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Batch Removal of Chromium (VI) By Biosorption onto Sugarcane Bagasse (Saccharum Officinarum L.)

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Abstract: In the present study sugarcane baggase (Saccharum officinarum L.) was studied as a cost effective biosorbent for chromium (VI) ions was investigated using batch technique. The effects of operational factors including solution pH, biosorbent dose, initial lead (II) ions concentration, contact time and temperature on the biosorption efficiency were studied. The experimental equilibrium biosorption data were fitted by four widely used two-parameters Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin isotherm equations. Simple kinetic models such as pseudo-first-order, pseudo-second-order, Elovich equation and Weber and Morris intraparticle diffusion rate mixing equation were employed to determine the adsorption mechanism. Thermodynamic studies were also carried out. The results showed that sugarcane baggase (Saccharum officinarum L.) was a low-cost capable sorbent to seize chromium(VI) from wastewater

Keywords: Adsorption kinetics, biosorption, Chromium (VI) ions, Thermodynamic study. Biosorption ,chromium (VI), sugarcane baggase (Saccharum officinarum L.),adsorption isotherm,

I. INTRODUCTION

Environmental pollution by heavy metals because of industrial activities tends to accumulate throughout the food chain which results in serious ecological and health hazard. Heavy metals are non-biodegrable and toxic to all forms of life including humans. Chromium is listed among top pollutants and is ranked 16 th harmful pollutant due to its carcinogenic and teratogenic characteristics on the community (Selomulya et al 1999; Geleel et al 2013). Chromium occurs frequently as Cr (VI) and Cr (III) in aqueous solutions (Dakiky et al 2002).

Hexavalent chromium, which is primary present in the form of chromate (CrO4 2-) and dichromate (Cr2O7 2-) possesses significantly higher level of toxicity than the other valence states (Smith and Lec 1972;Sharma et al 1995). Cr (VI) discharge into the environment can be due to various large numbers of industrial functions like dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining, etc (Pattterson 1985). Major diseases caused by toxic hexavalent chromium ions are bronchial asthma and lung cancer. The conventional methods for removing heavy metal ions from industrial effluents include oxidation/reduction, filtration by membranes, chemical precipitation, coagulation, solvent extraction, cementation, freeze separation, reverse osmosis, ion etc. These methods have found limited application because they often involve high capital and operational cost. The study was extended with the objective for estimation and calculation of various parameters affecting the biosorption such as solution pH, biosorbent dose concentration, initial concentration of heavy metals, contact time, temperature and agitation rate. Adsorption isotherms model and kinetics models was employed to understand the probable biosorption mechanism. Thermodynamic study was also carrying out to estimate the standard free change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0).

II. MATERIALS AND METHODS

Chemical and reagent: All the chemicals and reagents used were of analytical reagent (AR) grade. Double distilled water was used for all experimental work including the preparation of metal solutions. The desired pH of the metal ion solution was adjusted with the help of dilute hydrochloric acid and sodium hydroxide.

A. Preparation of Chromium (VI) Solution

The stock solution of 1000 ppm of chromium (VI) was prepared by dissolving 0.7072 g of potassium dichromate (K Cr O) in 250 ml of double distilled water

B. *Preparartion of Biosorbent*

The Sugarcane bagasse (*Saccharum offcinarum* L.) was collected locally and washed with several times with distilled water to remove the surface adhered particles, dirt, other unwanted material and water soluble impurities and water was squeezed out. The washed biosorbent was then dried at 50^0C overnight and grounded in a mechanical grinder to form a powder. The powder was sieved and a size fraction in the range of 100-200 µm will be used in all the experiments. This powder was soaked (20 g/l) in 0.1 M nitric acid for 1 hour. The mixture was filtered and the powder residue was washed with distilled water, several times to remove any acid contents. This filtered biomass was first dried at room temperature and then dried in an oven at 105ºC for 1-2 hrs. For further use, the dried biomass was stored in air tighten plastic bottle to protect it from moisture.

