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Isotherm and Kinetics studies, Adsorption of Chromium (III) Ions from Wastewater Using Cane Papyrus

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ABSTRACT

Cane Papyrus, a novel plant material, were found to exhibit excellent adsorption capacity over a wide range of Cr(III) concentration. It was characterized by Fourier transform infrared spectroscopy and Scanning Electron Microscopy to support the adsorption of Cr(III) ions. Effect of different parameters likes pH, contact time, initial concentration and different electrolytes was investigated using batch process to optimize conditions for maximum adsorption. The adsorbent data were analyse using Langmuir, Freundlich, isotherm equations at 30°, 40° and 50 °C. Thermodynamic parameters such as standard enthalpy change($\Delta H°$), free energy change ($\Delta G°$) and entropy change ($\Delta S°$)were also evaluated and the results indicated that adsorption of Cr(III)spontaneous and endothermic. Various kinetics models including the Pseudo- first -order kinetics, Pseudo-second-order kinetics and Intra particle diffusion models have been applied to the experimental data to predict the adsorption kinetics. Kinetic study was carried out by varying initial concentration of Cr(III) at constant temperature and it was found that pseudo-second-order rate equation was better obeyed than pseudo- first -order equation supporting that chemisorptions process was involved.

Keywords:*Adsorption; Cane papyrus; Chromium (Cr); Isotherms; Kinetics.*

I. INTRODUCTION

Chromium(III) result from Industrial process has conventional much concentration due to the main environmental impact connected with the two mainly common chromium oxidation states, Cr(VI) , and Cr(III). Chromium(VI) has larger environmental impact because the Cr(VI) in soluble state is regularly engrossed further simply a crosses the cell of body membranes more willingly. Therefore it is more poisonous and more steady than chromium(III). Global environmental values in wastewater involve chromium should not go above 5 mg/L for Cr(+3) and 0.05 mg/L for Cr(+6).The chromium(III) compounds are mainly toxic components of tannery wastewater, and they are used in various industries such as metallurgy, production of pigments, electroplating, aircraft painting ,pesticide, wood preservative, Textile manufacturing, dyeing, cement industry, metal finishing, photography industry, leather tanning etc (Zhonghua *et al.*,2003) by applications for conservation stabilization of proteins of animal hides. Consequently, tannery wastewaters contain large quantities of chromium; a major potential contributor has existed for chromium pollution in the environment. There are many health effects of chromium likes Ingestion, Erosive to stomach, hemorrhaging and death are likely eyes, direct eye contact with chromic acid or chromate dusts can cause permanent eye damage. Respiratory Tract :Hexavalent chromium can irritate the nose, throat and lungs. Repeated or prolonged exposure can damage the mucous membranes of the nasal passages and result in ulcers. Skin prolonged skin contact can result in dermatitis and skin ulcers. Some workers develop an allergic sensitization to chromium . In sensitized workers , contact with even small amounts can cause a serious skin rash. Trivalent chromium is an essential trace element and hazardous at relatively high doses interest in respiration (Nilima S. Rajurkar *et al.*,2011). The chromium is relatively stable and slowly oxidized to the much more toxic hexavalent chromium. Therefore elimination of hexavalent chromium has gained much more interest. Chromium is a metal that exists in several oxidation or valence states, ranging from chromium(III) to chromium(+VI). chromium compounds are very stable in the trivalent state and occur naturally in this state in ores such as Ferro-chromites, or chromites ore. Chrome (III) is an essential nutrient for maintaining blood glucose levels. The hexavalent, Cr(VI) or chromate, is the second most stable state. It rarely occurs naturally. Different strategies need aid being used to those evacuation about overwhelming metals from those streamlined release yet adsorption innovation organization need been discovered with show helter skelter effectiveness clinched alongside detoxifying effluents (A. Shoaib *et al.*,2014). Adsorption uses the capacity with gather great metals from wastewater toward probably metabolically intermediate or physiochemical uptake way. Characteristic materials have phenomenal possibility Concerning illustration modest adsorbents. Different adsorbents have been utilized within secret word quite some time for chromium particle removal, however, those investigation Furthermore improvement for new adsorbents may be constant. Biomaterials for example,. cashew nut shells (S.Tangjuank *et al*.,2009),low cost Fly Ash(Dr.V.Chitradevi1 *et al*.,2015), ground nut shell(Tasrina Rabia Choudhury *et al*.,2012), zeolite NaX(P. K. Pandey *et al*.,2010), Activated Carbon Derived from Tendu (Diospyros melanoxylon)(Mane P. C *et al*.,2010), Modified and Nonmodified Carbon Nanotubes.(Muataz Ali Atieh *et al*.,2010), ionic liquid functionalized multi walled carbon nanotubes as a super sorbent (A. Santhana Krishna *et al*.,2015), Spheroidal Cellulose Adsorbent(Minghua Liu *et al*.,2001), natural marl(Maher Jabari *et al*.,2009),Synthetic Polymers(FARAH KANWALa *et al*.,2012), modified walnut shells(Altun T, Pehlivan *et al*.,2012), modified clays (Arfaoui S. *et al*.,2008)etc. have lately been utilize the Cr(III) elimination from wastewater .Cane Papyrus flora are medium size plants or plant with flowers to look like a Cane Papyrus since of the cylindrical stalk.

