significant environmental and occupational concerns. High exposure and ingested levels of chromium may cause stomach upset, ulcers, convulsion, liver or kidney damage, lung cancer or death [4]. According to the World Health Organization, the permissible limit of total chromium is 0.05 mg/L for potable water and 0.1 mg/L for discharge to inland surface water [43].

The progressive increase of industrial technology utilizing chromium, leads to increased pollution, and in turn increases the effort to minimize these hazardous pollutants due to their adverse effects. Conventional

methods of chromium ion removal in wastewater include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, adsorption, electrochemical treatment and membrane technology [10], [35], [39].

Adsorption technology is one of the more promising methods due to the efficiency of the removal of heavy metals ions from aqueous solutions, the easy separation of sorbent after treatment, and the low cost of the initial materials used as sorbents. In adsorption heavy metals are adsorbed by surfaces either electrostatically by physical adsorption, which produces relatively weak complexes, or chemically by chemisorption, which produces strong complexes [9]. Metals adsorbed on the surface of the granular medium or sediment can be substituted by other cations via cation exchange process.

The most common industrial adsorbents are activated carbon, silica gel, and alumina, because they present enormous surface areas per unit weight. These commercially available adsorbents are still considered expensive, and as a result, there is a need to study alternative substitutes which have high adsorption efficiency and are low in cost. For instance, the use of charcoal, pumice, coal, sawdust, hazelnut, almond husks, rice husks and coffee husks, tea wastes have been studied [17], [22], [23], [27], [31], [42], and [45]. Reference [15] conducted studies that identified charcoal as an effective adsorbent of heavy metals with removal efficiencies exceeding 80%.

To provide an understanding of the reaction pathways, the mechanism of the reactions and the adsorption behavior of different adsorbents, different diffusion and isotherm models have been widely employed [12],[16].The pseudo-first and -second-order kinetic models are the most well-liked models to study the biosorption kinetics of heavy metals and quantify the extent of uptake in biosorption kinetics. Langmuir and Freundlich equations are the most widely used adsorption isotherm models [14], [29], [36].

Acacia tortilis tree is commonly found worldwide. It is very common in African countries. It is a competitive species and potentially very invasive. This makes it readily available, low cost and a cheap biomaterial. The objective of this study was to evaluate the potential of acacia tree charcoal for the removal of chromium (VI) from aqueous solution. The influences of experimental parameters of contact time, pH, and initial chromium ion concentrations were studied. First-pseudo and Second-pseudo- order Sorption Kinetics models and Langmuir and Freundlich Isotherm models were investigated to understand the controlling reaction pathways and mechanism, as well as to quantify the adsorptive capacity of the adsorbent.

2. Materials and Methods

This research study was conducted at the Food Science and Technology lab in Jomo Kenyatta University of Agriculture and technology, Kenya.

2.1 Preparation of Adsorbate
Chromium stock solution was prepared by dissolving Potassium Dichromate ($K_2Cr_2O_7$) 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.

2.2 Preparation of Charcoal adsorbent
Charcoal made from acacia tree (Acacia tortilis) was obtained from Makueni County in Kenya. The Charcoal was rinsed with distilled water until the effluent turbidity was lower than 0.1 NTU and then dried in an oven at 100° C for 24 hrs. The raw sample was then crushed, and sieved to particle size fraction of 20 mesh size (0.841 mm). Standard method was used to analyze the adsorbent physically and chemically in the laboratory.

2.3 Analysis
The concentrations of chromium (VI) in the solutions before and after adsorption were determined using 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 before adsorption was determined using Hanna HI 98129 pH meter, Woonsocket, Rhode Island, USA.