C. *Instrumentation*

The pH of the solution was measured by digital pH meter (EQUIP-TRONICS, model no. Eq-610) using a combined glass electrode. The concentration of Lead(II) in the solutions before and after equilibrium was determined by using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) technique. Biosorbent was characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM) and X-ray diffraction (XRD).

D. *Experimental Procedure*

The static (batch) method was employed at temperature (300C) to examine the biosorption of Chromium(VI) by biosorbent. The method was used to determine the adsorption capacity, stability of biosorbent and optimum biosorption conditions. The parameters were studied by combining biosorbent with Lead(II) solution in 250 ml separate reagent bottles. The reagent bottles were placed on a shaker with a constant speed and left to equilibrate. The samples were collected at predefined time intervals, centrifuged, the content was separated from the adsorbent by filtration, using Whatmann filter paper and amount of Chromium(VI) in the supernatant/filtrate solutions was determined by ICPAES. The following equation was used to compute the percent removal (% Adsorption) of chromium (VI) by the adsorbent,

$$\%\ \mathrm{Ad} = \frac{(\mathrm{C_i} - \mathrm{C_e})}{\mathrm{C_i}} \times 100$$

where C_i and C_e are the initial concentrations and equilibrium concentrations of the Lead(II) in mg/L. The equilibrium adsorptive quantity (qe) was determined by the following equation,

$$\boldsymbol{q_e} = \frac{(C_i - C_e)}{w} \times \boldsymbol{V}$$

where q_e (mg metal per g dry biosorbent) is the amount of chromium (VI) biosorbed, V (in liter) is the solution volume and w (in gram) is the amount of dry biosorbent used.

III. RESULTS AND DISCUSSION

A. *Effect of pH*

The biosorption capacity of the biosorbent and speciation of metals in the solution is pH dependent. The optimization of pH was done by varying the pH in the range of 1-8 for bisorption of chromium (VI) and pH trend observed in this case is shown in Figure 1. It was found that at pH 3 the biosorption process was maximum with 44.25 % and after increasing pH, biosorption was decreases. As the pH of the solution increases, charges on the surface of biosorbent becomes negative, this leads to generation of repulsive forces between chromium (VI) and biosorbent and inhibits biosorption and resultantly percent chromium (VI) uptake may decrease.

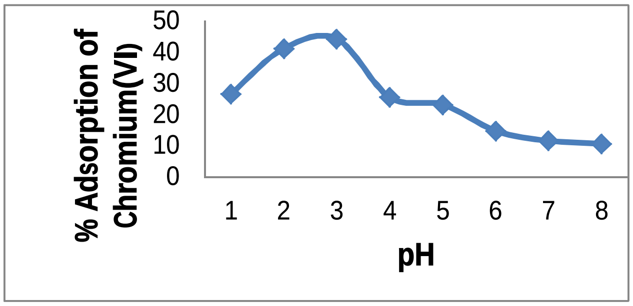


Figure 1: Effect of pH on Chromium(VI) biosorption by Sugarcane bagasse (Saccharum offcinarum L.) (biosorbent dose concentration: 5 g/L, Chromium(VI) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30^0C

A. *Effect Of Biosorbent Dose Concentration*

Biosorbent dosage is an important parameter studied while conducting batch mode studies. The sorption capacity of sugarcane bagasse on to chromium (VI) ions by varying its dosage from 1 g/L to 15 g/L as shown in Figure 2. From the results it was found that biosorption of chromium (VI) ions increases with increase in biosorbent dosage and is highly dependent on biosorbent concentration. Increase in biosorption by increase in biosorbent dose is because of increase of ion exchange site ability, surface areas and the number of available biosorption sites (Naiya et al., 2009). The point of saturation for silica gel immobilized banana peels (L.) was found at 5 g/L of biosorbent dose with 39.72 % of removal efficiency. The biosorbent dose 5 g/L was chosen for all further studies..

