POTENTIAL OF BANANA PEELS (MUSA SAPIENTUM BIOMASS) IN ADSORPTION OF HEXAVALENT CHROMIUM: EQUILIBRIUM AND KINETIC STUDY

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ABSTRACT

Chromium heavy metal released into the environment has caused serious contamination of water and soils with significant environmental and occupational concerns. The removal of the Cr (VI) ions from aqueous solutions is investigated in this study using of banana peels (Musa Sapientum Biomass) as a low cost biosorbent material. Sorption of Cr (VI) onto banana peels was carried out in batch at room temperature, with parameters of initial Cr (VI) concentrations and contact time being investigated. The removal of Cr (VI) was observed to increasewith increasing contact time, and reduce with increasing initial Cr (VI) chromium concentration. Kinetic model simulations showed that the pseudo-second –order kinetic model (R^2>0.998) best describes the kinetic sorption of Cr (VI) onto banana peels. Adsorption isotherm models results also indicated Langmuir (R^2>0.997) and Freundlich (R^2>0.988) modesl agreevery well with experimental data. The R_L(0.004 and 0.29) and n (1.328 and 2.967) values observed proved the favorability of Cr (VI) adsorption onto banana peels.

Keywords: Chromium ions, Banana peels, Adsorption isotherms.
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1. INTRODUCTION

Water is a precious natural resource, vital for life, development and the environment. Water resources 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 (Rodda, [17]). 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 (Winters, [23]). 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 concentration 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 (Mancuso and Hueper, [9]).

Chromium ion mainly occurs in two forms; Trivalent (CrIII) 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 (Hlihor and Gavrilescu, [5]). According to the World Health Organisation (WHO, [24]), 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 chromium removal in wastewater include chemical precipitation, chemical oxidation or reduction,

filtration, ion exchange, adsorption, electrochemical treatment and membrane technology (Song *et al*., [19]; Tiravanti*et al.,* [21]).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 (Evangelou, [4]; Parineeta&Shubhangi, [13]). Adsorption operations using activated carbon, silica gel, and alumina are widely used in industrial applications of water and wastewater purification.However, these industrial adsorbents are expensive, especially for developing countries, resulting in a need to study alternative substitutes of adsorbents which are low cost. Researchers have been studied some of these low cost biosorbent including the use of coal, sawdust, hazelnut, rice husks and coffee husks (Castro *et al.,* [3]; Memon*et al.,* [11]; Ramos *et al*., [15]; Valdimir& Danish, [22]).

This study evaluate the feasibility of banana peels for the removal of Cr (VI) from aqueous solution using batch studies, and investigate the influences of experimental parameters of contact time and initial Cr (VI) concentrations on adsorption. It also seeks to develop an understanding of controlling reaction pathways and mechanism, as well as quantify the adsorptive capacity of the adsorbent. This is done using first-pseudo and second- pseudo kinetic models and Langmuir and Freundlich isotherm models. Results of this study can be utilized in assessing the ability of banana peels for chromium heavy metal at the field scale.

2. MATERIALS AND METHODS

2.1 Preparation of Absorbate

Chromium (VI) stock solution was prepared by dissolving Potassium Dichromate (K_2CrO_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 Banana peels adsorbent

Banana peels (*Musa Sapientum*biomass),and mature banana with yellow peel, were collected from a local market in Juja, Kenya. The biomass was dried in the sun for fifteen days and then washed with tap water to remove any dust or foreign particles attached to biomass. The biomass was then thoroughly rinsed with distilled water. The washed biomass was cut into small pieces (1-2 cm) and was then oven dried at 100°C for 24h. Finally the biomass was ground to powder with a kitchen grinder and sieved to particle size fraction of 100 mesh size (0.150mm).

2.3 Analysis

The concentrations of chromium in the solutions before and after equilibrium were determined by Perkin –Elmer 3100 Atomic adsorption spectrometer 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.

2.4 Adsorption experiment

Batch adsorption experiments were performed by contacting 1g of banana peels, with a rangeof different concentrations of Cr (VI) solution from 5-50 mg/l.The adsorbent was agitated in 100 ml of the Cr(VI) solution. Agitation contact time was kept for 3 hrs with a constant agitation speed of 150 rpm at room temperature. A pH value between 4.0 and 5.0 was 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 was analyzed to evaluate the amount of Cr (VI) adsorbed. The Cr (VI) concentration retained in the adsorbent phase was calculated using equation 1:

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

Where, q_e is the Cr (VI)adsorbed (mg/g), C_i and C_e are the initial and final concentration (mg/l) of Cr (VI) solution respectively; V is the volume and W is the dry weight of biosorbent.