2.4 Batch experiment
Batch adsorption experiments were performed by contacting 1g of acacia tree charcoal, with a range of different concentrations of chromium (VI) solution from 5-50 mg/L. The adsorbent sample was agitated in a 250 ml beaker with 100 ml Cr (VI) aqueous solutions. Agitation contact time was kept for 3 hrs with a constant agitation speed of 150 rpm at 24° C. A pH value of between 4.0 and 5.0 were maintained throughout the experiment by adding 0.1 N NaOH or 0.1 N HNO_3 before each experiment. The mixture was then filtered using a Whatman filter paper No.597 (45 mm) and the filtrate analyzed to evaluate the amount of chromium (VI) adsorbed. The Cr (VI) concentration retained in the adsorbent phase was calculated using equation 1 [8].

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

Where, q_e is the metal ion adsorbed (mgg⁻¹), C_i and C_e are the initial and final concentration (mg/L) of metal ion in solution respectively; V is the volume of the solution (l) and W is the dry weight of adsorbent (g).

To evaluate the effect of contact time, 3g of acacia tree charcoal was contacted with 300ml stock chromium (VI) solution of concentration 20 and 50 mg/L at natural solution pH of 4.45 and at 24°C. The solution was then stirred using a magnetic stirrer at a speed of 150 rpm for a specified time. 20 ml samples the solution was taken after 1, 5, 10, 15, 20, 30, 60, 90, 180 and 200 minutes. The samples were then filtered and the filtrate was analyzed to evaluate the amount of Cr (VI) adsorbed. Effect of contact time on chromium sorption was carried out at time interval 1-180 minutes.

The effects of pH on adsorption were evaluated by contacting 1g acacia charcoal in 100ml of Cr (VI) solution at concentrations of 20 and 50 mg/L. The pH range of 2.0-10.0 was used and adjusted by adding 0.1N NaOH and HNO₃ before each experiment. Agitation contact time was kept for 3 hrs with an agitation speed of 150 rpm. The solution was then filtered and filtrate analyzed for Cr (VI).

Evaluation of the effect of initial chromium concentration was investigated in the range of 5, 10, 20, 30, 40 and 50 mg/L at pH values between 4.0-5.0. The contact time was kept at 3hrs with adsorbent doses of 1g in 100ml Cr (VI) solution and at 24°C. The solution was then filtered and filtrate analyzed for Cr (VI) concentration.

2.5 Desorption studies
Desorption of chromium ion from the used acacia tree charcoal was studied by agitation of 0.5g of contaminated material with 50 ml, 2M HNO₃ at 30°C at 150 rpm for 3 hrs. The mixture was then filtered using a Whatman filter paper and the filtrate analyzed for the recovered Cr (VI).

2.6 Modeling
To evaluate the adsorption mechanism, and adsorption capacity, the data obtained from the adsorption experiments were fitted into first-pseudo and second-pseudo Kinetic models and Langmuir and Freundlich adsorption models.

3. Results and Discussion

3.1 Characterization of the adsorbent
The physical and chemical analysis of the adsorbent was carried out and the results are presented in Table 1.

Table 1: Chemical characterization of acacia charcoal

Constituents	% by weight
CaO	3.00 %
K₂O	0.55 %
Loss on ignition (LOI)	95.00 %
Density (g/cm³)	0.21
Porosity	0.19

Table 1 shows that loss of ignition accounts for more than 95% of the total weight, which may be associated to carbon. The value of porosity reveals that the adsorbent is adequately porous nature.