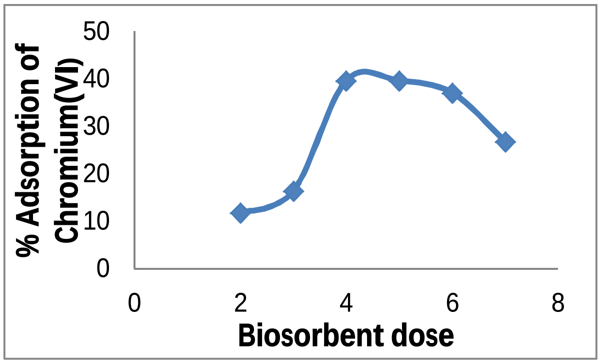


Figure 2: Effect of biosorbent dose concentration on Chromium(VI) biosorption by Sugarcane bagasse (Saccharum offcinarum L.) (biosorbent dose concentration: 5 g/L, Chromium(VI) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30^0C

B. *Effect Of Initial Chromium(Vi) Concentration*

The effect of initial chromium (VI) concentration from 10 mg/L-300 mg/L on the removal of chromium (VI) from aqueous solutions at biosorbent dose 5 g/L and at optimum pH 3 at 30 C was studied. On increasing the initial chromium (VI) ions concentration, the total chromium (VI) ions uptake decreased slightly at chromium (VI) ions concentration ranges from 10 mg/L- 300 mg/L.

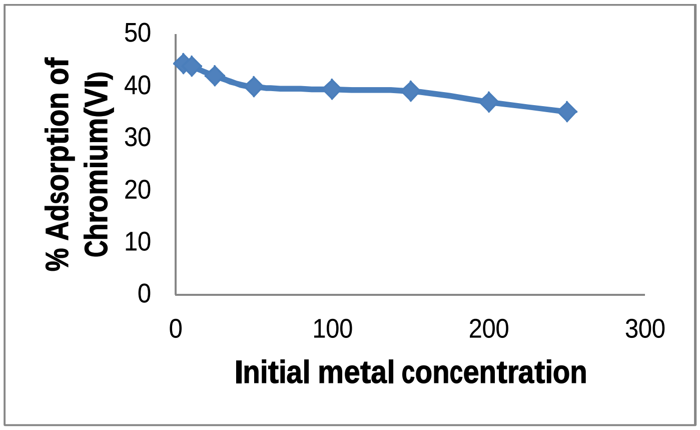


Figure 6: Effect of chromium(VI) concentration on Chromium(VI) biosorption by Sugarcane bagasse (Saccharum offcinarum L.) (biosorbent dose concentration: 5 g/L, Chromium(VI) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30^0C)

C. *Effect Of Contact Time*

In order to optimize the contact time for the maximum uptake of metals ions, contact time was varied between 10 minute-240 minute on the removal of chromium (VI) from aqueous solutions in the concentration of chromium (VI) 10 mg/L and adsorbent dose 5g/L at optimum pH 3.0 at 30 C. The results obtained from the biosorption capacity of chromium (VI) Sugarcane bagasse (Saccharum offcinarum L.) showed that the biosorption increases with increase in contact time until it reached equilibrium. The optimum contact time for biosorption of chromium (VI) ions onto Sugarcane bagasse (Saccharum offcinarum L.) was 180 minutes with 49.60% removal. The rapid uptake of chromium (VI) is due to the availability of ample active sites for sorption. So a contact time of 180 min was fixed for further experiments.

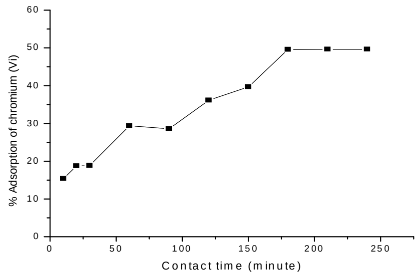


Figure 4: Effect of contact time on Chromium(VI) biosorption by Sugarcane bagasse (Saccharum offcinarum L.) (biosorbent dose concentration: 5 g/L, Chromium(VI) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30^0C)

D. Effect Of Temperature

The effect of temperature on removal of chromium (VI) ions from aqueous solutions using banana peels (L.) was studied at different temperatures from 20^o C-40^o C. The influence of temperature is depicted in Figure 5. Maximum sorption was seen at 30 C with percentage removal 40.63%.