This worth of effort need been embraced should investigate the adsorption behavior Of this guaranteeing novel material stick papyrus towards Cr(III) ions. Those impact about parameters for example, introductory result pH, substantial metal concentration, and contact run through might have been analyzed. A few characterization strategies (FTIR, SEM) were likewise utilized to recognize those progressions On stick papyrus should determine its materialness in the adsorptive evacuation for Cr(III). This substance up till now need to be tried in favor of the adsorption about overwhelming metals from watery result Also In this way it's phenomenal adsorption capacity, simplicity about availability, non-toxic nature, inexpensiveness and so forth. Provide for those principle advancement of the display investigation.

II. MATERIALS AND PROCEDURE

The Preparation of adsorbent

The Adsorbent Preparation (Cane Papyrus) was collected from farmlands in the marshes of Messan, south of Iraq . The grass were cautiously separate from the plant stalk and wash carefully by valve hose to get rid the mud, and remains soil particles after that dried by sun for l0 days. The dehydrated biomass was ground to fine particles by a hammer mill also weigh. Powder resultant was classified by systematic sieves. The Particles in l00-300 µm were used for simulated wastewater samples. The adsorbent showed a fluffy and highly porous and rough microstructure containing some voids and cracks which is suitable for the adsorption of Cr^{+3} ions . The Cr^{+3} ions concentration in aqueous solution was analyzed using Atomic Absorption Spectrometer (AAS). Mechanical shaker with regulating velocity, time was used for agitation and pH meter was used for all pH measurements. The chemical composition of the adsorbent was analyzed using X-ray Fluorescence spectrometer . The chemical composition of the adsorbent is presented in (Table l).

Table l : Chemical Composition of Cane Papyrus

Compound	Wt %	Compound	Wt %
Na_2O	l.l7	K_2O	ll.7
MgO	6.93	CaO	23.9
Al_2O_3	6.l5	SiO_2	23.6
TiO_2	l.33	P_2O_5	2.42
MnO	0.778	Fe_2O_3	l2.8
SO_3	5.68	SrO	l.24
Cl	l.09	BaO	0.52l

Surface area of the adsorbent was l.96 m^2 /g (Table 2). The Cane Papyrus normal diameter was in range l0 < D < 1000 × $l0^{-8}$ cm and the adsorbent was classified as a meso porous material . Similarly, reported BET surface areas of l.083 m^2 /g and 2.52 m^2 /g for activated carbon from macadamia nuts used for phenol removal and maize tassels for heavy metal removal from polluted waters, respectively although adsorbents with higher surface areas have been widely reported in literature.

Table 2 : Characteristics of Cane Papyrus

Physical Parameters	Result
BET surface area (m^2 /g)	l.96
Micropore surface area (m^2 /g)	l.75
Total pore volume (cm³/g)	0.01
Micropore volume (cm³/g)	0.0095
Average pore diameter(Ao or $l0^{-8}$ cm)	500

Used 1g of milled Cane Papyrus to adsorption Cr^{+3} ions onto the surface of Cane Papyrus using mechanical shaker at 25C^o and speed at 200 rpm. The adsorbent dosage effect was investigate by changeable the adsorbent initial mass between (5–100) g. The most favourable dosage obtain was use for consequent process. Likewise, the pH effects, Cr^{3+}initial concentration removal was initiated by contacting (0.0 to 5.0) g of the adsorbent with a 100 ml Cr^{3+} solution in a closed cylindrical plastic vessel of 250 ml volume.

and (5–l20) min, respectively. The percentage removal of Cr^{+3} ions from aqueous solution was estimated by using Equation (l):

$$\textbf{Adsorption}(\%) = \frac{[\text{Ci}-\text{Cf}]}{\text{Ci}} \times \mathbf{100} \qquad \textbf{(l)}$$

where, C_f and C_i are the final and initial metal ions concentrations, respectively.

$$\mathbf{qe} = \frac{(\text{Co}-\text{Ce})\text{V}}{\text{w}} \qquad \textbf{(2)}$$

where, qe is the amount of metal adsorbed in mg/g, C_i and C_e represent initial and equilibrium concentrations of metal ions in aqueous phase. V is the volume of the solution in litters (l) and W is the weight of the adsorbent used in grams.