3.2 Effect of Contact time
The effects of the contact time on chromium sorption are shown in figure 1. Results show that the rate of chromium ion removal is rapid in the initial and thereafter chromium removal becomes relatively constant. Initial Cr (VI) uptake of 1.31 mg/g and 2.61 mg/g for 20 and 50 mg/l concentrations were observed in just 1 minute (Figure.1).This is probably due to the availability of large number of active binding sites initially available in the charcoal adsorbent and consequently large numbers of Cr (VI) ions are bound onto the charcoal.
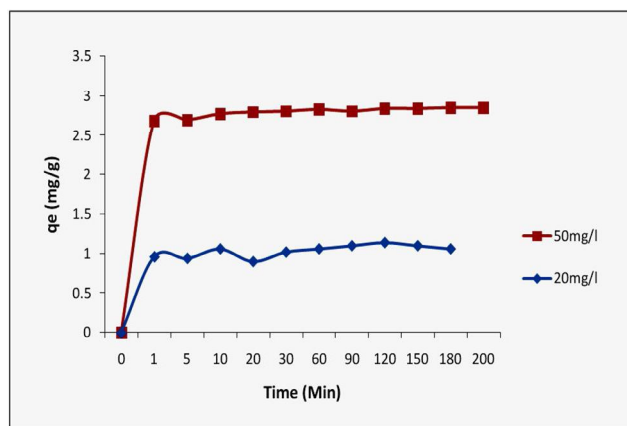

Fig.1. Effect of contact time on Cr+ removal on acacia charcoal at 20 and 50 mg/L concentrations

As the contact time increases the Cr (VI) removal rate decreases, as the sites available for adsorption begin to decrease. This could also be attributed to the formation of repulsive forces between the chromium on the solid surface and the liquid phase [1].
Equilibrium time of chromium ion was observed to have been obtained within 120 min. At equilibrium time, Cr (VI) uptake of 1.41 mg/g and 2.84 mg/g was attained for 20 and 50 mg/l concentrations respectively. However, the equilibrium time was observed to be lower than that obtained from untreated charcoal, which attained

equilibrium at 150 min in Cr (VI) removal [38]. Results also indicate that low initial concentrations of 20 mg/l provided higher Cr (VI) uptake rates than at initial concentrations of 50 mg/l. This may be as a result of higher numbers of chromium ions creating high competition for available adsorbent sites and repulsive forces.

3.3 Effect of Initial Concentration

The effects of initial concentration on removal efficiency of chromium ion by acacia tree charcoal are presented in Figure. 2. 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 chromium removal efficiency was found to be 48.6 %, while at levels of 50mg/l the removal efficiency was at 20.7%. The decrease in percentage Cr (VI) uptake with increase in initial concentration can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration [48]. At lower concentration almost all the metal ions could interact with binding sites facilitating maximum adsorption [49]. As the initial concentration increases, there is an increase in number of metal ions competing for available binding sites. At higher concentration more chromium ions are left unadsorbed in the solution due to saturation of adsorption sites [50], resulting in observed decreased Cr (VI) uptake. Hence the removal of chromium is observed to be dependent on the initial concentration of chromium present in the solution. This corroborates the results obtained using bone charcoal [37].
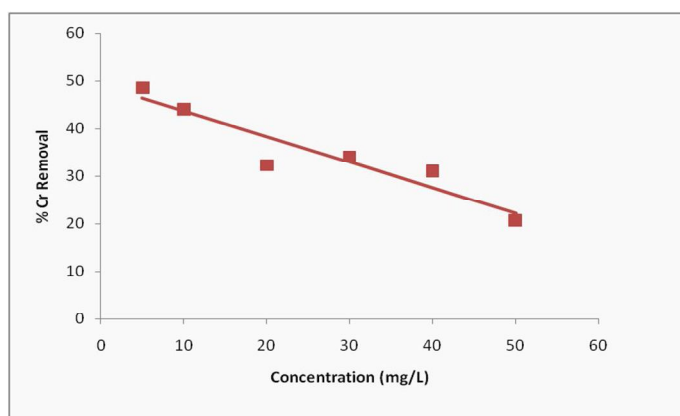

Fig 2. Effect of Initial Chromium concentration (mg/L) on Cr$^+$ removal using acacia tree charcoal (adsorbent: 10g/L, agitation: 180min)