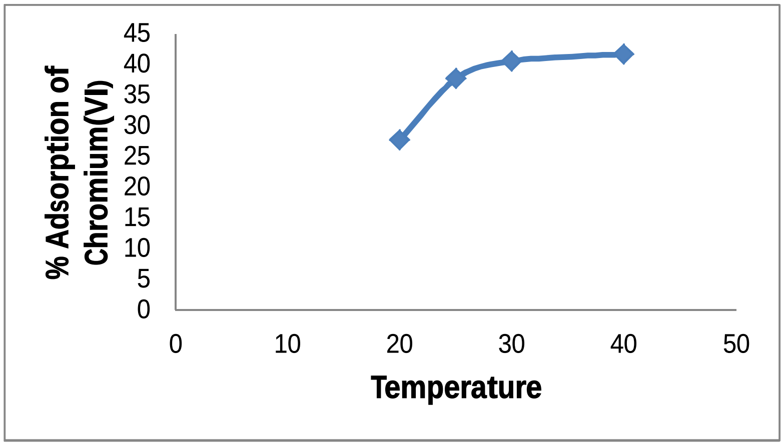


Figure 8: Effect of temperature on Chromium(VI) biosorption by Sugarcane bagasse (Saccharum offcinarum L.) (biosorbent dose concentration: 5 g/L, Chromium(VI) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30^0C)

E. Effect Of Agitation Rate

The effect of agitation rate on removal of chromium (VI) from aqueous solutions at biosorbent dose 5 g/L and at optimum pH 4 was studied at different rpm such as 40 rpm, 80 rpm, 120 rpm, 160 rpm and 200 rpm. The efficiency was highest at 120 rpm with percentage removal 44.25%. So, 120 rpm was chosen for all further biosorption studies

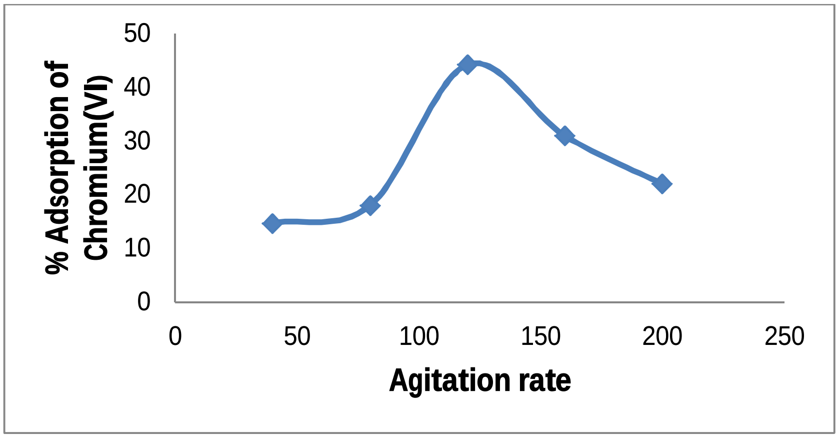


Figure 6: Effect of agitation rate on on Lead (II) biosorption by Sugarcane bagasse (Saccharum offcinarum L.) (biosorbent dose concentration: 5 g/L, Lead (II) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30^0C)

F. Adsorption Isotherm Models

The analysis of the adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. The experimental data were applied to the two-parameter isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin

G. Langmuir Adsorption Isotherm (Langmuir, 1918)

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by:

$$q_e = \frac{q_m\, b\, C_e}{1+bC_e}$$

where qm is the maximum biosorption capacity of adsorbent (mg g-1). b is the Langmuir biosorption constant (L mg-1) related to the affinity between the biosorbent and biosorbate. Linearized Langmuir isotherm allows the calculation of adsorprtion capacities and Langmuir constants and is represented as:

$$\frac{1}{q_e} = \frac{1}{q_m\, b\, C_e} + \frac{1}{q_m}$$

The linear plots of 1/q vs 1/ce is shown in Figure 10 (a). The two constants b and qm are calculated from the slope (1/qm·b) and intercept (1/qm) of the line. The values of qm, b and regression coefficient (R 2) are listed in Table 1.