2.4.1 Effect of time

To evaluate the effect of time, 3g of banana peels was contacted with 300ml stock chromium solution of concentration 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.

2.4.2 Effect of initial concentration

Evaluation of the effect of initial Cr (VI) concentration was investigated in the range of 5 - 50 mg/l at pH values between 4 .0-5.0. The contact time was kept at 3hrs with adsorbent doses of 0.01g/ml and at room temperatures. The solution was then filtered and filtrateanalysed for Cr (VI).

3. RESULTS AND DISCUSSION

3.1 Effect of Contact time

Effect of contact time on chromium sorption was carried out at time interval 1-180 min and the adsorbed Cr (VI) is shown in Figure1 in terms of % Cr(VI) uptake and Cr(VI) uptake in mg/g.

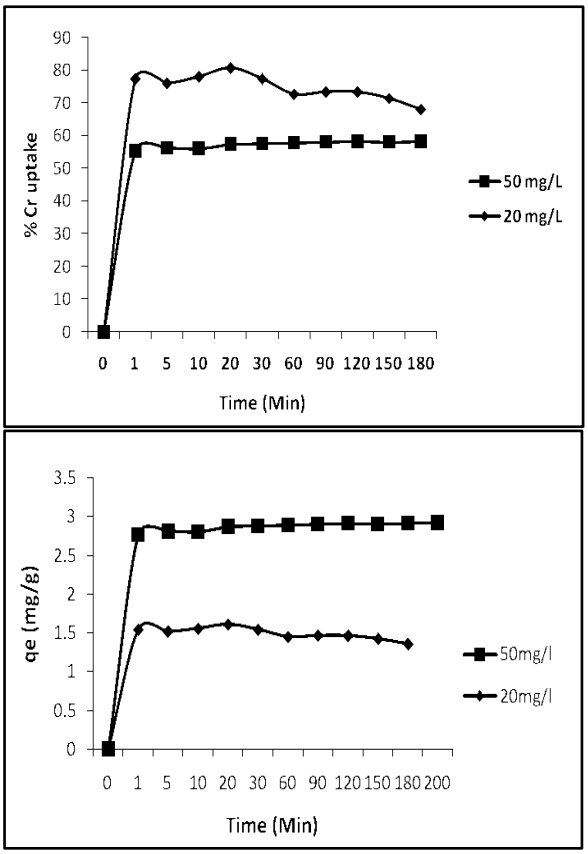

Fig.1: Effect of contact time on % Cr (VI) removal by acacia charcoal at 20 and 50 mg/l concentration (adsorbent: 0.01 g/ml, agitation: 180 min)

The plot reveals that the rate of chromium ion removal is rapid in the beginning, with Cr (VI) uptake of 77.3% and 55.3% for 20 and 50mg/l concentrations in just 1 minute (Figure 1). This was then followed by a slow increase and thereafter the rate of Cr (VI) removal tends to become relatively constant. This is probably due to the availability of large number of active binding sites initially in the banana peel adsorbent and consequently large numbers of Cr (VI) are bound onto the banana peel. The equilibrium time of Cr (VI) was observed to have been obtained within 20 min. Similar trends of equilibrium time were also observed in studies conducted by Memon*et al*., [11] in Cr (III) removal.Results also showed that low initial concentrations of 20 mg/l indicated higher Cr (VI) removal rates than at initial concentrations of 50 mg/l. Cr (VI) uptake of 80.6 %(1.6mg/g) and 57.3% (2.9mg/g) was attained at 20min.This Cr (VI) uptake showed similar trends to previous studies conducted using banana peels (Al-Azzawi*et al.*,[2]; Memon*et al.*,[11]; Memon*et al.*,[10]). Banana peels uptake of Cr (III) of 60-79% at higher adsorbate concentrations (10-100 mg L^{-1}) and 80-99% at lower adsorbate concentrations (0.5-8 mg L^{-1}) have been observed (Memon*et al.*,[11]). Hence, with uptake rates of 58%, banana peels is reflected as an efficient adsorbent material for the removal Cr (VI) from aqueous solution.

