Removal of Chromium Ions From Industrial Effluents by Adsorption Technique (Batch and Column) Studies

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ABSTRACT:

Chromium(III) salts are the most widely used chemicals for tanning processes, but70% of total chromium salts react with the hides. In other word, about 30% of the chromium amount remains in the solids and liquid wastes (especially spent tanning solutions). Therefore, the removal and recovery of the chromium content of these wastewaters is necessary for environmental protection and economic reasons. The possibility of using bypass cement kiln dust (BCKD) as a low cost and natural adsorbent is investigated in this study for the removal of Cr(III) from synthetic and real wastewater. The parameters studied include contact time, adsorbent dose, initial chromium ion concentration, ph and temperature. The adsorption followed pseudo second order reaction rate and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity obtained from the Langmuir isotherm plots were 142.7, 142.97, 142.323, 142.85 and 166.69 mg/g respectively at an initial ph 2.5 at 25, 30, 50, 70 and 90^{o}C. The temperature variation study showed that the chromium ion adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the ph of the chromium ion solution.

The percentage adsorption increased with decrease in ph and showed maximum removal of Cr(III) at initial ph value 2.5. Desorption of Cr(III) from the spent BCKD has also been investigated. Desorption process suggest that the adsorption of Cr(III) ions on BCKD involves physisorption mechanism. Column studies have been carried out to compare these with batch capacities. Removal of Cr(III) from tannery wastewater by BCKD was testified.

Keywords: *Adsorption, Tannery effluent, Chromium, BCKD, Fixed bed.*

1. INTRODUCTION

Environmental pollution due to the development in technology is one of the most important problems of the century and the future. Heavy metals like chromium, copper, lead, cadmium, ..etc. in wastewater are hazardous to the environment. These metals cannot be degraded or readily detoxified biologically and have tendency to accumulate in living materials. Bedside that, heavy metals discharge in the wastewater can be toxic to aquatic life and render natural waters unstable for human consumption, (Khan & Mohamad, 2007).

Chromiuom is present in aquous solutios mainly in two stable oxidation states, *Cr(III)* and *Cr(VI)*. Hexavalent chromium, which is primarily present as an anion in chromate ($Cr_2O_4^-$), and dichromate ($Cr_2O_7^{--}$), possesses significantly higher levels of toxicity than other valence states, (Sharma & Forster, 1993). *Cr(III)* is less health concern, because its low water solubility than *Cr(VI)*, but has a widely used as a tanning agent in the leather industry, and is an important source contamination due to the large volume of wastewater discharges and solid sludge's produced. There is no doubt that its compounds at higher concentrations are both accurately and chronically toxic and can generate serious trouble and diseases such as nausea, skin ulceration's and lung cancer, (Costa, 1997).

The main sources of *Cr* pollution are mining, leather tanning, the cement industry, use in dyes, electroplating, production of steel, photographic material and corrosive paints (Leyva et al., 1994). The principal techniques for recovering or removing *Cr* from wastewater are chemical reduction and precipitation, adsorption by several types of adsorbents; such as activated carbon (Leyva et al., 1994 & 1995), Pinus sylvestris bark (Alves et al, 1993), fly ash and wollastonite (Panday et al., 1984), sphagnum moss peat (Sharma & Forster, 1993) and bone charcoal (Dahbi et al., 2002), ion exchange (Tahir et al., 1998 and; Tiravanti et al., 1997) and membrane technologies (Chaudry et al., 1997). Most of these methods suffer from some drawback such as high capital and operational costs. Therefore, there is a need for search and development of low cost, easily available materials, which can adsorb *Cr* economically.

The main objective of this study was to evaluate the possibility of using bypass cement kiln dust (*BCKD*) as adsorbent for the removal of *Cr(III)* from aquous environment. *BCKD*, commercially available in Libya, is a byproduct from dry process of Potrland cement industry. The effect of contact time, initial chromium ion concentration, *BCKD* dose, pH vlaue and temperature on *Cr(III)* adsorption are described here in detail.

2. MATERIAL AND METHODS

2.1. Adsorbent

The adsorbent was by-pass cement kiln dust (*BCKD*) are collected from Al-Burg cement factory (Zliten city/Libya) which was undesired byproduct from the Portland cement manufacturing due to its high alkalinity content. The powder of *BCKD* was sieved according as required 20 *μm*. The chemical composition of the *BCKD* constituents are shown in Table.1.

Table.1: X-ray analysis of BCKD

Constituents	***Composition*, (wt%)***
SiO_2	12.47
Al_2O_3	3.58
Fe_2O_3	2.37
CaO	39.35
MgO	1.67
K_2O	3.08
Na_2O	0.865
Cl	5.306
SO_3	6.301
Free lime	13.108
Loss on Ignition (LOI)	11.9

** Average value of six samples*

2.2. Adsorbate

Stock solution 1000 *mg/l* of *Cr(III)* was prepared by dissolving 3.77 *g* of basic Chromium sulfate salt ($Cr_2(SO_4)_2OH_2$) into 1 *liter* of deionized distilled water (*DDW*) and stir *Cr(III)* solutions of different concentrations for sorption experiments were prepared by diluting stock solution with *DDW*.

2.3. Experimental procedure

All experiments were carried out by batch system using a definite volume of *Cr(III)* ion solution with known initial concentration in 250 *ml* Erlenmeyer flasks, then mixed with a definite amount of *BCKD*. The mixture was agitated for a certain time at known temperature using a controlled temperature shaker bath.

The *Cr(III)* ion suspension at equilibrium time were centrifuges for 5 minutes at 200 *rpm* using a rotary centrifuge, the residual concentrations of *Cr(III)* ions for the supernatant solutions were measured by *AAS* to studying paramaters effect on adsorption process (Contact time, initial concetration, adsorbent dose and pH values).

The analysis on the *AAS* was carried out according to standard methods (Rand et al., 1995). The experiments were triplicate for quality control and statistical purposes. The percent standard deviation (*S.D.*) of the sorption parameters was under 1.5%. All data represents the mean ±*S.D.* of three independent experiments. All statistical analysis was done using Microsoft Excel 2007, Version office XP.

Each one the Adsorption capacity of *Cr(III)* calculated based on the mass balance principle (Eqn.1) and the percent removal of *Cr(III)* ions was determined based on (Eqn.2).

$$q = \frac{V(C_o - C)}{W} \qquad \text{………………..} \ (1)$$

$$R\% = \frac{(C_o - C)}{C_o} * 100 \qquad \text{………………..} \ (2)$$

Where, C_o and C are initial and final (or equilibrium) concentrations, W is the weight of adsorbent (*g*), R is the removal percentage, (*%*) and q is the adsorbent capacity, (*mg/g*)

2.3.1. Equilibrium isotherms

Adsorption isotherms were obtained by batch method at optimum conditions, using 0.5 *g* of *BCKD* added to 100 *ml* of *Cr(III)* ions solution with a known initial concentration ranged (100-1000 *ppm*). The equilibrium adsorption data obtained are analyzed by the Langmuir and Freundlich isotherms.