H. Frenudlich Adsorption Isotherm (Frenudlich, 1939)

Freundlich equation is represented by;

$$q = KC_e^{1/n}$$

where K and n are empirical constants incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively. Linearized Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as

$$\log q_e = \log K + \frac{1}{n}\log C_e$$

Equilibrium data for the adsorption is plotted as log q vs log Ce, as shown in Figure 10 (b). The two constants n and K are calculated from the slope (1/n) and intercept (log K) of the line, respectively. The values of K, 1/n and regression coefficient (R 2) are listed in Table 1

Table 1: Adsorption isotherm constants for Chromium(VI) biosorption by Sugarcane bagasse (Saccharum offcinarum L.)

Langmuir parameters			Freundlich parameters			DKR parameters				Temkin parameters		
q_m	*B*	R^2	*K*	*1/n*	R^2	*B*	q_m	*E*	R^2	A_T	b_T	R^2
57.1428	0.0028	0.9999	7.9359	1.4224	0.9985	$-2\text{x}10^{-5}$	10.2985	0.1581	0.6703	0.1174	438.941	0.8882

Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm (Dubinin and Radushkevich, 1947): Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as;

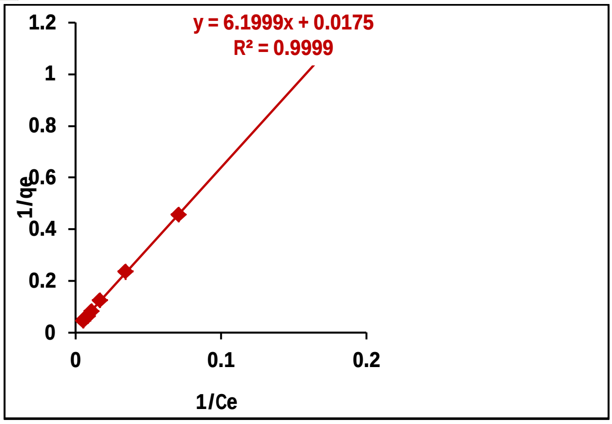
$$\ln q_e = \ln q_m - \beta\, \varepsilon^2$$

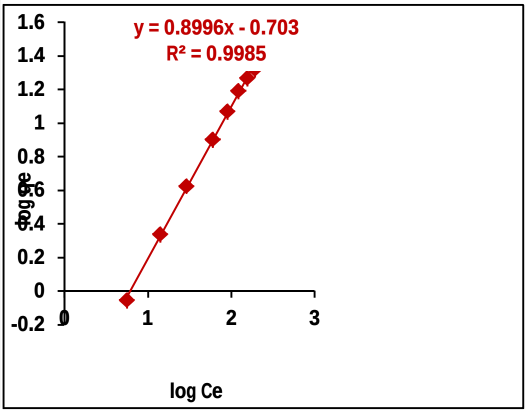
where qm is the maximum biosorption capacity, β is the activity coefficient related to mean biosorption energy and ε is the polanyi potential, which is calculated from the following relation;