Adsorbate solution

Preparing Chromium solution (1,000 mg /L) by dissolve desired quantity of the green oxide Cr_2O_3 (industrial type) in double distilled water (DDW). Chromium sulphate ($Cr_2SO_4.3H_2O$) as in equation (3) [formed by dissolved Cr_2O_3 in acid (H_2SO_4)] was used as the source of Cr^{3+} ion in a simulated effluent solution.

$$\mathbf{Cr_2O_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3.3H_2O} \qquad \textbf{(3)}$$

Sulphuric acid and sodium hydroxide solutions with 1M concentration were used to adjust the pH value.

Temperature Studies

The temperature effect on the Cr(III) adsorption was studied through changeable the doses of adsorbent starting 0.1 to 1.0 gm on initial concentration of Cr(III) 50 mg /L ,with constant volume (50 ml) of the solution . These beakers were reserved into water bath shaker at diverse temperatures (30,40 and50)°C used for 5hr and after that filtered.

pH Studies

Cr(III) solution in 50 ml volume, containing50 mg /L Cr(III) was in use in a glass as well as adjusted the solution through adding 0.1 M H_2SO_4 or 0.1 M NaOH with pH meter, after that The solution treat with the adsorbent in 0.5g after the equilibrium achievement and final Cr(III) concentration determined. The % adsorption calculated from Eq.(1) by subtract initial concentration from final concentration. The equilibrium or final also record. To study electrolyte effect, similar method repeat with(50 mg/L)solution of Cr(III) set within KNO_3(0.5 M).

Study the Capacity of Breakthrough

The study used glass column was taken 1gm adsorbent. Cr(III) ions solution in 50 mg/L concentration and 1000ml, the flow rate in the column was 10ml/min initial concentration (C_0) was passed through . In 500 ml fractions the effluent was collected and to the (AAS). By plotting volume versus C/C_0 of the effluent was obtained the capacity curve of breakthrough.

Electrolytes Studies

The different electrolytes effect likes Na_2SO_4,$CaSO_4$, $NaHCO_3$, NaCl , $MgSO_4$ and H_2SO_4 on the adsorption of Cr(III) was investigated. Solution in 50 ml volume and (50 mg/L) Cr(III) concentration was ready on top of electrolytes treat through 0.5 g of adsorbent. The Cr(III) quantity adsorbed in these electrolytes attendance were after that determined because its describe before.

Adsorption Study

Adsorption investigations were conveyed out by clump procedure. The measure about 0.5g adsorbent might have been set for a tapered flask to which 50 ml Cr(III) result for fancied focus might have been included to a 250ml tapered the mixture and flask might have been shaken over temperature-controlled shaker hatchery to 24h. For filtration paper used filter paper (No. 50) kind(Whatman). The final solution of metal ions in the filtrate analysed by atomic Absorption spectrophotometer (AAS). Total Cr(III) ions adsorbed was intended with subtract last concentration from first concentration.

III. RESULTS AND DISCUSSION

Infra-red Spectroscopy

The results from the Fourier transform infra-red showed a broad peak at 3000 cm^{-1} with a high transmittance frequency, which can be attributed to either –OH or –NH groups. As shown in Fig. l, the band observed at 2550 cm^{-1} is possibly due to C–H stretching vibrations of saturated aliphatic compounds , while the band at l750 cm^{-1} can be attributed to –NH bending vibration of primary amines . A small peak was observed at l350 cm^{-1} and corresponds to v(C–C) stretching vibrations of aromatic rings . The peaks observed at l200 cm^{-1} and l150 cm^{-1} corresponds to the C–O stretch of alcohols, carboxylic acids, esters or ethers. The absorption band at 500 cm^{-1} can be due to the presence of an alkyl halide. Also confirmed that mucilage extracted from Diceriocaryum species contains carboxyl functional group. The presence of acidic functional groups is responsible for its adsorptive property . The stated clearly from their studies of natural plant materials that the biochemical characteristics of acidic functional groups are responsible for their metal ion uptake(S. E. Ghazy *et al*.,2008).