2.3.2. Desorption

Desorption studies were carried out after adsorption experiments for 200 *ml* of solution with various initial concentration of *Cr(III)* ions (200, 400, 600, 800 and 1000 *ppm*) and 0.5 *g* of *BCKD* are done at (25±2 ^oC, particle diameter 20 μm, initial value of pH equal to 2.5 and 200 *rpm* agitation rate for 30 *minutes*), then the chromium-laden adsorbent samples, separated by centrifuge, were gently washed with *DDW* to remove any unadsorbed *Cr(III)*. The spent adsorbent samples were then agitated with 250 *ml* of *DDW* and sulfuric acid (98% *wt.*) was added to samples to various pH values ranging from 0.25 to 2.0 and desorbed *Cr(III)* was estimated by analyzing the acid solutions by *AAS*.

2.3.3. Tests with real effluents

The tannery effluent contained very high concentration of *Cr(III)*. Tanning solutions obtained from two different location tanneries effluent. The wastewater samples obtained from theses tanneries after the tanning operation was filtered to obtain a tanning solution then then reduction process for their content of *Cr(IV)* to *Cr(III)* which done (Ibrahim, 2010), the produced solution is to be further treated for *Cr(III)* removal. *Cr(III*) content in the filtrate (tanning solution) was determined using *AAS*. The initial concentrations of *Cr(III)* in tanning solutions were treated were 2336 and 4320 *mg/l* respectively. These both tanneries batches are taking from two different national tanneries effluents wastewater.

2.3.4. Column studies

Adsorption experiments were conducted using fixed bed column. The column diameter was 2.54 cm and its height was 55 cm. To avoid fluidization, the column was packed with BCKD between two supporting layers of glass wool. Experiments were run with 15, 20 and 25 cm, bed height.

The filtered *Cr(III)* bearing wastewater is fed up the column, using peristaltic pump, at 10.5 $ml.min^{-1}$. Two samples of wastewater, that have initial concentrations 2336 and 4320 $mg.l^{-1}$ were treated. The *Cr(III)* concentration in filtered and treated samples was measured using Atomic Absorption Spectroscopy (Varian, model SpectrAA50). Samples from treated water (column effluent) were analyzed for *Cr(III)* every 15 *minutes*. Experiments were carried out at 25±2 ^oC temperature, and the initial pH value of wastewater was 2.5±0.1 for all runs (optimum conditions for adsorption (Ibrahim, 2010).

3. RESULTS AND DISCUSSION

3.1 Paramtetrs effect on adsorption process

3.1.1. Effect of contact time

The effect of contact time on the residual concentration is shown in Figure (1), whereas the residual concentration of *Cr(III)* ions decrease with increase a contact time between *Cr(III)* ions and *BCKD*, sharply decreases occur through period (1 to 10 *minutes*) then a sluggish decrease in residual concentration of *Cr(III)* ions in a solution through the period (10-15 *minutes*), then the concentration values remain a constant in the range (15-60 *minutes*). This behavior refer to that the system reaches to equilibrium very fast and reached to equilibrium at 15 *minutes*. Similar results were reported by El-Awady & sami (1997) and; Jamali et al., (2009).

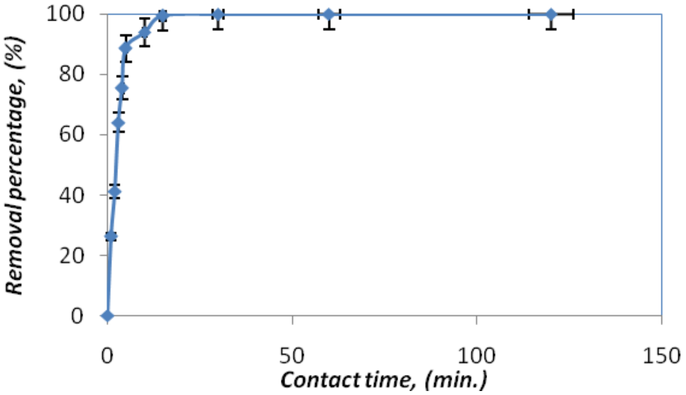

Figure .1: Effect of contact time on adsorption removal percentage of Cr(III), *Conditions:* (C_o*=500 ppm, BCKD dose=0.25g /50 ml, particle diameter =20 µm, agitation rate =200 rpm, initial pH= 2.5 and temperature 25±2* ^oC*)*

3.1.2. Effect of adsorbent dose

The effect of the amount of *BCKD* on the removal of *Cr(III)* form synthetic solution is shown in Figure (2). The results showed that the *Cr(III)* removal percentage increases as the dose of the *BCKD* also increase. Similar adsorption behavior of *Cr(III)* was observed by Potgeiter et al., (2005) when using palygorskite clay as an adsorbent, also by Babel & Opiso (2007) when using volcanic ash soil for removal *Cr* from synthetic wastewater. This was attributed to increased *BCKD* surface area and availability of more number of adsorption sites (Arivoli et al., 2008).

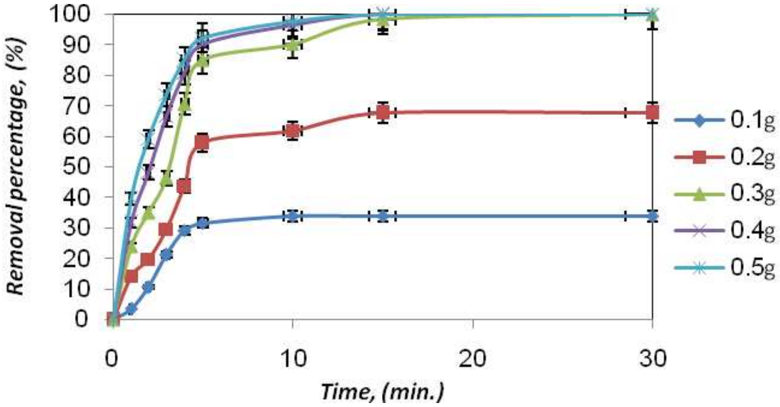

Figure.2: Effect of adsorbent dose variation on adsorption removal percentage of Cr(III), *Conditions:(C_o=500 ppm, particle diameter =20 µm, Agitation rate =200 rpm, solution volume= 200 ml, initial pH= 2.5 and temperature =25±2 °C)*

3.1.3. Effect of Variation of Initial Cr(III) concentration

The initial *Cr(III)* concentration is important parameter since a given amount of *BCKD* can adsorb a certain amount of *Cr(III)*. Figure (3) represent the effect of variation of initial *Cr(III)* concentration(ranged 200- 1000 ppm) on the percentage removal. It was found that, the removal increases by decreasing the initial concentration of *Cr(III)*, the data show that the contact time necessary for removal to reach maximum value in each case is approximately is 15 *minutes*.

