On the Adsorptive Detoxification of Chrome Tan Liquor: Kinetics, Thermodynamics and Mode of Transport.

Abstract:

Aim: The aim of this study is to regenerate spent activated carbon (RGAC) for use as adsorbent and to study the kinetics, thermodynamics and mode of transport of removing chromium from spent chrome tanning effluent (TEff).

Methodology: The chemical regeneration approach was adopted in the recycling. Regenerated adsorbent was characterized using FTIR, SEM and classical methods. A batch adsorption experiment was carefully followed to de-chrome the chrome tan effluent. Equilibrium phase chromium was quantified with Atomic Absorption Spectrophotometer (AAS). Adsorption phenomena were investigated with Kinetic, thermodynamic and transport (diffusion) models to study the behavior of Cr uptake. Kinetic models viz; First order, pseudo-second order, Elovich and Bhattacharya-Venkobachor kinetic models were subjected to three model applicability tests. Thermodynamic parameters which include changes in free energy (ΔG), entropy (ΔS) and enthalpy (ΔH) were monitored in standard states. Prediction of applicable diffusion model was based on comparing film diffusion, intra-particle diffusion and intraparticulate diffusivity models.

Results: Highlights from this study unveiled the influential roles of parametric factors (Initial effluent concentration on vol./vol. bases, solution pH, particle size, adsorbent dose, contact time and temperature). R^2 values for models considered showed good fit except for the Bhattacharya-Venkobachor kinetic model. The rate law of the adsorption kinetics is best explained using the Pseudo-second order kinetic model. The chromium adsorption efficiency using both Commercial and regenerated GAC are in good agreement at 95 % confidence interval. The regenerant-chromium mode of diffusion, as predicted by the "best-fit'' transport models, was not suitable for use in the intraparticle diffusion mode (with least R^2 and high transport rate) as it does for the film diffusion. In addition, thermodynamic parameters of sorption have also been determined in favour of spontaneity and chemisorptions mechanism.

Conclusion: An overall from this study is the recommendation of regenerated adsorbent as a sure economically viable substitute to the commercial activated carbon for chrome tan effluent de-chroming. This generalization was based on statistical test of significance which reports good agreement between the two adsorbents for the investigated adsorption phenomena.

Keywords: Regenerated, Tannery effluent, Rate, Diffusion, Regenerant, Diffusion, Film Diffusion

1. Introduction

The wastewaters, which are by-products from industrial activities (Tanneries, mining, painting and printing processes, plumbing, automobile batteries and petrochemical industries) contains very high concentration of heavy metals ions. Which may include either, some or all of lead, cadmium, mercury, chromium, nickel, zinc and copper, are non-biodegradable and are often toxic and carcinogenic, even at very low concentrations [1].

Owing to the property of metals which is its toxicity and non-degradable nature, researchers the world over has focused on the removal of these metals from solutions and industrial effluents. Different treatment techniques have been developed and tried out in the removal of dissolved metals in soils and wastewaters, these methods include: reverses osmosis, ion flotation, chemical precipitation, membrane filtration, membrane processes, ion-exchange, electrochemical, the application of complexing agent and membrane filtration. Notably, the techniques mentioned above are not without their diverse disadvantages, which can be in terms of, ability to completely remove the metals, requires use of a large quantity of reagents, low selectivity, not financially prudent and generation of secondary waster (e.g. sludge) which are usually difficult to treat. Bearing this is mind; technologies, which are cost-effective in the treatment of metal-contaminated wastes streams, are paramount. Adsorption method of metal removal has proved to be one of the reliable and cost-effective methods, which is uncomplicated, cheap and selective for the remediation of metal polluted wastes [1]. One of the heavy metals that have been a major focus in wastewater management is chromium; this metal is introduced into the environment via industrial discharges from leather tanning, textiles, paint and pigment, electroplating, canning, glass and ceramic industries. At high concentrations, all compounds of chromium are toxic, its ingestion may result to diarrhea and sevear vomiting, nausea and epigastric pains [2]. Ghosh and Singh [3], affirmed that the range of chromium toxicity for most agronomic plants varies from 5 to 100 mg/kg of available chromium in soil. Because of its high oxidizing potential, Cr(VI) causes mutagenic and carcinogenic effects on biological organisms.