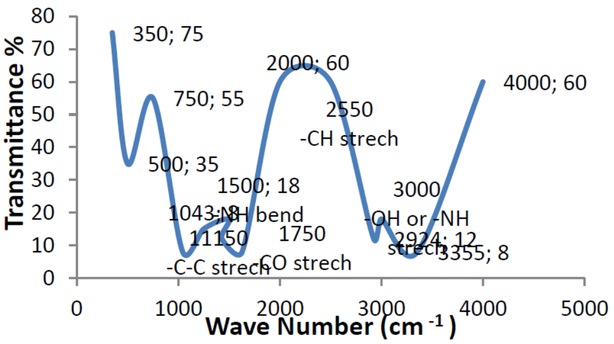

Figure 1: Infra-red spectra of the Cane Papyrus.

Zero charge Point

The zero charge point of the adsorbent was determined by addition of solid method . 50 ml DDW transfer to a sequence of beakers and these solutions has initial pH adjusted roughly among 1 to 10 with each 0.1 M NaOH or 0.1 M H_2SO_4 solution. The solutions in these initial pH was correctly record, after that add 0.5 g adsorbent to every beaker and allowable the mixture 24 h to equilibrate, with irregular manual trembling. The supernatant solution final pH was then noted (Babic BM ***et al*.,1999)**

Effect of pH

The % Cr(III) adsorption increased by raise the initial pH and reach to greatest pH at 6. Adsorption also affected with final pH or the equilibrium solution pH . The adsorption mechanism can be explain on the initial pH basis, equilibrium pH, the adsorbent surface charge and the metal speciation. The effect of pH on Cr^{+3} ions adsorption onto Cane Papyrus is shown in **Fig. 2**. Chromium(III) ion elimination was fast affected by change in the equilibrium solution pH . Adsorption of Cr(III) was 40 % at pH 1, 65% at pH 4, 90% at pH 5 and 98.5% at pH 6. The removal efficiency was decrease in experiential at pH value of after 7 (90%) and 75% at pH 8. This may be because at and after pH 7 [Cr(III) exist as Cr^{+3} ions (in great amount) with the formation of $Cr(OH)_3$ (tiny amount)] .The maximum adsorption of Cr^{+3}ions occur at pH=6. Higher values of pH (pH>7), Cr^{+3}ions started precipitation(Farinella NV *et al*.,2007).

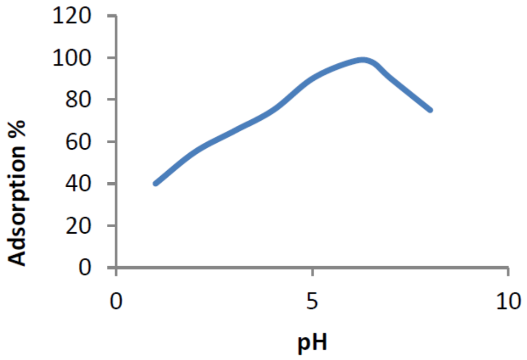

Figure 2: Effect of pH on the adsorption efficiency of Cr^{+3}ions onto Cane Papyrus

Breakthrough capacity

The most efficient column method creating the best use of the concentration gradient between the residual in the solution and that solute adsorbed by the adsorbent is breakthrough curve. The column is operational until the metal ions in the effluent start appearing and for practical purposes the working life of the column is over called breakthrough point. That is essential in the method design since it straight affect the possibility and process economics Fig. 3 show to Cr(III) solution in 220 ml could be passed through column with no detect Cr(III) in the waste matter. The capacity of breakthrough be establish to be 45 mg/g (Fourest E, Roux J. *et al*.,1992).

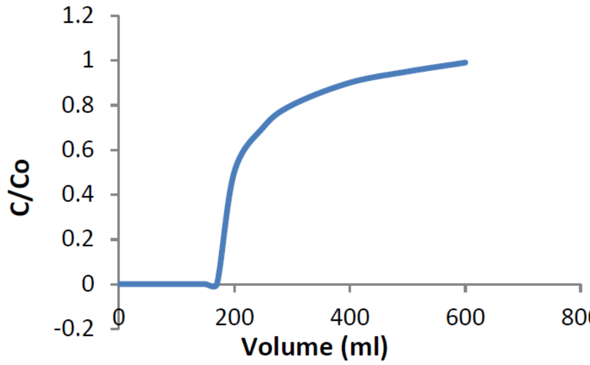

Figure 3 : Breakthrough curve of Cr(III)