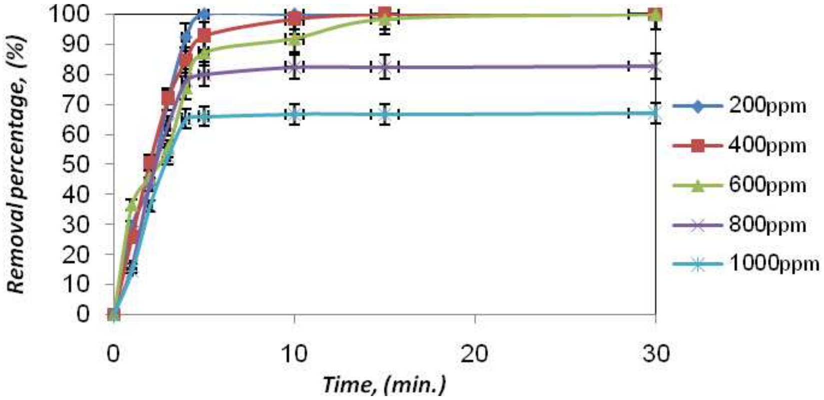

Figure.3: Effect of initial concentration variation on adsorption removal percentage of Cr(III), *Conditions: (BCKD dose =0.5g/200 ml, particle diameter =20 µm, agitation rate =200 rpm, initial pH= 2.5 and temperature =25±2 °C)*

3.1.4. Effect of pH

The effect of pH on adsorption percentage of *Cr(III)* in presence of *BCKD* was studied various values of pH 1, 2, 3, 4 and 5. All experiments were done at adsorbent dose 0.5 *g*, initial concentration = 500 *ppm*, temperature 25±2 *°C*, agitation rate 200 *rpm*, solution volume = 200 *ml* and 30 minutes were used as a contact time to carry out the experiments.

Figure (4) shows the effect of initial pH on adsorption percentage of *Cr(III)* in the presence of adsorbent, it was found that the removal percentage increases by increasing pH values in which were 47, 90.4 and 99.99% in cases pH values 1, 2 and 3 respectively. Then the opposite trend occurs in which the removal percentage decreases by increasing pH values from 4 to 5 as 88 and 81% respectively.

To explain this behavior a plot of removal percentage by adsorption/ precipitation of *Cr(III)* done as shown in Figure (5). A maximum adsorption of 99.99% was attained at an initial pH= 2.5 (Final pH=3.1). For kinetic and isotherm studies care was taken that no tests were performed at an initial pH > 4 [Figure (5)], because *Cr(III)* precipitation could occur) in order to find out the ability of *BCKD* to remove *Cr(III)* by adsorption rather than precipitation.

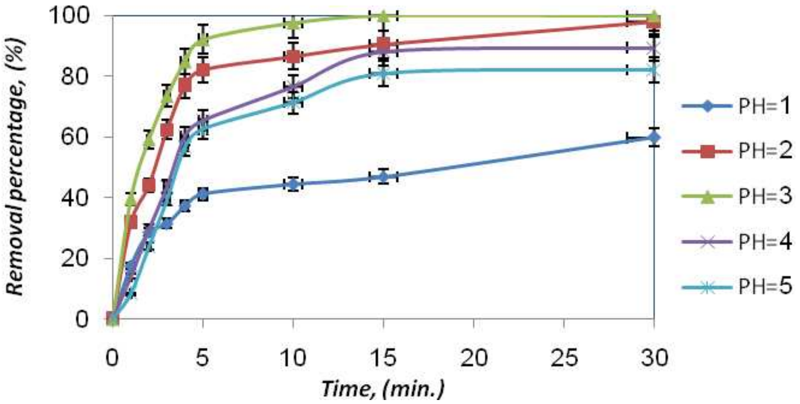

Figure.4: Effect initial pH values variation on adsorption percentage removal, *Conditions: (Initial concentration = 500 ppm, BCKD dose =0.5 g/200 ml, particle diameter =20 µm, agitation rate=200 rpm and temperature =25±2 °C)*

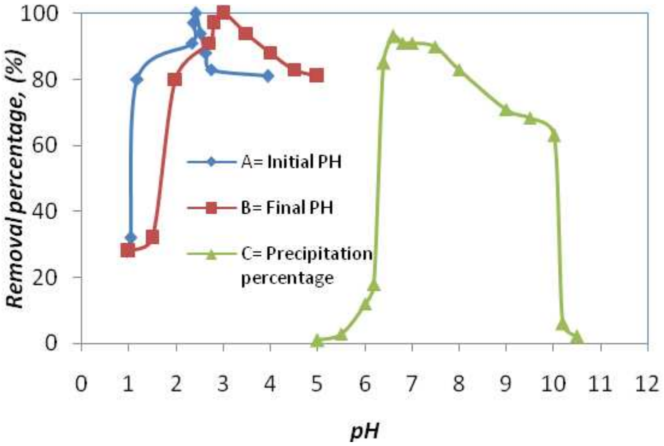

Figure.5: Effect of pH on removal percentage of Cr(III),

A*= Adsorption percentage vs. Initial pH;* ***B****= Adsorption percentage vs. Final pH; and*

C*= Precipitation percentage vs. pH. (by precipitation of Cr(III) as Cr(OH)$_3$ in the absence of BCKD).*

Conditions: (Initial concentration = 500 ppm, BCKD dose =0.5 g/200 ml, particle diameter =20 µm, agitation rate=200 rpm and temperature =25±2 °C)

3.2. Equilibrium isotherms and Thermodynamic parameters

3.2.1. Equilibrium isotherms

Analysis of equilibrium data is important for developing an equation that can be used to design and optimize an operating procedure, (Sahmoune et al., 2008). To examine the relationship between adsorbent and aqueous concentration at equilibrium, various adsorption isotherm models are widely employed for fitting data.

Figure (6) shows the equilibrium adsorption of *Cr(III)* (q_e *vs.* C_e) using *BCKD*. The isotherm rises sharply in the initial stages for low C_e and q_e values. This indicates that there are plenty of radially accessible sites. Eventually a plateau is reached, indicating that the adsorbent is saturated at this level. The decrease in the curvature of the isotherm, tending to a monolayer, considerably increasing the C_e values for a small increase in q_e, is possibly due to less active sites being available at the end of the adsorption process and/or the difficulty of the edge molecules in penetrating the adsorbent due to *Cr(III)* molecules partially covering the surface sites.

In order to optimize the design of a sorption system to remove *Cr(III)* from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Langmuir and Freundlich isotherm equations have been tested. The goodness-of-fit between experimental data and the model predicted values was expressed by the correlation coefficient (r^2, values close or equal 1), it's not to ascribe more meaning to it than is warranted to obtaining the constants of the models from the best fitting. Just because r^2 is close to 1 does not mean that the fit is necessarily good (Chapra & Canale, 1998). So, the conformity between experimental data and the model predicted values was expressed by the total mean error ($\in \%$), is the discrepancy between the experimental data and the predicted values and given in Eqn.(3), (Press et al., 1989);

$$\in \ \% \ = \frac{\sum_{i=1}^{n} \left| \left(q_{e\ (Exper.)} - q_{e(Calc.)} \right) \right|}{\sum_{i=1}^{n} q_{e(Eper.)}} \qquad \text{…………… (3)}$$

A relatively low ($\in \%$) value indicate that the model successfully describes of the equilibrium isotherms and kinetics of *Cr(III)* adsorption on *BCKD*.