3.4 Effect of pH

Cr (VI) uptake was observed to continuously increase as the pH value increases from 3.0 to 6.0, after which it decreases as the pH value is increased to 10.0 (Figure 3).
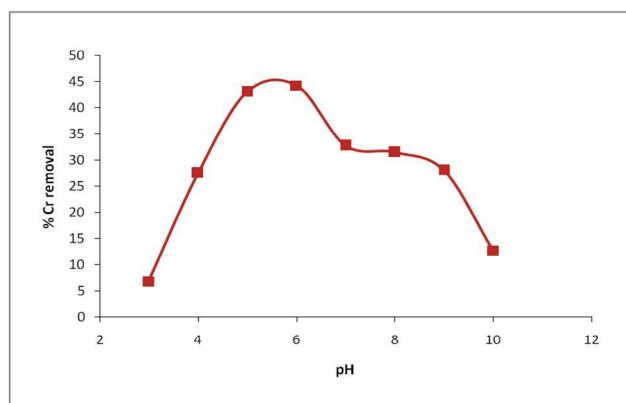

Fig 3. Effect of pH on adsorption of Chromium ions on acacia tree charcoal (Cr$^+$ concentrations: 50mg/L, adsorbent: 10g/L agitation 180min)

The maximum Cr (VI) removal was observed to between pH 5.0 and 6.0, with 42% of Cr (VI) removal being attained at pH 6.0. Solution pH plays a major role in controlling the adsorption process. At very low pH values, the uptake of Cr (VI) was observed to be low. This is may be due to the fact that activated carbon surfaces are closely associated with hydronium ions (H$_3$O$^{+)}$, which restricts approach of metal ions as a result of repulsive forces [41]. As the pH increases from 3 to 5, Cr (VI) ions uptake increases due to more ligands with negative charge being exposed with the subsequent increase in attraction sites to positively charged metal ions. At higher pH values (pH>6), precipitation of metal may occur which could lead to decrease in the adsorption of metal ions. This decrease may be due to the formation of soluble hydroxyl complexes. Similar literature studies conducted indicated maximum adsorption at pH 5, as precipitation of Cr (VI) in aqueous solution was observed at higher pH [30], [46].

3.5 Adsorption Kinetic study

The kinetics of Cr (VI) adsorption process onto acacia tree charcoal was analyzed using pseudo-first-order and pseudo-second-order kinetic models. Adsorption kinetics not only describes the adsorption mechanism of metals on adsorbents but also describe the metal adsorption rate which controls the contact time of metals at the solid-liquid interface [19].

3.5.1 Pseudo-first-order model

The pseudo-first-order kinetic model can be expressed linearly as [32], [19]:

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

Where q_e and q_t are the amounts of metal 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 Figure 4. The linear plot of the experimental data and the calculated parameters are summarized in Table 2. It was observed that the experimental data is not well fitted to the pseudo- first-order kinetic equation (R^2<0.552). The regression coefficient indicates that the adsorption process of Cr (VI) on acacia charcoal is not a first-order reaction.
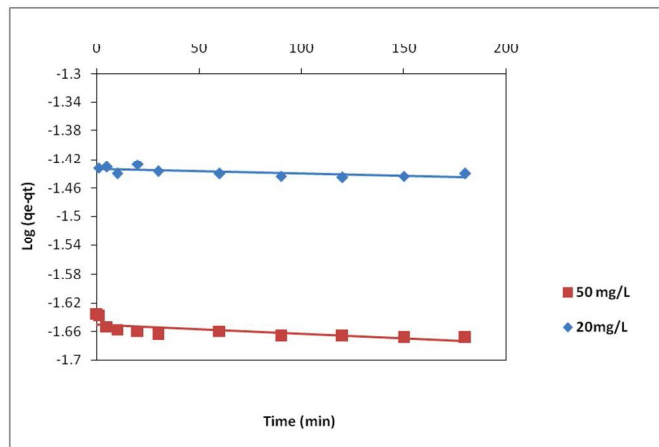

Fig. 4. Linear plot of Pseudo-first-order equations of Chromium ions adsorption on acacia charcoal at 20 and 50 mg/l concentrations