Contact time and Cr(III) initial concentration Effect

The contact time Effect on the adsorption of Cr(III) ions was determined through analyse the remaining Cr(III) into solution after contact time starting (5 to 300) min. Batch process Experiments were perform using at room temperature. 1gm add of adsorbent to100ml solution in diverse Cr(III) initial concentrations (10–50 mg/L).The Samples were withdrawn from beakers after specific time period and analyse for remaining metal content. The metal mechanism uptake normally depends on the adsorbent mass that contact with the heavy metals initial concentration. Small concentrations the specific site is dependable for adsorption, whilst in case of increase concentrations of metal the specific site is saturated with adsorption sites are packed. The Cr(III) initial concentration effect on the amount of adsorption that is shown in Fig.4. Increasing adsorption with time and achieve maximum for all the concentrations. Capacities of the adsorption 10, 30 and 50 mg/l, initial Cr(III) concentrations were establish to be 2.4, 2.7 and 3 mg/g , respectively. Increasing driving force by means of increasing Cr(III) ions concentration might be causes this result. The metal ions uptake at any particular concentration increased with contact time. Fig.4 show that the rate is rapid then it slow down awaiting it reach stability. This is due to the fact that a great amount of residual vacant plane site is obtainable for adsorption through first step by the time raise , the residual vacant plane site is not easy to be in use because of disgusting forces between the bulk phases and solute molecules on the solid. On the other hand, by increasing Cr(III) ions initial concentration also increasing the contact time and need to achieve equilibrium. From experimental the equilibrium is attain at (50,15 and 5)min for (50, 30 and10) mg/L of Cr(III) concentrations, respectively.

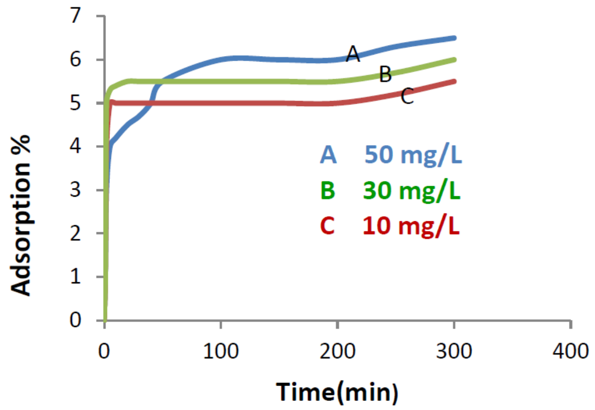

Figure 4 : Efficiency adsorption of Cr^{+3} ions with contact time onto Cane Papyrus.

Adsorption isotherms

To optimize the adsorption design system for the Cr(III) ions removal from wastewater , it is significant to give details about association among equilibrium concentration of residual metal ion in solution (Ce) and adsorbed Cr(III) ions per unit mass of adsorbent (q_e). The adsorption isotherm figures study by correct them to diverse isotherm models of adsorption is significant step to get the appropriate isotherm model of adsorption to use for design purpose. investigational data were fitted within the , Freundlich, Langmuir models at different temperatures. To calculate the data suitability, determination coefficient (R^2) that evaluate between calculated data and experimental data for both model. Consistent with model of Langmuir (Langmuir I. *et al*.,1916) adsorption occurs on a homogenous surface form adsorbate monolayer with steady adsorption temperature for all sites with no interface among adsorbed molecules . The Langmuir model may be known as linear form :

$$\frac{l}{qe} = \frac{l}{qmax} + \{\frac{l}{bqmax}\}\frac{l}{Ce} \qquad \textbf{(4)}$$

where, Ce is the equilibrium concentration ions of Cr(III) in the solution (mg/L), q_e is the Cr(III) adsorbed quantity per adsorbent unit weight (mg /g), q_{max} is the Cr(III) required amount to form monolayer (mg/g) and b is a constant related to adsorption energy (L/mg) that represent enthalpy of adsorption that differ with temperature. The q_{max} and b values were calculated at diverse temperatures from the intercept and slope of the linear plots of $1/C_e$ versus $1/q_e$. From this model, the data obtain indicate that is applicability at diverse temperature (30,40 and 50) °C , however data were fixed greatest by high temperatures (40 and 50)°C like indicate through high determination coefficient (R^2). The value of q_{max} and b increase by rising temperature representing adsorption higher heat by rising temperature and confirm the adsorption endothermic nature. **Fig. 5** representing that the adsorption conform to langmuir model indifferent temperature . The adsorption capacity and the greatest Cr^{+3} ions concentration adsorbed was calculate from the intercept and slope of the scheme. The adsorption process agreement to langmuir model was determined using Equation (5):

$$\mathbf{Rl} = \frac{l}{(\mathbf{l+bCo})} \qquad \textbf{(5)}$$

where, (R_l)separation factor, (C_o) initial concentration of metal (mg/L) and (b) langmuir coefficient (l/mg). R_l > l indicate an unfavourable adsorption monolayer process, R_l = l linear, 0 < R_l < l favourable and R_l = 0 irreversible. From this study the result obtain is R_l values between (zero to one), representing a favourable adsorption process. This implies that chemisorptions process duly explains the Cr^{+3} ions adsorption onto Cane Papyrus.