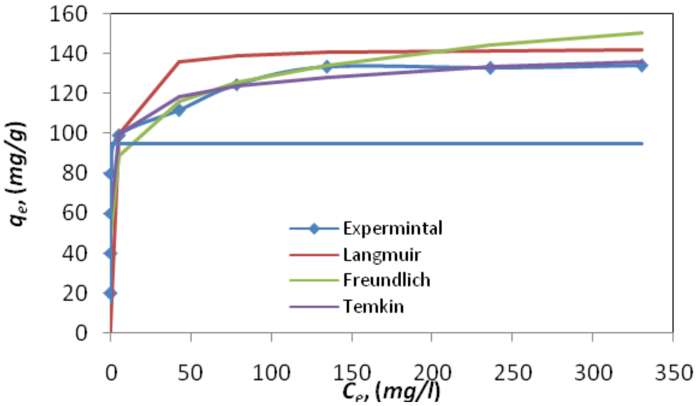

Figure.6: Equilibrium isotherms of Cr(III) on BCKD,

Conditions (0.5g/ 100 ml, 25±2 °C, particle diameter =20 µm, agitation rate 200 rpm, initial pH= 2.5and temperature =25±2 °C)

3.2.1.1. Langmuir isotherm

The widely used Langmuir isotherm has found successfully application in many real sorption processes (Özacar, 2003) and is expressed in a linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \qquad \text{……………….. (4)}$$

Therefore a plot of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and intercept $1/K_L$ in Figure (7). The values of the Langmuir constants a_L, K_L and Q_o with the correlation coefficient are listed in Table(2) for the *Cr(III)/BCKD* system and the Langmuir isotherm is plotted in Figure (6) together with the experimental data points. The mean total error ($\in$ %) between this models with the experimental data was 33.47 %. Observed that the monolayer saturation capacity (Q_o) is 142.756 *mg/g*.

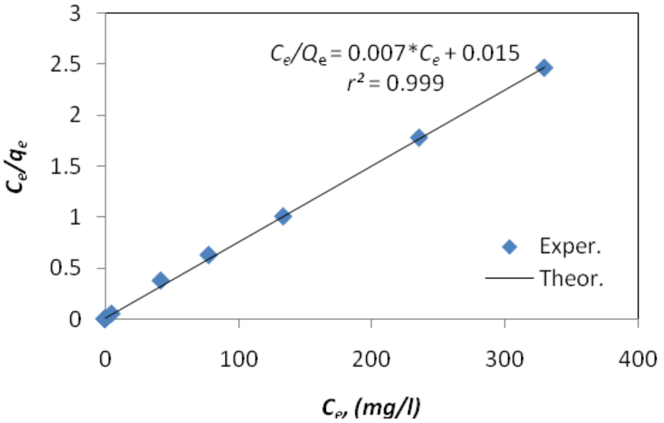

Figure.7: Linear form of Langmuir isotherm of Cr(III)/BCKD system,
Conditions: (0.5g/ 100 ml, 25±2 °C, particle diameter =20 µm, agitation rate 200 rpm, initial pH= 2.5and temperature =25±2 °C)

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimension less constant separation factor or equilibrium parameter, R_L (McKay et al., 1980) in which values of R_L presented for *Cr(III)/BCKD* system are ranged between (0.020964-0.002137) for initial concetration ranged (100-1000 *ppm*) . The parameter indicates the shape of the isotherm between 0 and 1 at different concentrations indicate favorable adsorption of *Cr(III)* on *BCKD.*

Table.2: Langmuir and Freundlich isotherm constants

Langmuir Isotherm					*Freundlich Isotherm*			
K_L	a_L	Q_o	r^2	∈	K_F	n	r^2	∈
(l/g)	(l/mg)	(mg/g)	--	%	(l/g)	--	--	%
66.667	0.467	142.756	0.999	33.468	72.443	7.936	0.856	2.546

3.2.1.2. Freundlich isotherm

The well known Freundlich isotherm is often used for heterogeneous surface energy systems (Schneider et al., 2007; Cooney, 1999; and Bhargava & Sheldarkar, 1993). A linear form of this expression is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \ldots\ldots\ldots\ldots\ldots\ldots.. (5)$$

A linear plot of *log* q_e versus *log* C_e shown in Figure (8). The values of the Freundlich constants together with the correlation coefficient are presented in Table (2) and theoretical data of Freundlich equation is shown in Figure (6). The value of *n* of this model falling in the range 1-10 indicates favorable adsorption (Sahmoune et al.,2008 and; Aksu & Kustal, 1991). Value of the total mean error (∈ %) is much lower than value of Langmjuir isotherm model, which is reach up to 2.546%. This trend is due to the high surface area of the adsorbent, and multilayer of adsorption on the *BCKD*. This trend was investigated also by Schneider et al. (2007) of adsorption *Cr(III)* onto activated carbon, in which Freundlich isotherm gives a best fit.

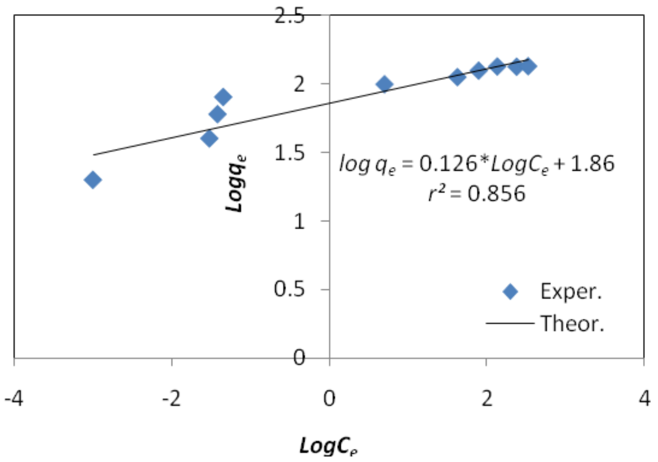

Figure.8: Linear form of Freundlich isotherm of Cr(III)/BCKD system,
Conditions: (0.5g/ 100 ml, 25±2 °C, particle diameter =20 µm, agitation rate 200 rpm, initial pH= 2.5 and temperature =25±2 °C)

3.2.2. Thermodynamic parameters

For study of adsorption isotherm the temperature ranged from 25 to 90 ^{o}C. Adsorption rate of *Cr(III)* increases with temperature (Figure.9). Thermodynamic parameters of the adsorption process such as change in standard free energy (ΔG^{o}), enthalpy (ΔH^{o}), and entropy (ΔS^{o}) were obtained from experiments at various temperatures to predict nature of adsorption process.