At concentrations of 20mg/l the adsorption was observed to decrease after 20 min. This decrease may be associated with temperature changes. Studies conducted have shown Cr (VI) adsorption onto activated carbon to be an endothermic process (Wu et al., [25]; Tamirat et al., [20]). At higher temperatures the energy of system facilitates the chromium (VI) attachments onto biosorbent surfaces. Therefore, at low temperature, the adsorption sites with lower active energy were occupied first, and the other sites with higher active energy had decreased adsorption rates. Higher adsorption rates in the first 20 min may have been as a result of high temperature. The higher temperature may have resulted to an increase in the rate of intraparticle diffusion of Cr (VI) into the pores of the adsorbent, which indicates that

the diffusion reactions play an important role in the process of adsorption (Lyubchik et al., [8]). As the temperature decreased after 20 min, the rate of adsorption was observed to decrease due to decreased active energy.

3.2 Effect of Initial Concentration

The effect of initial concentration on removal of Cr (VI)ion on the adsorption efficiency by banana peels was investigated as shown 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 Cr (VI)removal efficiency was found to be 53 %, while at levels of 50 mg/l the removal efficiency was at 35%.This indicates that the removal of Cr (VI)is dependent on the initial concentration of Cr (VI)present in the solution.

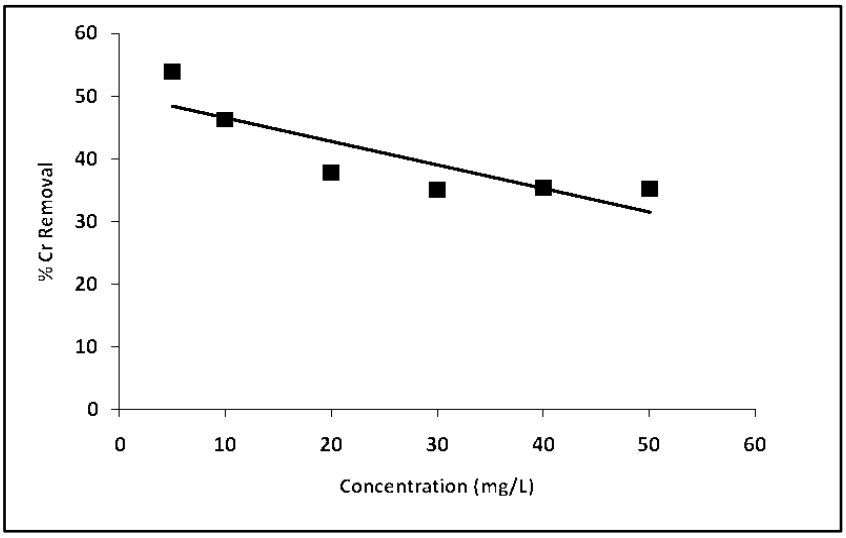

Fig. 2: Effect of Initial concentration on Cr (VI)removal (adsorbent: 0.01g/ml, Initial Concentration: 50 mg/l, agitation: 180min)

It was also observed that the removal efficiencies at initial concentrations of 20mg/l and 50mg/l were lower than efficiencies recorded in the analysis of contact time. With the adsorbent doses being kept at 0.01g/ml for both studies, the differences in the removal efficiencies may be due to variances in temperature changes. This may also be as a result of the amounts of adsorbent dosage used of 1g/100ml compared to the adsorbent dosage used in the effect of contact time of 3g/300ml. The adsorbent amount of 1g/100ml was utilized for the full 180 min in evaluating the effect of initial concentration, while in the evaluation of contact time; subsequent sampling of the solution at time interval may have resulted in high adsorbent being available in the residual solution. This may have resulted to higher removal efficiencies as a larger amount of banana peel adsorbent was available.

3.3 Adsorption Kinetic study

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

3.3.1 Pseudo-first-order model

The pseudo-first-order kinetic model can be expressed linearly as (Ho and McKay, [7]):

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

Where qe and qt 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 (qe-qt) against t as shown in Figure 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 as the R^2 values were low (R^2<0.676). This hence shows that the adsorption process of Cr (VI)onto banana peels is not a first-order reaction.