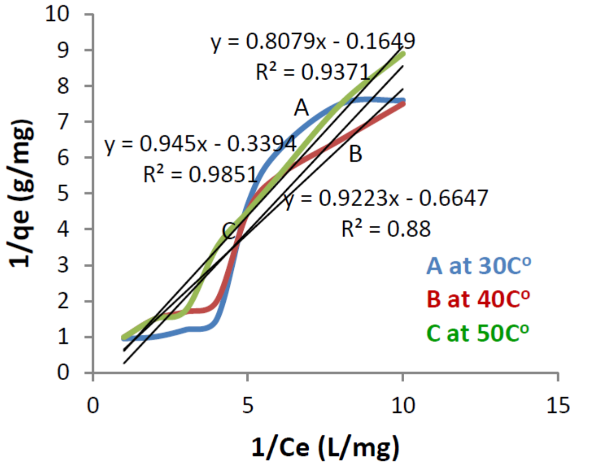

Figure 5 : Langmuir Isotherm adsorption plot for Cr^{+3} ions onto Cane Papyrus in different temperature.

The Freundlich model (Freundlich HMF. *et al*.,1906) is an empirical equation based on the adsorption of adsorbate onto heterogeneous surface. The linear form of Freundlich model can be represented as.

$$q_e = K_f C_e^{l/n} \qquad (6)$$

where Ce is the equilibrium concentration in mg/L , K_f is the Freundlich constant which indicate the adsorbent qualified adsorption ability correlated to bonding energy and n is the heterogeneity factor representing the difference from linearity of adsorption and is also recognized as Freundlich coefficient. Equation (7) was obtained by taking the logarithm of Equation (6):

$$\log q_e = \log K_l + \frac{l}{n} \log C_e \qquad (7)$$

A plot of log qe versus log Ce in different temperature should produce directly line and values of 1/n and K_f can be calculated from the slope and intercept. The data obtain from this model indicate that the values of K_f and n increased with the increase in temperature from 30 to50 °C as shown in Fig. 6. Freundlich model was best obeyed at 50 °C because of high R^2. The n values between 0.0 and 1.0 indicated favourable adsorption.

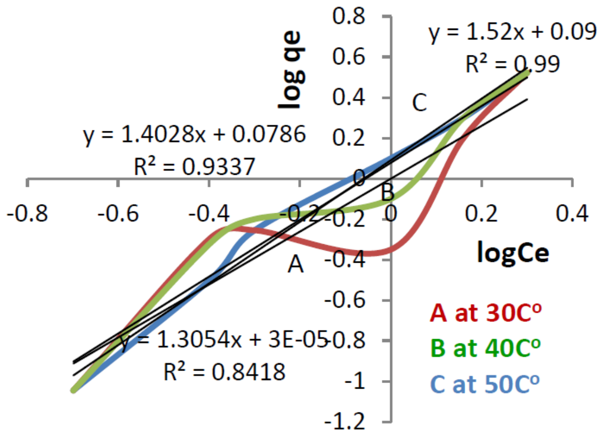

Figure 6 : Freundlich Isotherm adsorption plot for Cr^{+3} ions onto Cane Papyrus in different temperature.

Adsorption kinetics

The rate constants were calculated using pseudo-first-order (Lagergren S. *et al*.,1898) and pseudo-second-order kinetics models. The first-order rate expression is given below

$$\log(qe - qt) = logqe - \{\frac{Kt}{2.303}\} \qquad (8)$$

where q_e is the amount of Cr(III) adsorbed per unit weight of adsorbent at equilibrium or adsorption capacity (mg/g), qt is the amount of Cr(III) adsorbed per unit weight of adsorbent at any given time t, K_1 is the rate constant for pseudo-first-order model. The values of K_1 and qe were calculated from slope and intercept of the linear plot of lin (q_e - q_t) versus t at various concentrations. A plot of log (q_e - q_t) versus t gave straight lines confirming the applicability of the pseudo-first-order rate equation Fig.7.