The thermodynamic parameters of the adsorption process such as change in standard free energy (ΔG^{o}), enthalpy (ΔH^{o}), and entropy (ΔS^{o}) were obtained from experiments at various temperatures using the following equations (Wang & Li, 2005):

$$\Delta G^{o} = -RT\ln a_L \qquad \text{………………..} \; (6)$$

$$\ln a_L = \frac{\Delta S^{0}}{R} - \frac{\Delta H^{0}}{RT} \qquad \text{………………..} \; (7)$$

where a_L are the Langmuir constants (*l/mol*), R is the ideal gas constant (8.31 *J/mol.K*), and T is the absolute temperature. ΔH^{o} and ΔS^{o} were calculated from the slope and intercept of Eqn. (7).

Langmuir equilibrium isotherms are shown in Figure (9) at varies temperature then and isotherm constants tabulated in Table (4) for the experimental data.

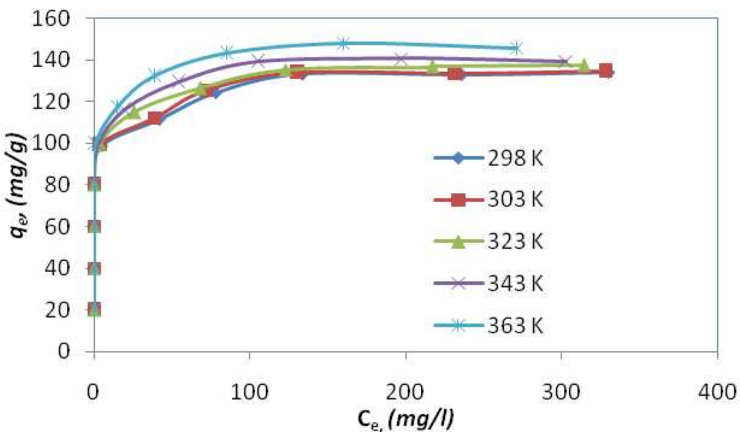

Figure.9: Equilibrium isotherm at different temperature values for Cr(III)/BCKD system

These constants using to apply *Van't Hoff* plot to carry out the computation of the thermodynamic parameters (Ajmal et al., 1998). The Langmuir constants at varies temperatures show a comparatively linear variation with temperature (Figure.10) and hence used to calculate the thermodynamic parameters (Table.3).

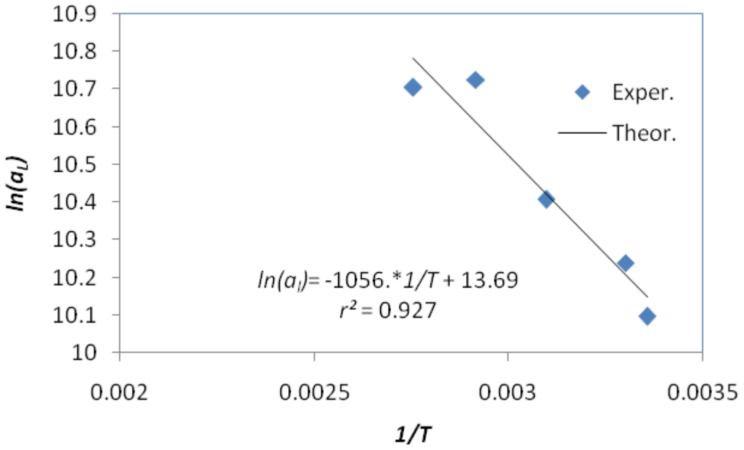

Figure.10: Van't Hof plot for adsorption of Cr(III)/BCKD system.
Condition: (0.5g/ 100 ml, particle diameter =20 µm, agitation rate 200 rpm,initial pH= 2.5 and temperature =25±2 °C)

The negative values of the Gibbs free energy change (-25017.5, -25793.8, -27947.4, -30585.8 and -32306.5 *J/mol* at 25, 30, 50, 70 and 90 °*C*, respectively) indicate that the adsorption process is spontaneous nature for all five temperatures studied; the positive enthalpy (8779.584 *J/mol*) reveals that energy is absorbed as adsorption proceeds, and the extent of the endothermic reaction will increase at higher temperatures (Sandler, 1999 and; Namasiavayam & Yamuna, 1999).

Table.3: Thermodynamic parameters for adsorption of Cr(III)/BCKD system

Temperature, *K*	Q_o *mg/g*	a_l *l/mg*	$\ln a_l$ *l/mol*	ΔG^o *J/mol*	ΔH^o *J/mol*	ΔS^o *J/mol.K*
298	142.7	0.467	10.09757	-25017.5	8779.584	113.86
303	142.979	0.538	10.2391	-25793.8		
323	142.85	0.6364	10.40707	-27947.4		
343	142.857	0.875	10.72547	-30585.8		
363	166.69	0.857	10.70468	-32306.5		

The entropy changes in this study were found to be positive; meaning that increased disorder appeared on the *BCKD*-solution interface during the adsorption process (Low & Lee, 1991). The positive entropy change (113.86 *J/mol.K*) may be due to the release of water molecules and the sulfate anions which are present on the surface or in the interlayer spaces of *BCKD* after the ion exchange reaction with the *Cr(III)* adsorbate.

3.3. *Cr(III)* desorption and regeneration studies

Regeneration of spent *BCKD* and recovery of *Cr(III)* would make the treatment process economical. Also desorption studies help elucidate the mechanism of adsorption, (Arivoli et al., 2008; Namasivayam & Höll, 2004; and Namasivayam & Yamuna, 1999). The effect of various reagents used for desorption studies (DDW, sulfuric acid and acetic acid) indicate that, sulfuric acid is a better reagent for desorption, because get more 96% removal of adsorbed chromium ions. The general trend of increasing desorption with decreasing solution pH as shown in Figure (11) is in keeping with both the present observation of diminished uptake at lower pH and many similar reports (Huang et al., 1990; and Treen-Sears et al., 1984). Increased H^+ concentrations are recognized either to compete with or displace cationic species from anionic *BCKD* binding sites and pH adjustment has previously been used as an effective method of metal recovery (Holan et al., 1993).

The percent desorption decreased from 97.767% to 20.66% when the pH was increased from 0.25 to 2 for initial concentration 200 *ppm*; and decreased from 92.96% to 8.23% when the pH was increased from 0.25 to 2 for initial concentration 1000 *ppm*. Only the *Cr(III)* ions that were adsorbed by ion exchange, not the chemisorbed species, might be desorbed from the adsorbent surface at acidic pH.

The reversibility of adsorbed *Cr(III)* ions in mineral acids is in agreement with the pH dependent results obtained. The desorption of *Cr(III)* ions by mineral acids medium indicates that the *Cr(III)* ions were adsorbed onto the *BCKD* through by physisorption mechanisms same behavior obtained by Arivoli et al., (2008) for *Cr(III)* adsorption onto activated carbon; Tobin & Roux, (1998) for adsorption *Cr(III)* onto waste industrial Mucor meihi biomass and Namasivyam & Yamuna, (1999) for *Cr(III)* adsorption onto residual slurry. Both adsorption kinetic and desorption studies also thermodynamic studies suggest that the physisorption might be the major mode of removal of *Cr(III)* by adsorption on *BCKD*.