Leather is material a product of specific reaction among carboxylic groups of protein fiber network or matrix of animal skin (collagen) and tanning regents, which gives it a reasonable resistance, good chemical stability and acceptable thermal behavior. Tanning industries use large quantities of water (15 to 20 m^3) per ton of raw skin. The major public concern over tanneries has traditionally been about odours and water pollution from untreated discharges. Important pollutants associated with the tanning industry include chlorides, tannins, chromium, sulphate and sulphides as addition to trace organic chemicals and increasing use of synthetic chemicals such as pesticides, dyes and finishing agents, as well as from the use of newer processing chemical solvents. The tannery effluents are characterized by high COD and BOD andconductivity values. The composition of the effluent varies according to the tanning process used and the type of leather to be obtained. Tannery wastewater contains large amount of chemical compounds, mostly toxic in nature [4,5]
Chromium tanning is a reaction between collagen and Cr^{+3} ion. Six coordination positions (octahedron) are available, and stereo-isomers are possible. In solution, chromium III nitrate is thought to give a complex ion of the form $[Cr\ (H_2O)_6]^{+3}$ in solution. Reaction sites for chrome tanning are the ionised carboxyl groups on side chains of the collagen. The lateral cross-linking of chrome complexes is presented in Figure 1.

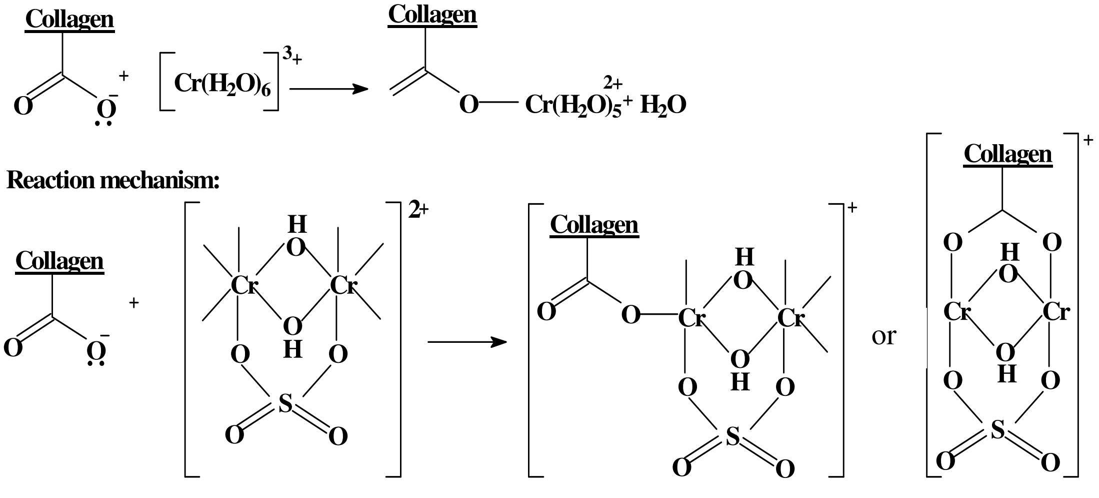

Fig. 1: Proposed Chromium (III) tanning mechanism [6]
The manufacture of leather has evolved into a significant source of livelihood in many industrialized and developing countries. Bosnic *et al* [7] reported an estimated production

capacity of 1.8 billion metric tons of leather yearly, with a larger part of the product processed in Africa and Asia, factored by the high labour intensity involved in leather manufacture. Procedures employed by most developing countries in leather tanning are still at the traditional level and are not technologically compactable or designed for use with chemical and water. As estimated, the total wastewater discharge from tanneries runs to about 400 million m^3 each year. This industry has been painted negatively in the society owing to its high pollutant composition. The difficulty in treating tannery effluent results from the complex nature of the wastewater produced, leading to various environmental regulations and laws in many developing countries being passed especially in the last ten years

The tannery industry is known for its deterring impact on the environment. High quantities of polluted water are discharged containing large amounts of chemicals which include lime, sodium chloride and chromium salts from which the discharge of heavy metal (Cr) into the environment is known [8]. It is noteworthy that the chromium present in chrome tan by-products is in the trivalent state and considered harmless, which under noncontrollable conditions, however, the Cr (III) can be oxidized to the mutagenic chromium (VI) and become threatening to man and the environment [9]. Biochar dechroming uses the leather as the source of organic carbon to convert the chromium, in which the oxygen in the leather is excluded to create the biochar. The chromium in the wastes will combine with the biochar to produce chromium carbide at higher temperatures. Thus, the chromium can be captured by the biochar [10]. This may however end up as constituent of chrome liquor. The literature suggests that chromium-tanned leather waste may be managed through more sustainable technological alternatives, namely by wet treatment [11].