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

Parameter	First –order Kinetic Model			Second-order Kinetic Model				
Initial Cr (VI) Concentration. (mg/L)	K_1 (1/min)	$q_{e \cdot cal}*$ (mg/g)	R^2	K_2 (mg min)	$q_{e \cdot cal}*$ (mg/g)	h	R^2	$q_{e \cdot exp}**$ (mg/g)
50	0.0002	0.022	0.552	4.031	0.025	0.003	0.983	0.028
20	0.0002	0.037	0.480	11.205	0.012	0.002	0.987	0.011

$q_{e \cdot cal}*$- calculated values of q_e; $q_{e \cdot exp}**$ -experimental values of q_e

3.5.2 Second -pseudo -order model

The pseudo-second-order equation can be represented in the linear form as [19]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

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

$$h = K_2 q_e^2 \qquad (4)$$

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 Figure 5. The calculated parameters for the data of second-order-kinetic model are summarized in Table 2. Results indicated a good fit (R^2>0.983) 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) on the acacia charcoal follows the pseudo-second-order kinetic model. As the initial concentration of Cr (VI) increases adsorption capacity at equilibrium q_e and the initial sorption rate (h) increases, while the adsorption rate (K) decreases.
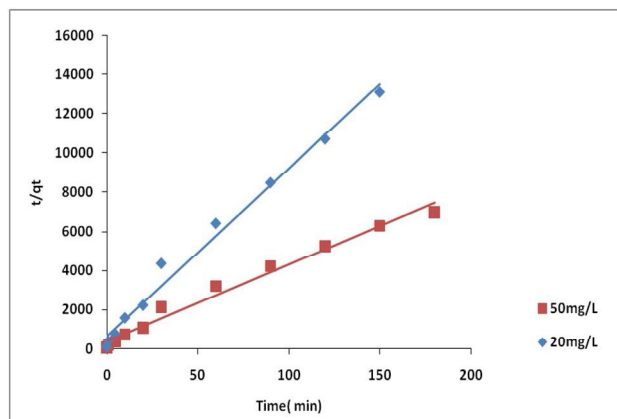

Fig. 5. Linear plot of Pseudo-Second-order equation for Chromium ions adsorption on acacia charcoal at 20mg/l and 50 mg/l concentrations

3.6 Adsorption Isotherms

Adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate. The adsorption isotherm relates the amount of adsorbate on the adsorbent as a function of its pressure or concentration at constant temperature. To describe the experimental data, the most widely accepted adsorption models for single solute systems, Langmuir and Freundlich isotherms, were used.

3.6.1 Langmuir Isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. The model assumes that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface. In addition, it assumes that the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane [20], [26]. The linear form of Langmuir isotherm model is described as:

$$C_e\big/q_e = 1\big/K_L q_m + C_e\big/q_m \qquad (5)$$

Where C_e is the equilibrium concentration in liquid phase (mg/l), q_e is the amount of metal ion adsorbed at equilibrium (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 [2], [6].

The slope and intercept of plots of C_e/q_e versus C_e (Fig.6) were used to calculate q_m and K_L and the Langmuir isotherm parameters are summarized in Table.3. The maximum monolayer adsorption capacity, q_m were found to be 9.009 and 1.536 mg/g for 20 and 50 mg/L Cr (VI) concentrations respectively. The correlation Coefficients ($R^2 = 0.999$) clearly suggest that the adsorption of Cr (VI) ions onto acacia charcoal follows the Langmuir isotherm.
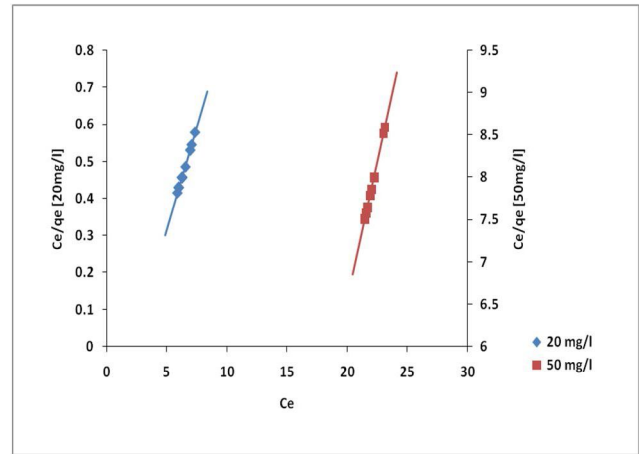