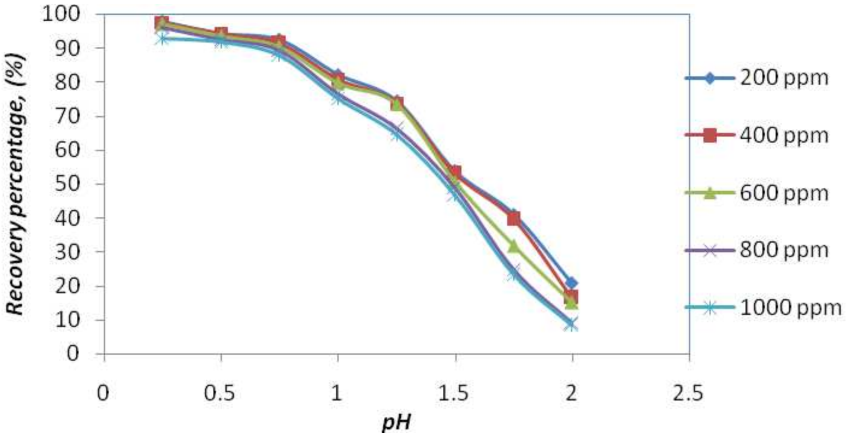

Figure.11: Effect of pH on desorption of Cr(III) from –Cr(III) loaded.
Conditions: (0.5g/ 200 ml, particle diameter =20 µm, agitation rate 200 rpm and agitation time 30 minute)

3.4. Tests with tannery wastewater

Figure.12 shows the effect of adsorbent concentration on the adsorption of *Cr(III)* from both tannery wastewater effluents containing 2336 and 4320 *mg/l* respectively an initial pH of 2.5. A complete removal of *Cr(III)* was obtained at a *BCKD* concentration of 5.5 *g*/250 *ml* (about 22 *mg/l*). The increase of adsorbent dose required to removal of *Cr(III)* in the real wastewater compared to synthetic wastewater due to increase the amount of initial concentrations of *Cr(III)* ions and due to the presence of other constituents present in the tannery wastewater, which compete with *Cr(III)* species for adsorption.

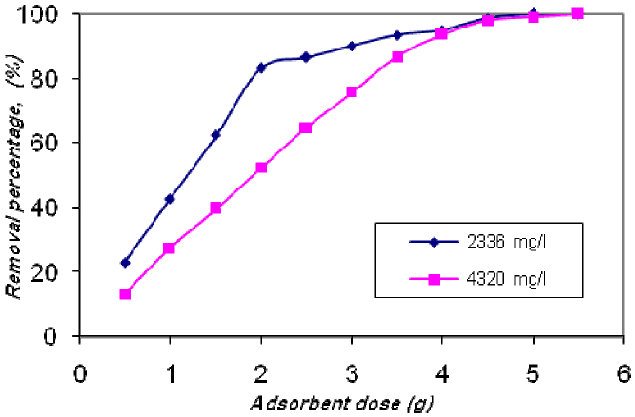

Figure.12: Variation of Cr(III) removal versus adsorbent dose for both batches, *Conditions: (particle diameter =20 µm, agitation rate =1200 rpm, solution volume= 250 ml, initial pH= 2.5 temperature = 25±2 °C and contact time=30 min)*

3.5. Column Studies Results

Figure.13 shows breakthrough curves for three different heights of the *BCKD* bed. Breakthrough times, at C/C_o=0.1, exhaust times, at C/C_o=0.9, and the corresponding volumes, of treated wastewater, at both points, are listed in Table.4 for two chromium concentrations, 2336 $mg.l^{-1}$ and 4320 $mg.l^{-1}$.

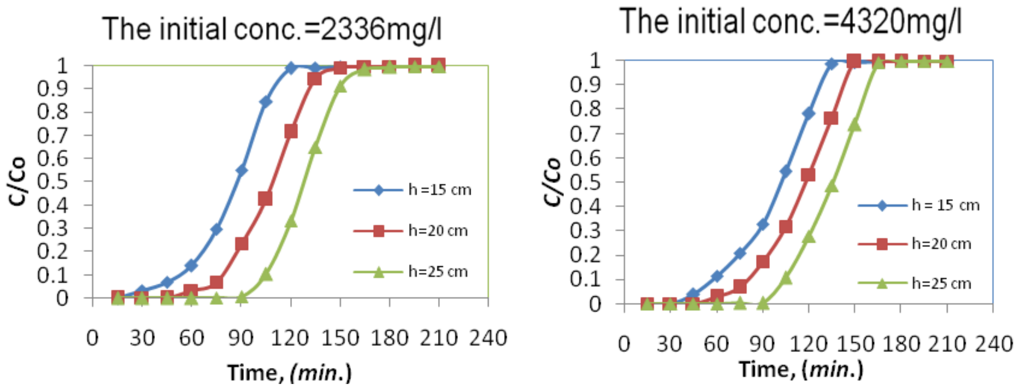

Figure.13: Breakthrough curves of Cr(III) removal by BCKD packed columns of different bed depth for both samples

Table.4: Data of the breakthrough and exhaust points

At C_o=2336 *mg/l*				
Bed depth	**Breakthrough point**		**Exhaust point**	
(*cm*)	**Time (*hr*)**	**Volume (*l*)**	**Time (*hr*)**	**Volume (*l*)**
15	0.9333	0.5880	1.7166	1.0815
20	1.3533	0.8526	2.1333	1.3440
25	1.7283	1.0888	2.4583	1.5487
At C_o=4320 *mg/l*				
Bed depth	**Breakthrough point**		**Exhaust point**	
(*cm*)	**Time (*hr*)**	**Volume (*l*)**	**Time (*hr*)**	**Volume (*l*)**
15	0.9833	0.6195	1.9666	1.2390
20	1.4733	0.9282	2.3833	1.5015
25	1.7366	1.0941	2.6516	1.6705

This type of asymptotic breakthrough curves is desirable, because they are translated to constant mass transfer zone with respect to both position and time. Different parameters for column, such as time required for the exchange zone to move its own height (t_z), height of exchange zone (h_z), rate at which the exchange zone is moving up (U_z) are calculated.

To calculate column and process parameters, Bohart and Adams model was used for this purpose. The simplified equation of Bohart and Adams model (1920) is as follows:

$$t = \frac{N_o}{C_o V} x - \frac{1}{C_o K} ln\left(\frac{C_o}{C_B} - 1\right) \quad \text{........} \quad (8)$$

where C_o is the initial concentration of solute ($mg.l^{-1}$), C_B is the concentration of solute at breakthrough ($mg.l^{-1}$), K is the adsorption rate constant ($l.mg^{-1}.hr^{-1}$), N_o is the adsorption capacity ($mg.l^{-1}$), x is the bed depth of column (cm), V is the linear flow velocity of feed to bed ($cm.hr^{-1}$) and t is the service time of column under above conditions (hr).