De-chroming (by Chrome shaving, dechromed splits, Oxidation dechroming or reduction with hydrogen peroxide, Hydrolysis dechroming, Alkaline hydrolysis dechroming, Enzymatic hydrolysis dechroming, reduction with glucose and sodium disulphite) [12] in tanning is carried out in order to achieve maximum elimination of chromium from the leather sample without affecting the molecular structure of collagen fibres thereby generating chrome liquor. This is different from reduction of chromium from the environment or receiving water bodies. In this study we focused on detoxifying the generated chrome tan effluent using adsorption; a clean and economically viable technology with an attempt to overcome the high cost of activated carbon by considering regeneration and reuse of spent adsorbent.

2. MATERIALS AND METHODS

All of the used reagents were analytical grade,purchased and applied without further purification. FTIR spectrum was recorded on a Fourier Transform Infrared Spectrometer (Agilent technologies Cary 630), scanning electron microscope (SEM) images of virgin, effluent loaded and Chemically regenerated activated carbon at selected magnifications was observed using SEM (Phenomenon Prix, MVE016477830). UV-Visible (Agilent 8453E) Spectrophotometer was used to study the absorbance of both treated and untreated effluent. The procedure was carried out at a pre-determined wavelength (λ max) of 353 nm. Atomic adsorption Spectrophotometer (Varian AA240FS) was used to estimate the concentrations of Cr.

The spent activated carbon used in this work, with already exhausted adsorption efficiency, came from an initial filtrate obtained in a previous experiment.

2.3 Sampling

Methods described by Kawser *et al.* [13] and Islam *et al.* [14] was followed. The Chrome tannery effluent (Liquor) was sampled by lowering a pre-cleaned 4L glass bottle (previously washed with 0.1M HNO_3 and rinsed with distilled water), allowed to overflow, withdrawn, sealed and stored at 4^oC till required for analysis.

2.1 Chemical regeneration of activated carbon

Regeneration of exhausted activated carbon was carried out in the laboratory using method adopted from Abbas and Waleed [15]. The exhausted activated carbon (50 g) was weighed by electric balance (Mettler AE200) and mixed with 600 mL of 20% ethanol in a pyrex beaker of 1L. The mixture was agitated using a magnetic stirrer (IKA Hitachi RT5) at 200 rpm for 4 h at 25 ± 2^oC (room temperature). The washing liquid was replaced three times during this process, then with 0.1 M NaOH then rinsed with distilled water, the pH of the activated carbon was neutralized (pH 7) using 0.1 M HCl and dried in the oven (Gallenkamp BS 0V-160) at 200^oC for 3 h.

A batch adsorption experiment was carried out using the regenerated granular activated carbon. The efficiency of the regenerant is judged on the adsorption quantity of activated carbon. This efficiency was calculated using the relation:

$$Regeneration\ Efficiency\ (RE\ \%) = \frac{q_r}{q_0} \times 100 \qquad (1)$$

Where q_0 and $q_r$are quantity of Cr (or adsorbate) adsorbed per unit weight of commercial activated carbon and quantity of Cr (or adsorbate) adsorbed per unit weight of activated carbon, respectively [16]

2.2 Chromium Estimation

Chrome tan liquor was digested accordingly [17]. The digest was quantitatively transferred to a volumetric flask and diluted to 50 mL volume with deionized water and analysed for heavy metal (Cr) using AAS.

2.3 Adsorption Studies

2.3.1 Effect of agitation time on adsorption of Cr onto activated carbon

One gram activated carbon was placed in five well labeled 250 mL Erlenmeyer flasks, each containing 50 mL of tannery wastewater. The flasks were agitated continuously for 20 minutes. The resulting mixture was filtered using Whatman No.2 filter paper and stored in a well labeled glass bottles at normal room temperature for further analysis. The same procedure was repeated for for 40, 60, 80 and 100 minutes agitation time [18].

2.3.2 Effect of temperature on adsorption of Cr onto activated carbon

The activated carbon (1g) was mixed with 50 mL of sample and treated using the Gallenkamp temperature controlled water bath shaker. The instrument was set at 20^oC for 1hr, after which the sample was taken off and filtered using the Whatman No.2 filter paper, stored in a well labeled glass bottle at normal room temperature for further analysis. The same procedure was repeated for samples at temperatures of 40^oC, 60^oC, 80^oC and 100^oC for 1hr each [18].

The amount of Cr adsorbed by the adsorbent was evaluated using equations described by Vijayakumar *et al.* [19].