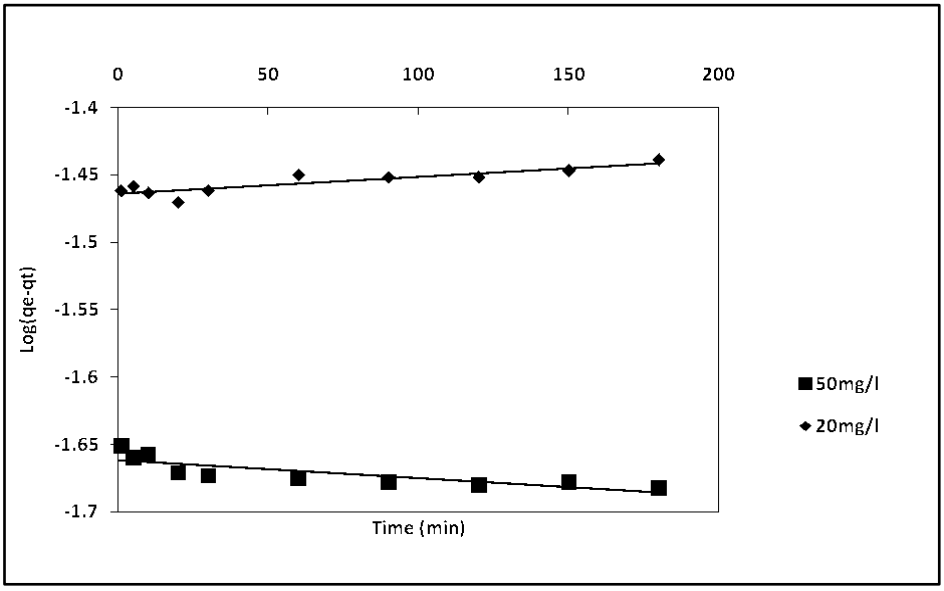

Fig. 3: Linear plot of Pseudo-first-order equations of Cr (VI)Ions adsorption on banana peels at 20 and 50 mg/l concentrations.

3.3.2 Pseudo- Second-order model

The pseudo-second-order equation can be represented in the linear form as (Ho & McKay, [7]):

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (3)$$

Where, K2 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:

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

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 4. The calculate parameters for the data of second-order-kinetic model were summarized in Table 1. Results indicated a good fit (R^2>0.998) 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 banana peels 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.

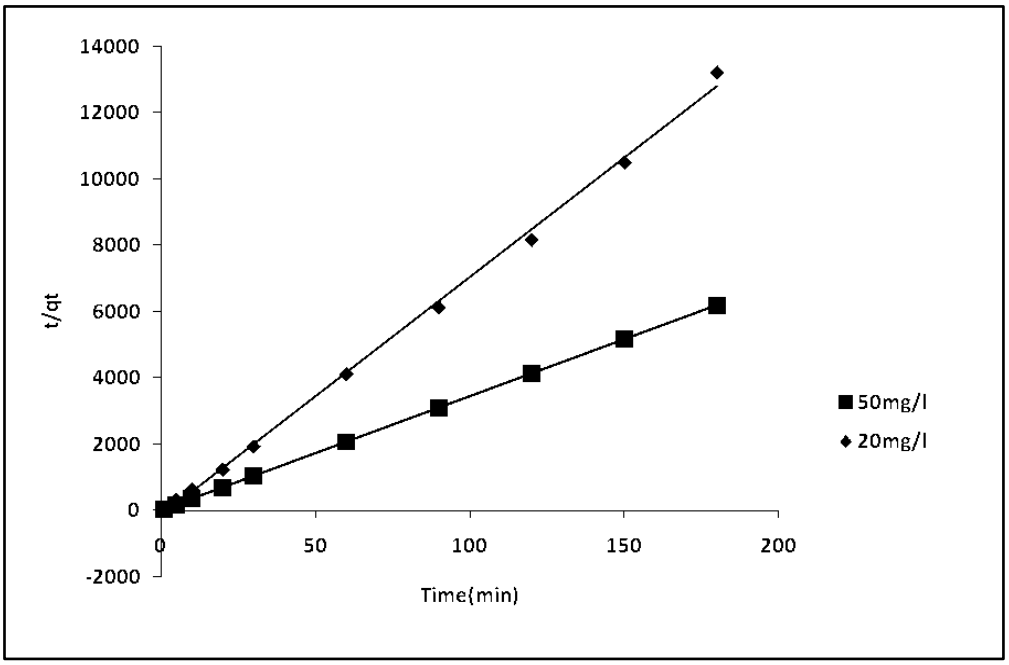

Fig. 4: Linear plot of Pseudo-Second-order equation for Cr (VI)adsorption on banana peels at 20 and 50 mg/l concentrations