Eqn.(8) can be used to determine the service time (t_z)of a column of bed depth (x) given the values of (N_o, C_o and K) which must be determined for laboratory columns operated over a range of velocity values (V).

To collect the required laboratory data, a technique requires only three column tests to collect the necessary data. In this technique, given by Hutchins, (1973), called the bed depth service time (BDST) approach, the Bohart-Adams equation is expressed as;

$$t = ax + b \quad \text{........} \quad (9)$$

where:

$$a = slope = \frac{N_o}{C_o V} \quad \text{........} \quad (10)$$

$$b = intercept = \frac{1}{KC_o} ln\left(\frac{C_o}{C_B} - 1\right) \quad \text{........} \quad (11)$$

Figure.14 shows the plot of depth versus service time (BDST) for 10 and 90% saturation of column for both samples. The equations of these lines were as follows:

At C_o=2336 $mg.l^{-1}$

For 90% saturation: $t = 0.074x + 0.619$

For 10% saturation: $t = 0.079x - 0.251$

At C_o=4320 $mg.l^{-1}$

For 90% saturation: $t = 0.068x + 0.963$

For 10% saturation: $t = 0.075x - 0.108$

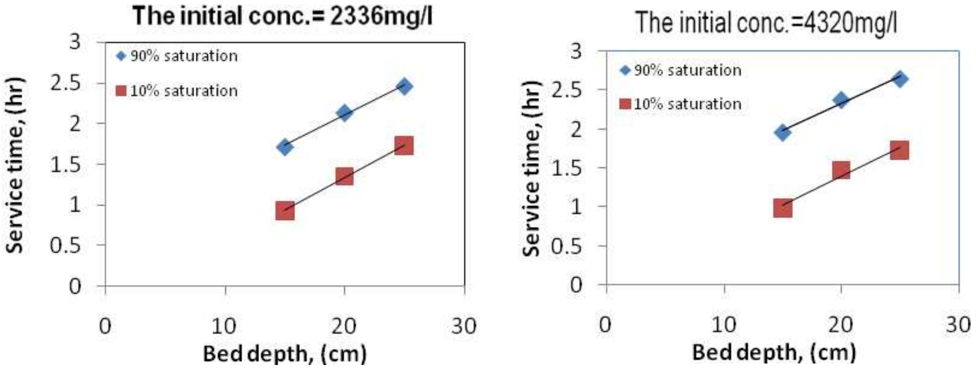

Figure.14: BDST curve for Cr(III) removal

From the slope, it was found that these lines are, almost, parallel and the horizontal distance between the lines is called the height of exchange zone (h_z). The heights of the exchange zone for each bed depth and sample's concentration are shown in Table 5.

Table.5: Values of estimated exchange zone height

	t_z, (*hr*)		**h_z, (*cm*)**	
Bed depth	**C_o = 2336 *mg/l***	**C_o =4320 *mg/l***	**C_o =2336 *mg/l***	**C_o =4320 *mg/l***
15 *cm*	0.783	0.9833	10.6868	14.2292
20 *cm*	0.78	0.91	10.2592	13.5429
25 *cm*	0.73	0.915	9.8315	12.5429
Average value	0.7644	0.93611	10.2592	13.548

From the slope and intercept of the 10% saturation lines, N_o and K were calculated out using Eqns. (10) and (11), respectively. These values are presented in Table 6.

Table.6: Important column design parameters

	For 10% saturation		For 90% saturation	
Parameter	C_o = 2336 $mg.l^{-1}$	C_o =4320 $mg.l^{-1}$	C_o =2336 $mg.l^{-1}$	C_o =4320 $mg.l^{-1}$
A	0.079	0.075	0.074	0.068
B	-0.251	-0.108	0.619	0.963
N_o, ($mg.l^{-1}$)	22956.38	40304.03	--	--
K, ($l.mg^{-1}.hr^{-1}$)	0.00375	0.00471	--	--

High values of N_o indicate the high capacity of BCKD for Cr(III) adsorption and hence, its removal from water media.

4. CONCLUSIONS

The following conclusions were drawn from the present study:

- The obtained results showed that pH, adsorbent dose, initial metal concentration uptake time and solution temperature highly affected the *Cr(III)* ions removal by *BCKD*.
- The optimum conditions for chromium removal operation from aqueous solution are 15 *minutes* contact time and 200 *rpm* agitation rate in presence of 5.5 *g* of adsorbent per one *liter* of aqueous solution of *Cr(III)* ions at initial concentration value equal to 2.5.
- Adsorption followed Freundlich isotherm and the monolayer saturation capacity (Q_o) is 142.756 *mg/g* at pH 2.5.
- The calculated thermodynamic parameters showed that reactions were endothermic and spontaneous in nature that proceeds.
- Desorption data obtained reveal to that, the adsorption process of *Cr(III)* onto *BCKD* are physical-sorption in nature.
- It is a cheap and abundant material, which has high capacity, and represents an alternative to more costly materials. Breakthrough curves indicated, beside high capacity, uniform structure and constant transfer zone with position and time.
- Application of *BCKD* for the removal of *Cr(III)* from tannery wastewater has been demonstrated. The data may be helpful for designing and fabricating tannery wastewater treatment plants for the removal of *Cr(III)*.

These all facts confirmed that *BCKD* can be used for the effective removal of trivalent chromium from aqueous solution with high uptake capacity.

5. REFERENCES

Ajmal, M.; Khan, A.H.; Ahmed, S. and; Ahmed, A. (1998). "Role of saw dust in the removal of copper (*II*) from industrial wastes"; *Wat. Res.*; **32**: 3085–3091.

Aksu, Z. and; Kutsal, T. (1991). "A bio-separation process for removing lead (*II*) ions from waste water by using C. vulgaris"; *J. of Chem. Technol. And Biotechnol*.; **52(1)**: 109-118.

Alves, M.M; Gonzalez-Beca, C.G.; Guedes de Carvalho, R.; Castanheira, J.M.; Sol-Pereira, M.C. and; Vasconcelos, L.A.T. (1993). "Chromium removal in tannery wastewaters “polishing” by Pinus sylvestris bark"; *Wat Res.;* **27**: 1333-1338.

Arivoli, S.; Hema, M.; Karuppaiah, M. and; Saravanan, S. (2008). "Adsorption of Chromium ion by Acid Activated low Cost Carbon-Kinetic, Mechanistic, Thermodynamic and Equilibrium Studies"; *E-Journal of chemistry*; **5(4)**: 820-831.

Babel, S. and; Opiso, M. (2007). "Removal of *Cr* from synthetic wastewi8;;ater by sorption into volcanic ash soil"; *Int. J. Environ. Sci. Tech.*; **4(1)**: 99-107.

Bhargava, D.S. and; Sheldarkar, S.B. (1993). “Use of *TNSAC* in Phosphate Adsorption Studies and Relationships. Isotherm Relationships and Utility in the Field”; *Wat. Res*.; **27(2)**: 325-335.