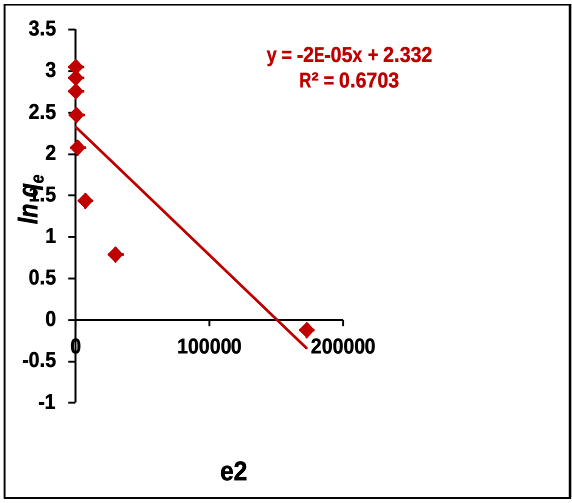
$$\varepsilon == RT\ln\left(1+\frac{1}{C_e}\right) \quad (10)$$

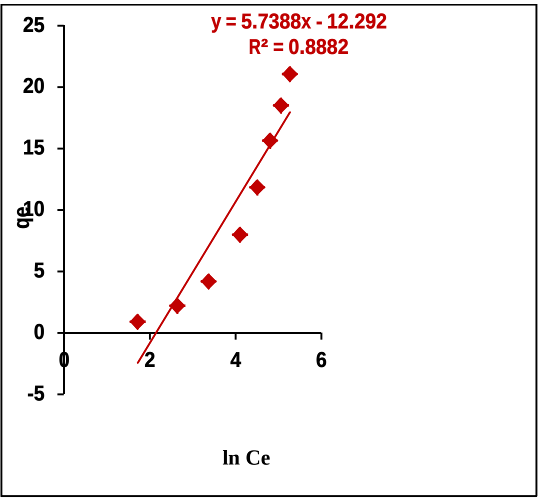
Equilibrium data for the adsorption is plotted as lnqe vs ε2 , as shown in Figure 10 (c). The two constants β and qm are calculated from the slope (β) and intercept (lnqm) of the line, respectively. The values of adsorption energy E was obtained by the following relationship,

$$E = \frac{1}{\sqrt{-2\beta}} \quad (11)$$







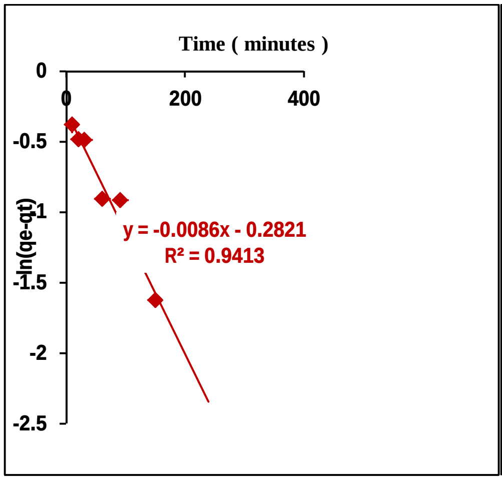


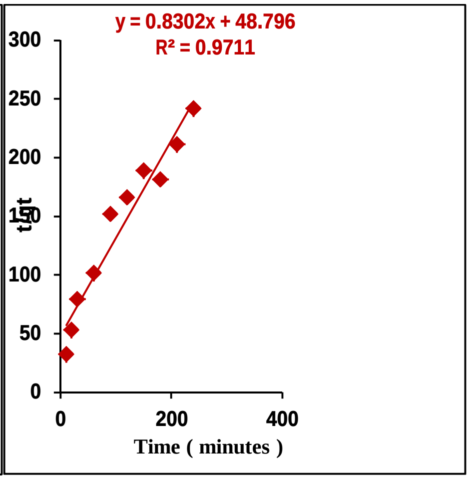
Temkin adsorption isotherm (Temkin and Pyzhev, 1940):

Linearized Temkin adsorption isotherm is given by the equation;

$$q_e = \frac{RT}{b_T}\ln(A_T C_e) \quad (12)$$

where bT is the Temkin constant related to heat of biosorption (J/mol) and AT is the Temkin isotherm constant (L/g). Equilibrium data for the adsorption is plotted as qe vs lnCe, as shown in Figure 10(d). The two constants bT and AT are calculated from the slope (RT/bT) and intercept (RT/bT· lnAT) of the line.