Fig.6. Langmuir Isotherm of Chromium ions adsorption on acacia charcoal at 20 mg/L and 50 mg/L concentrations.

Table 3: Parameters of the Langmuir and Freundlich isotherm

Parameter	Langmuir isotherm				Freundlich Isotherm		
Initial Cr+ Concentration (mg/L)	q_m	K_L	R_L	R^2	K_F	n	R^2
50	1.536	0.101	0.003	0.999	33.497	1.245	0.999
20	9.009	0.461	0.172	0.999	3.365	2.045	0.998

Separation factor, R_L, is a dimensionless constant which is essential characteristic of Langmuir isotherm model. The separation factor was calculated as the following equation:

$$R_L = 1\big/1 + K_L C_i \qquad (6)$$

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_L value based on isotherm

R_L Value	Type of Isotherm
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable
$R_L = 1$	Linear

$R_L > 1$	Unfavorable

The calculated Values of R_L was found to be 0.172 and 0.003 for initial concentrations of Cr+ of 20 mg/L and 50 mg/L respectively. This confirms that the isotherm shape is favorable for Cr (VI) ion adsorption on acacia charcoal [32], [33].

3.6.2 Freundlich isotherm

The Freundlich isotherm is an empirical model that is based on adsorption on heterogonous surface and is an indicator of the extent of heterogeneity of the adsorbent surface. The linear form of Freundlich isotherm is expressed as [40], [24]:

$$Inq_e = InK_f + \frac{1}{n}InC_e \qquad (7)$$

Where, q_e represents the amount of adsorbed metal ions 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.

Freundlich equilibrium constants were determined from the plot of log q_e against log C_e (Fig.7) and the calculated parameters shown in Table 3. Based on the correlation coefficients values ($R^2 > 0.998$), the Freundlich isotherm model fitted well with the experimental data. The Freundlich constants K_f were found to be 3.365 and 33.497 for concentrations of 20 and 50 mg/L. The n value indicates the degree of nonlinearity between solution concentration and adsorption as shown in Table. 5 [3].
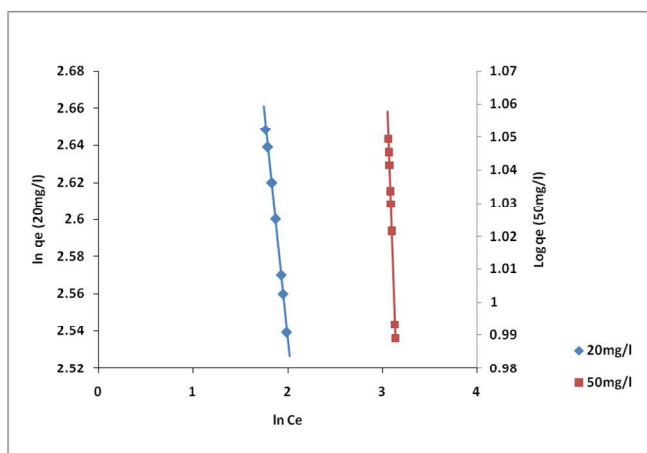
Fig.7. Freundlich isotherm of Chromium ions adsorption on acacia charcoal at 20 and 50 mg/L concentrations

Table.5: *n value based on isotherm*

n value	Type of isotherm

$n < 1$	Chemical Process
$n = 1$	Linear
$n > 1$	Physical process

High value of n indicates a strong bond between the adsorbent and the adsorbate [44] and if $n > 1$, this indicates a favorable sorption process [19], [21],[28]. The observed n values were higher than 1.0, indicating the physical biosorption of chromium ions onto acacia tree charcoal and that it is a favourable sorption process as $n > 1$.