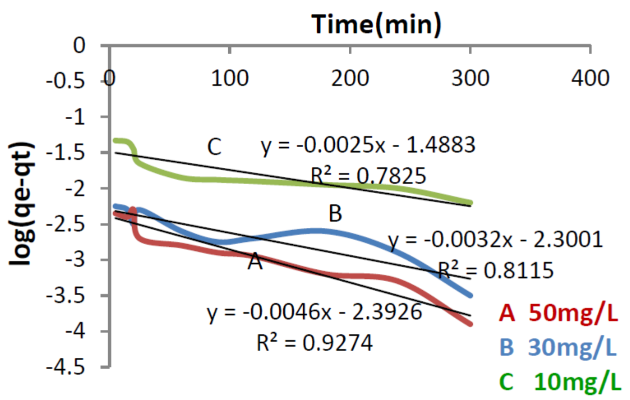

Figure 7 : Pseudo first order kinetics for Cr^{+3} ions adsorption onto Cane Papyrus.

The pseudo-second-order rate expression is used to describe chemisorptions involving valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange (Ho YS, McKay G. et al.,1998). The pseudo-second-order kinetic rate equation is given as

$$\frac{t}{qt} = \frac{1}{K2qt2} + \left\{\frac{1}{qe}\right\} t \qquad (9)$$

where K_2 is the pseudo-second-order adsorption rate constant in (g/ mg.min). The K_2 and q_e values were calculated from the intercept and slope of the linear plots of t/q_t versus t at various Cr(III) concentrations. directly line plots of t/q_t versus t indicate the pseudo-second-order model applicability (Fig,8).

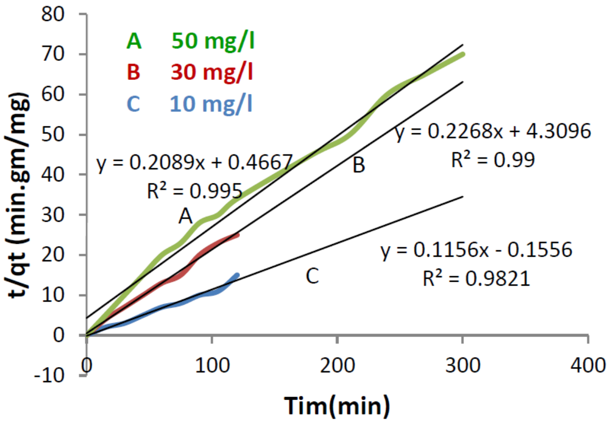

Figure 8 : Cr^{+3} ions Adsorption onto Cane Papyrus by Ho's Pseudo-Second-order model.

Table 3 : Cr^{+3} ions Adsorption on onto Cane Papyrus by Lagergren rate equation constants and Pseudo-second-order rate equation constant.

Concentr-Ation	Lagergren rate Equation		Pseudo-seconnd-order rate equation	
	K_1	R^2	K_2 g/ mg.min	R^2
10 mg/l	0.0025	0.7825	0.1156	0.9821
30 mg/l	0.0032	0.8115	0.2268	0.9900
50 mg/l	0.0046	0.9274	0.2089	0.9950

Table 3 provides data of pseudo-first-order rate constants K1, pseudo-second-order rate constants K_2, R_2, calculated equilibrium adsorption capability qe and investigational equilibrium adsorption capability qe at diverse initial Cr(III) concentrations. It establish that qe values from pseudo-first-order model differ significantly from the experimental values showing that system did not follow pseudo-first-order model. The values of qe were very close to qe values in pseudo-second-order kinetic model at different initial Cr(III) concentrations as compare to pseudo-first-order model representing that pseudo-second model was superior obeyed. The data also shows that the values of determination coefficient (R^2) for pseudo-first-order model(Table 3) lesser as compare to pseudo-second-order kinetic model at diverse initial concentration values.

Thermodynamic study

The effect of Cr(III) ions adsorption on the temperature was calculated on temperature range starting 30,40 and 50 °C. The Gibbs energy change (ΔG°) indicates the degree of spontaneity of an adsorption process, and a higher negative value reflects a more energetically favourable adsorption. Thermodynamic parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated using the following relations(Liu Y. et al.,2009) :

$$\Delta G^\circ = -RT\ln K_c \qquad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (11)$$

where R is the universal gas constant (8.314 J/mol. K), T is the temperature (K) and Kc is the thermodynamic equilibrium constant without units. The enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption are obtained from the following equation

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (12)$$

According to Equation (9), (ΔH°) and (ΔS°) parameters can be calculated from the slope and intercept of a plot of $\ln K_c$ versus 1/T, respectively **Fig.9**.