Bohart, G.S. and; Adams, E.Q. (1920). "Some aspects of the behavior of charcoal with respect to chlorine", J. Amer. Chem. Soc., **42**, 523-44.

Cooney, O. D. (1999). “*Adsorption Design for Waste-water Treatment*”; Lewis Publishers.

Costa, M. (1997). "Toxicity and carcinogenicity of Cr(VI) in animal models and humans"; *Critical Rev. Toxicol.*; **27(5)**: 431–442.

Dahbi, S.; Azzi, M.; Saib, N. And; de la Guardia, M. (2002). "Removal of trivalent chromium from tannery wastewaters using bone charcoal"; *Anal. Bioanal. Cem.*; **374**: 540-546.

El-Awady, M.H. and; Sami, M. (1997). "Removal of heavy metals by cement kiln dust"; *Bull. Environ. Contam. Toxicol.*; **59**: 603-610.

Holan, Z.R.; Volesky, B. and; Prasetyo, I. (1993). "Biosorption of Cadmium by biomass of marine algae; *Biotechnol. Bioeng*.; **41**: 819-825.

Huang, C.P.; Huang, C.P. and; Morehart, A.L. (1990). "The removal of *Cu(II)* from dilute aqueous solutions by Saccharamyces cerevisiae"; *Wat. Res*.; **24**: 433-439.

Hutchins, R. A. (1973). "New simplified design of activated carbon systems"; J. Am. Chem. Eng.; **80**; 133.

Chapra, S.C. and; Canale, R.P. (1998). “*Numerical Methods for Engineers*”; 3rd edition; McGraw-Hill Co.; USA.

Chaudry,A.; Ahmad, M.S. and; Malik, M.T. (1998). "Supported liquid membrane technique applicability for removal of chromium from tannery wastes"; *Waste Manag*.; **17**: 211-218.

Ibrahim, H.G. (2010). "Removal of chromium trivalent ions from aqueous solutions using bypass cement kiln dust and its application to tannery wastewater treatment", *Ph.D. dissertation*, West Coast University, LA, USA

Jamali, H.A.; Mahvi, A.H. and; Nazmara, S. (2009). "Removal of Cadmium from aqueous solutions by Hazel nut shell"; *World Appl. Sci. J.*; **5**: 16-20.

Khan, N.A. and Mohamad, H. (2007) Investigation on the removal of chromium (VI) from wastewater by sugarcane bagasse, *Water and Wastewater Asia*, January/February: 37-41.

Leyva R. R.; Juarez Martinez, A. and; Guerrero Coronado, R.M. (1994). "Adsorption of chromium (VI) from aqueous solutions on activated carbon"; *Water Sci. Techol.* **30**: 191–197.

Leyva, R.R.; Fuentes-Rubio, L.; Guerrero-Coronado, R. M. and; Mendoza-Barron, J. (1995). "Adsorption of trivalent chromium from aqueous solutions onto activated carbon"; *J. Chem. Technol. Biotechnol*.; **62**: 64-67

Low, K.S. and; Lee, C. K. (1991). "Cadmium uptake by the moss calympers delesertii"; *besch. Bioresour. Technol.;* **38***:* 1-6.

McKay, G.; Otterburn, M. S. and; Sweeney, A. G. (1980). "The removal of color from effluent using various adsorbents-IV. Silica: Equilibria and column studies "; *Wat. Res.*; **14**: 21-27.

Namasivayam, C. and; Höll, W.H. (2004). "Chromium(*III*) removal in tannery wastewaters using Chinese Reed (Miscanthus Sinensis), a fast growing plant"; *Holz. Roh. Werkst.*; **62**: 74-80.

Namasivayam, C. and; Yamuna, R.T. (1999). "Studies on Chromium(*III*) removal from aqueous solutions by adsorption onto Biogas residual slurry and its application to Tannery wastewater treatment"; *Water, Air, and Soil Pollution*; **113**: 371-384.

Özacar, M. (2003). "Equilibrium and Kinetic Modeling of Adsorption of Phosphorus on Calcined Alunite:; *Adsorption*; **9**: 125-132.

Panday, K.K.; Prasad, G. and; Singh, V.N. (1984). "Removal of Cr(IV) from aqueous solutions by adsorption on flyash-wollastonite"; *J. Chem. Tech. Biotechnol.*; **34A**: 367-374.

Potgeiter, J.; Potgeiter-Vermaak, S.and; Kalibatonga, P. (2005). "Heavy metals removal from solution by palygorskite clay"; *Minerals Engineering,* Article in Press. *Online available at: Elsevier Science Direct.*

Press, W.H.; Flannery, B.P.; Teukolsky, S.A. and; Vetterling, W.T. (1989). "*Numerical Recipes in Pascal: The Art of Scientific Computing*"; Cambridge University Press; Cambridge; UK.

Rand, M.C.; Greenberg, A.E. and; Taras, M.J. (1995). "*Standard methods for the examination of water and wastewater*"; 19th ed.; APHA, AWWA and WEF; Washington D.C.; USA.

Sahmoune, M.N.; Louhab, K. and; Boukhiar, A. (2008). "Kinetic and equilibrium models for the biosorption of *Cr(III)* on Streptomyces rimosus"; *Res. J. of Appl. Sci.*; **3(4)**: 294-301.

Sandler, S. I. (1999)."*Chemical and Engineering Thermodynamics*"; 3rd ed.; John Wiley & Sons; New York; USA

Sharma DC, Forster CF (1993) Removal of hexavalent chromium using sphagnum moss peat. Water Res 27:1201–1208

Schneider, R.M.; Cavalin, C.F.; Barros, M.A. and; Tavares, C.R.G. (2007). "Adsorption of Chromium ions in activated carbon"; *Chem. Eng. J.*; **132**: 355-362.

Tahir, H.; Saleem, M.; Afzal, M.; Ahmad, H.; Hussain, S.T. and; Afjal, J. (1998). "Estimation and removal of chromium ion from tannery wastes using Zeolite-3A"; *Adsorption Sci. Technol.*; **16**: 153-161.

Tiravanti, G.; Petruzzelli, D. and; Passino, R. (1997). "Pretreatment of tannery wastewaters by an ion exchange process for *Cr(III)* removal and recovery"; *Water Sci. Technol.* **36**: 197–207.

Tobin, J.M. and; Roux, J.C. (1998). "Mucor biosorption for chromium removal from tanning effluent"; *Wat. Res*.; **32(5)**: 1407-1416.

Treen-Sears, M.; Volesky, B. and; Neufeld, R.J.; (1984). "Ion exchange complexation of the uranly ion by Rhizopus biosorbents"; *Biotechnol. Bioeng.*; **26**: 1323-1329.

Wang, S. and; Li, H. (2005). "Dye adsorption on unburned carbon: kinetics and equilibrium"; *J. Hazard. Mater.*; **126 (1-3)**: 71-77.