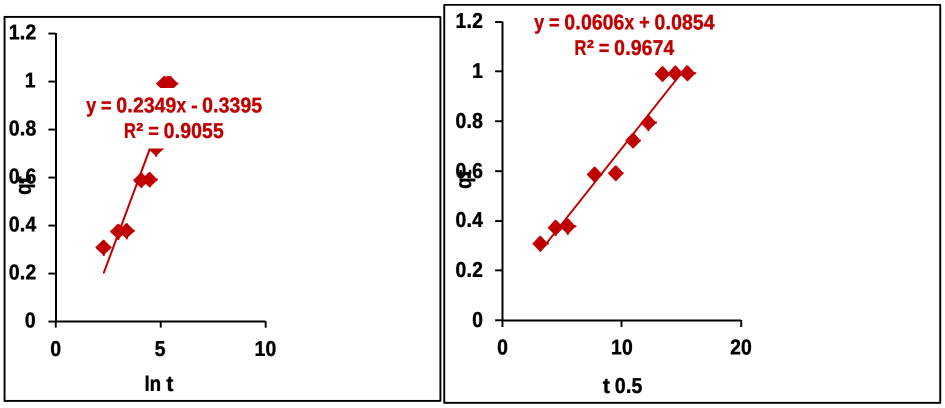


Figure 8: Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffussion equation, for biosorption of Chromium(VI) biosorption by Sugarcane bagasse (Saccharum offcinarum L.) (biosorbent dose concentration: 5 g/L, Chromium(VI) concentration: 10 mg/L, contact time: 180 minutes, temperature: 30^{0}C)

1) *Adsorption Kinetics:* As aforementioned, a lumped analysis of adsorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a) the pseudo-firstorder equation (Lagergren 1898) (b) the pseudosecond-order equation (Mckay et al., 1999) (c) Elovich equation (Chien and Clayton 1980) (d) Weber & Morris intra-particle diffusion equation (Weber and Morris, 1963) are presented below;

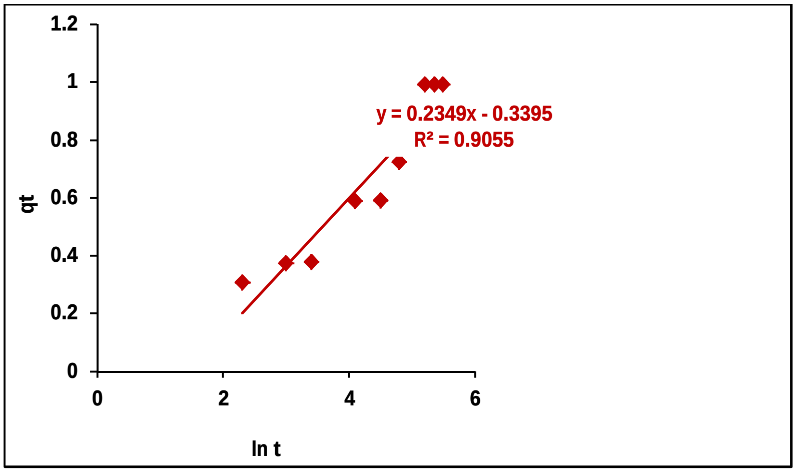


Figure 9: Plot of against for determination of thermodynamic parameters for biosorption of chromium (VI) by sugarcane bagasse (pH: 3.0, biosorbent dose concentration: 5 g/L, chromium (VI) concentration: 10 mg/L, contact time: 180 minutes)

$$\ln(q_e\text{-}q_t) = \ln q_e\text{-}k_1 t$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$$

$$q_t = k_i t^{0.5} + c$$

where qe (mg g-1) is the solid phase concentration at equilibrium, qt (mg g-1) is the average solid phase concentration at time t (min), k1 (min-1) and k2 (g mg-1 min-1) are the pseudo-first-order and pseudo-secondorder rate constants, respectively. The symbols of α (mg g-1 min-1) and β (g mg-1) are Elovich coefficients representing initial biosorption rate and desorption constants, respectively. k_i (mg g-1 min-1/2) is the intraparticle diffusion rate constant, c is intercept.