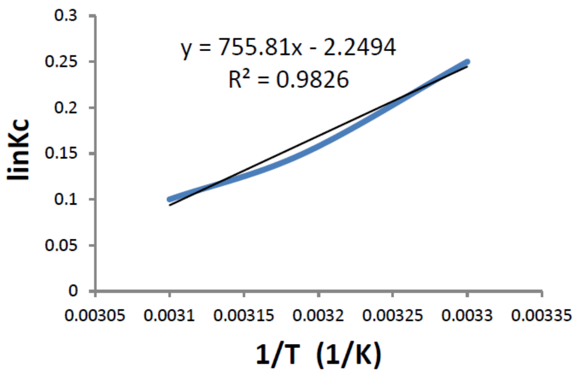

Figure 9 : Thermodynamic Parameters for Cr^{+3} ions Adsorption onto Cane Papyrus.

These parameters of thermodynamic can present imminent into the kind and method of an adsorption procedure. Free energy ΔG° values change are depressing confirm that adsorption of Cr(III) ions is thermodynamically and natural approving while ΔG° became further negative by raise into temperature(-0.27,-0.39 and-0.63)KJ/mol. at (30,40 and50)C^o respectively, representing high dynamic power and therefore resultant in upper capacity of adsorption by upper temperature. The ΔH° value in positive that indicate the process of adsorption is endothermic (0.756 KJ/mol.). A little but positive value of ΔS° (0.0225 KJ/mol.K)at the range of temperature from 30–50 °C recommended enlarged chance in the interface of solid-solution for the reason that a little molecules of water are dislodge through Cr(III) ions adsorption (Gonzalez JR. et al.,2006).

Effect of electrolytes

The contaminated water with Cr(III) also contains a new ions number that may possibly power the adsorption procedure. In this work evaluate the Cr(III) ions adsorption activities within the attendance salted solution in 0.05–0.1 M of different electrolytes like to sulphate , carbonate and chloride separately at the first concentration of Cr(III) ions 50 mg/L. Different electrolytes effect on the Cr(III) ions adsorption is listed in Table 6. Cr(III) ions adsorption is decrease by raise the electrolytes concentration like to Na_2SO_4,$CaSO_4$, NaCl,$NaHCO_3$, $MgSO_4$, H_2SO_4. That can be qualified to greater than before opposition for adsorption sites between Cr(III) ions and electrolyte ions as well as decrease the Cr(III) ions activity (Gladysz -Plaska A. *et al*.,2012). The electrolytes influence and their result in poisonous pollutants removal using natural materials has been observed in recent past (Pehlivan E. *et al*.,2011),(Pang Y. *et al*.,2011),(Rao RAK. *et al*.,2009),(Wang Q, Chang X. *et al*.,2011)and(Gupta VK. *et al*.,2001). Many studies showed that reduce the metal ions adsorption into the electrolytes ions attendance. However, Cr(III) ions adsorption enlarged by rising Na_2SO_4 concentrations which may be due to raise in final pH of the Na_2SO_4 solution with increased concentration (pH 7–8.5) as report in (Table 4).

Table 4 : The % adsorption onto electrolytes Influence of Cr^{+3}ions at 50 mg/l.

	%Adsorption	
Electrolytes	**0.05M**	**0.1M**
$MgSO_4$	82	54
Na_2SO_4	95	62
NaCl	44	19
$CaSO_4$	57	23
$NaHCO_3$	75	38
H_2SO_4	26	05

IV. CONCLUTION

The adsorption ability of powdered Cane Papyrus has been investigated and found effective for the removal of Cr(III) ions from wastewater. The removal concentration was dependent on the time of equilibrium. The experimental results showed that the adsorbent always had a higher capability to adsorb Cr(III) ions and the maximum adsorption could be possible from the aqueous solution at pH 6. At higher temperatures the isotherm of Freundlich , Langmuir were greatest obeyed. The Cr(III) ions adsorption was affected with rising the different electrolytes concentration. Kinetic data show the pseudo-second- order model confirm improved applicability that the Cr(III) ions adsorption was nature chemical sorption . Thermodynamic data indicate the Cr(III) ions adsorption was endothermic and natural. Column experiments showed that the breakthrough began at 220 ml.

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VI. CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

VII. ABBREVIATIONS

$\Delta H°$	Standard Enthalpy Change(KJ/mol.)
$\Delta G°$	Free Energy Change (KJ/mol.)
$\Delta S°$	Standard Entropy Change (KJ/mol. °K)
DDW	Double Distilled Water
AAS	Atomic Absorption Spectrometer
C_f	Final Concentration of Metal Ions(mg/L)
C_i	Initial Concentration of Metal Ions(mg/L)
W	Adsorbent Weight
R	Universal Gas Constant (J/mol. °K)
K_2	Pseudo-Second-Order Adsorption Rate Constant in (g/ mg.min)

VIII. REFERENCE

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