3.7 Desorption of Cr (VI)

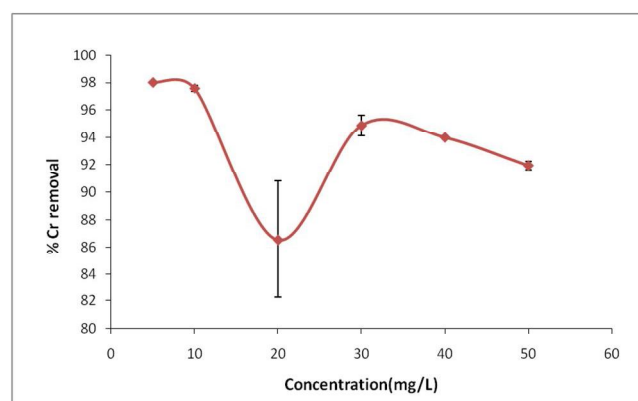Cr (VI) recovered from the acacia charcoal was presented as shown in Fig 8.

Fig. 8. Desorption of Chromium ions from acacia tree charcoal using 2M HNO$_3$.

Desorption studies of used adsorbents have been conducted to reduce the cost of operation in water treatment by ensuring the reuse of the adsorbents as well as recovering precious metals. The graph results indicated that the use of 2M HNO$_3$ is a good reagent for desorption of Cr (VI) ions, because we could get more than 92 % desorption. This also indicates that the adsorption of Cr (VI) ions process is a physical process, since H$^+$ released from the acids replaces the Cr (VI) ions on surface of the acacia tree charcoal. Literature observations indicate that adsorbed metals on adsorbents cannot be completely reversible [7], [11]. It is also observed that at low initial concentrations of 5 mg/L, the adsorbent adsorbed the most Cr (VI) ions at 48% (Fig. 2), and desorption provided the highest Cr (VI) ions removal. Desorption of Cr (VI) ions using 2M HNO$_3$ indicated that the adsorption is by physisorption mechanisms [5], [25], [47].The lowest value of Cr (VI) removal was observed at 20mg/L, which may be attributed to experimental error as indicated by the error bars.

4. Conclusion

The research investigated the use of untreated acacia tree charcoal to adsorb chromium (VI) ions from aqueous solutions in batch experiments. The adsorption was found to be dependent on initial metal ion concentration, pH and agitation time. Chromium adsorption increased with increase in contact time. Equilibrium was attained in 1 minute, and acacia tree charcoal was observed to be able to adsorb 2.7 mg/g (54%) and 1.3 mg/g (65%) of Cr (VI) at concentrations of 50 and 20 mg/L respectively. It can be concluded that acacia tree charcoal has a high capacity for Cr (VI) removal, although it presents lower values compared to other activated charcoal studies. Maximum Cr (VI) removal was achieved between pH 5.0 and 6.0. Chromium adsorption onto the acacia tree charcoal decreased with increase in the initial concentrations of Cr (VI). The adsorption of Cr(VI) onto acacia tree charcoal follows a pseudo- second-order kinetics and shows good fits with both the Langmuir (R^2=0.999) and Freundlich (R^2>0.998) isotherm models. Desorption studies conducted with 2M HNO_3 showed possibility of regeneration capacities of Cr (VI) at values higher than 92%. As the acacia tree is abundantly available in this region, it can be concluded that it provides a low cost favorable option for Cr (VI) removal in aqueous solution. However, replanting the trees should be encouraged to minimize negative environmental effects due to deforestation.

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