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

Parameter	First –order Kinetic Model			Second-order Kinetic Model				q_e ,Exp (mg/g)
Initial Cr(VI) Conc.	K_1 (1/min)	q_e,cal (mg/g)	R^2	K_2 (mg min)	q_e,cal (mg/g)	h	R^2	
50 (mg/L)	0.0002	0.022	0.676	96.821	0.029	0.082	1.000	0.028
20 (mg/L)	0.0002	0.034	0.785	33.498	0.014	0.006	0.998	0.011

q_e ,cal*- calculated values of q_e; q_e, exp** -experimental values of q_e

3.4 Adsorption Isotherms

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

3.4.1Langmuir 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 (Pehlivan and Cetin, [14]):

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

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 (Ageyi*et al.*,[1]).

The slope and intercept of plots of C_e/q_e versus K_L (Figure 5.) were used to calculate q_m and K_L and the Langmuir isotherm parameters are summarized in Table. 4. The maximum monolayer adsorption capacity, $q_m$was found to be 1.626and 11.111 mg/g for 20 and 50mg/L Cr (VI)Concentrations respectively. The correlation coefficients ($R^2 > 0.997$) clearly suggest that the adsorption of Cr (VI)onto banana peels follows the Langmuir isotherm.

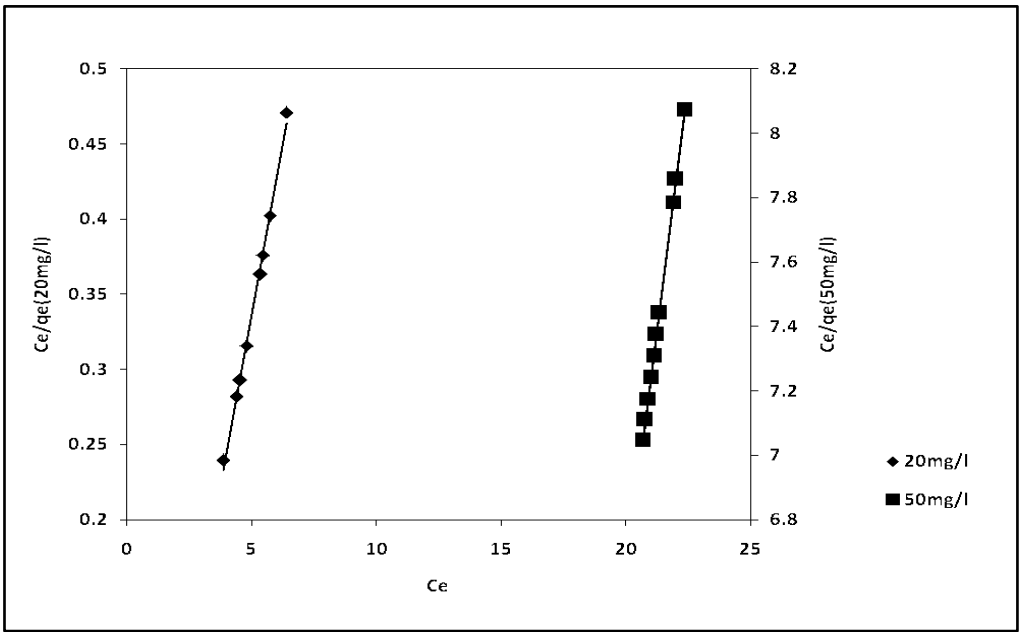

Fig. 5: Langmuir Isotherm of Cr (VI)adsorption onto banana peels at 20 and 50 mg/l concentrations

The separation factor was calculated as the following equation:

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

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.2. The calculated values of R_L were found to be 0.299 and 0.004 for initial concentrations of Cr (VI)of 20mg/L and 50mg/L respectively. This confirms that Cr (VI)adsorption onto banana peels is favorable (Samarghandi*et al*., [18]).