If the adsorption follows the pseudo-first-order model, a plot of ln (qe-qt) against time t should be a straight line. Similarly, t/qt should change lineally with time t if the adsorption process obeys the pseudo-second order model. If the adsorption process obeys Elovich model, a plot of qt against ln t should be a straight line. Also a plot of qt against t $^{0.5}$ changes lineally the adsorption process obeys the pseudo second order model. Kinetic plots depicted in Figure 8 (a) (b) (c) and (d) (Septhum et al., 2007).

I. Determination Of Thermodynamic

The effect of temperature on removal of Lead(II) from aqueous solutions in the concentration of Lead(II) 10 mg/L and biosorbent dose concentration 5 mg/ml with optimum pH 5.0 was studied. Experiments were carried out at different temperatures from 20^0C-40^0C. The samples were allowed to attain equilibrium. Sorption slightly increases from. The equilibrium constant (Catena and Bright, 1989) at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations;

$$K_c = \frac{C_{Ae}}{C_e}$$

$$\Delta G^0 = -RT \ln K_c$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where Kc is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and CAe is the amount of Lead(II) biosorbed on the biosorbent per liter of solution at equilibrium (mg/L). ΔG^0 , ΔH^0 and ΔS^0 are changes in standard Gibbs free energy (kJ/mol), standard enthalpy (kJ/mol) and standard entropy (J/mol K), respectively. R is the gas constant (8.314 J/mol K) and T is the temperature (K).

Table 2: Adsorption kinetic data for for Chromium(VI) biosorption by Sugarcane bagasse (Saccharum offcinarum L.)

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intraparticle diffusion model		
q_e	k_1	R^2	q_e	k_2	R^2	a	β	R^2	Ki	C	R^2
1.3259	0.0086	0.9413	1.2045	0.0141	0.9711	0.9967	4.2571	0.9055	0.606	0.0854	0.9674

The values of ΔH^0 and ΔS^0 were determined from the slope and the intercept from the plot of lnKc versus 1/T (Figure 12). The values of equilibrium constant (K_c), standard Gibbs free energy change (ΔG0), standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) calculated in this work were presented in Table 3.

Table 3: Thermodynamic parameters of Chromium(VI) biosorption by Polyvinyl alcohol- alginate- Glutaraldehyde immobilized Sugarcane bagasse (Saccharum offcinarum L.)

Sr. No.	Time (min)	K	Kc	$-\Delta G^0$	ΔH^0	ΔS^0
1	20^0C	293	0.3842	2.330	22.999	71.679
2	25^0C	298	0.6059	1.241		
3	30^0C	303	0.6843	0.955		
4	40^0C	313	0.7167	0.861		

IV. CONCLUSIONS

The present investigation revealed that Sugarcane bagasse (Saccharum offcinarum L.) used as inexpensive, excellent biosorbent for the removal of chromium (VI) from aqueous solutions. The optimal parameters such as solution pH, biosorbent dose, agitation rate, initial chromium (VI) concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of chromium (VI) Sugarcane bagasse (Saccharum offcinarum L.)Sorption equilibrium exhibited better fit to Langmuir isotherm than Freundlich isotherm, Temkin isotherm and Dubinin-KaganerRedushkevich (DKR) isotherm. The maximum chromium (VI) loading capacity of Sugarcane bagasse (Saccharum offcinarum L.) determined from Langmuir adsorption isotherm was found to be 57.14 mg g . The second order model was found to be correlate the experimental data strongest than other three kinetic models. The thermodynamic study confirmed that reaction of biosorption of chromium (VI) was spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that Sugarcane bagasse (Saccharum offcinarum L.) has considerable biosorption capacity, available in abundant, nonhazardous agro material can be used as an effective indigenous material for treatment of waste water stream containing chromium (VI).

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