Table.2 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

3.4.2 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 (Panahi*et al*., [12]):

$$\log q_e = \log K_f + {}^{1}/_{n} \log C_E \qquad (7)$$

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.

Freundlich equilibrium constants were determined from the plot of log qe against log C_e (Figure 6) and the calculated parameters shown in Table 3.

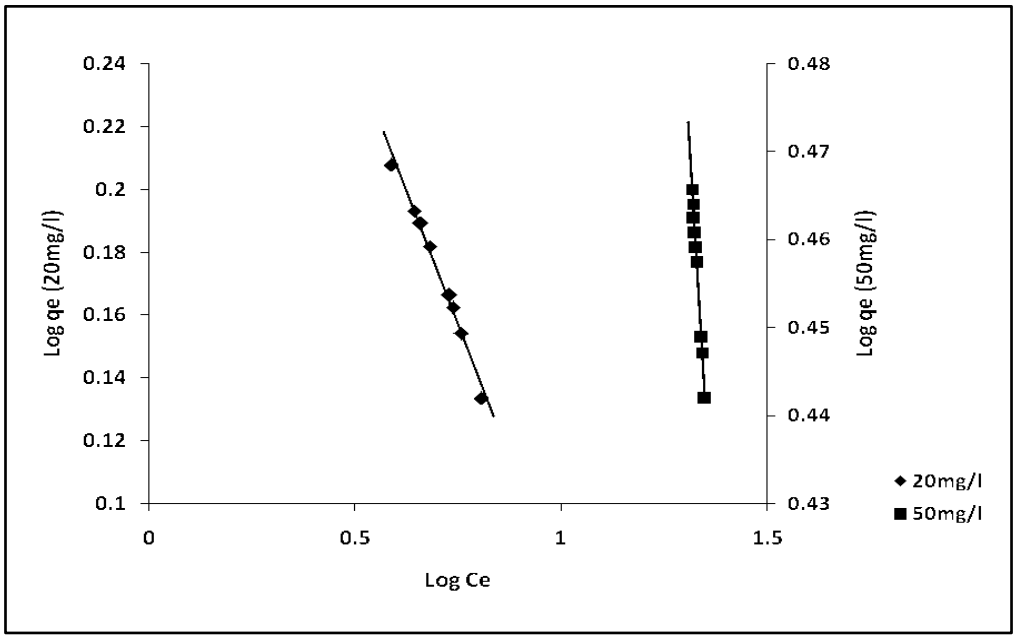

Fig.6:Freundlich Isotherm of Cr (VI)adsorption onto banana peels at 20 and 50 mg/l concentrations

Table 3: Parameters of the Langmuir and Freundlich isotherm

Parameter	Langmuir isotherm				Freundlich Isotherm		
Initial Cr+ Conc.	q_m	K_L	R_L	R^2	K_F	n	R^2
50 (mg/L)	1.626	0.108	0.004	0.999	28.708	1.328	0.999
20 (mg/L)	11.111	0.769	0.299	0.997	2.564	2.967	0.988

Based on the correlation coefficients values (R^2> 0.988), the Freundlich isotherm model fitted well with the experimental data. The Freundlich constants K_f were found to be 2.564 and 28.708 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 (Yakubu*et al.*,[25]), and if *n*> 1, this indicates a favorable sorption process (Ho &McKay,[7];

Huang *et al.*,[8]). The observed *n* values were higher than 1.0, indicating the physical biosorption of chromium ions onto banana peels and that its is a favourable process.

4. CONCLUSIONS

The research presents batch studies investigations on the use of banana peels (*Musa Sapientum*biomass)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 in20 minutes, and banana peels was observed to be able to adsorb 2.9 mg/g of Cr (VI)at concentrations of 50 mg/L. Cr (VI)adsorption onto banana peels was also observed to decrease as the initial concentrations of chromium increased. The adsorption Cr (VI) onto banana peels follows a pseudo- second-order kinetics and shows good fits with both the Langmuir (R^2> 0.997,q_m>1.626) and Freundlich (R^2>0.988) isotherm models. This study can conclude that banana peels provide a low cost favorable option from chromium removal in aqueous solution. However, recommendations are made to study the effect of the amount of adsorbate and temperature on the removal efficiency in order realize a good decontamination of leather wastewater.

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