For adsorption of Cr at equilibrium:

$$q_{e=\frac{(C_o-C_e)v}{w}} \qquad (2)$$

Where q_e, C_o, are equilibrium metal uptake sorption capacity, initial metal concentration (mg/L) and C_e is final metal concentration (mg/L). v is the volume of effluent solution in liters while w is the weight of adsorbent in grams. The percentage of Cr removed was calculated using the relation:

$$(\%)RE = \frac{(C_o - C_f)X\ 100}{C_o} \qquad (3)$$

RE represents the metal adsorption percentage or efficiency, C_o, the initial metal concentration (mg/L) andC_f is the final metal concentration (mg/L).

2.4 Adsorption kinetics

In order to evaluate the kinetic mechanism which controls the process, the Elovich, First-order, Pseudo second-order and the Bhattacharya-Venkobachor models were tested and the validity of the models were verified by their linear equation analysis.

2.4.1 Model applicability test for kinetic studies

Prediction of best fit model was based on the following:

(i) Regression analysis using the correlation of applicability (R^2) test.
(ii) Precision test, comparing q_e experiment and q_e calculated.
(iii) Statistical sum of error test:

$$SSE\ (\%) = \sqrt{(q_e\ exp - q_e\ cal)^2/N} \qquad (4)$$

where N is indicates the number of data points.

2.5 Adsorption thermodynamics

Adsorption experiment was carried out at varying temperature after which the Van't Hoff Plot was used to determine the thermodynamic conformity of the experiment. The thermodynamic parameters change in Gibb's free energy (ΔG^o), change in enthalpy ΔH^o, and change in entropy ΔS^o for the adsorption of Cr over the activated carbon was determined [20].

2.6 Mode of Transport (Diffusion)

Data generation from the sorption kinetic experiment was fitted into various diffusion models:

2.6.1 The intraparticle diffusion model

In many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t. Intraparticle diffusion model is expressed as:

$$q_t = k_{int} t^{1/2} \qquad (5)$$

k_{int} is the intraparticle rate constant. A plot of $q_t$versus $t^{1/2}$ should be a straight line with a slope k_{id} when the intraparticle is a rate limiting step. For Weber-Morris model, it is essential for the $q_t$versus $t^{1/2}$ to go through the origin if the intraparticle diffusion is the sole rate-limiting step [21]

2.6.2 Film diffusion model

Liquid film diffusion model is used to investigate if transport of metal ions from liquid phase to the solid phase boundary also plays a role in the adsorption process. The equation explaining this model is:

$$\ln(1 - F) = -\mathrm{k_{fd}} t \qquad (6)$$

F is the fractional attainment of equilibrium (F=qt/qe), K_{fd} is liquid film diffusion constant. Linear plot of –ln(1-F) versus t is used to fit this model[21].

2.6.3 Bhattacharya-Venkobachor model (for Diffusion coefficient)

This model is expressed as;

$$ln\left[1 - U_{(t)}\right] = K_{B}\cdot t \qquad (7)$$

$$U_{(t)} = (C_o - C_t)/(C_o - C_e) \qquad (8)$$

The effective diffusion coefficient is obtained from the equation:

$$D_2 = \frac{K_{B}\cdot I^2}{\Pi^2} \qquad (9)$$

r is particle radius. From the plot of ln[1-U (t)] versus t, the effective diffusion coefficient D_2 and rate constant, K_B can be determined [22].

3. RESULTS AND DISCUSSION

3.1 Physical Inspection

Physical examination of untreated effluent sample (Figure 2) revealed high pollution density as evident by brown colouration, foul odour, microbial activities etc. Similar result was reported by [5].

Fig. 2: Typical picture of Tannery (Top left), Effluent discharge point (Top right), Near point of impact (Bottom left) and Tan effluent (Bottom right)

3.2 FTIR and SEM Characterization

Figure 3 is SEM images (bottom) for GAC and RGAC with the corresponding FTIR Spectrum (top) of the adsorbents. Surface morphology of the image for regenerated adsorbent (RGAC) revealed more pore size development. This increased pore cavities observed for RGAC are linked to acid treatment during the regeneration process. FTIR spectrum of the RGAC indicated eight functional peaks, with two peaks higher than those reported for the GAC FTIR spectrum. This could be linked to residual regenerating agents (acids)

Table 1 is a summary of the FTIR spectral information for received tannery effluent (TEff) and treated tannery effluent (TTEff). By comparing the two spectra, dissimilar levels of observed frequencies and alteration of their peak intensities is an indication of adsorption of certain pollutant species onto the adsorbents. Results from this study unveiled only partial adsorption (%RE < 100) of such species.

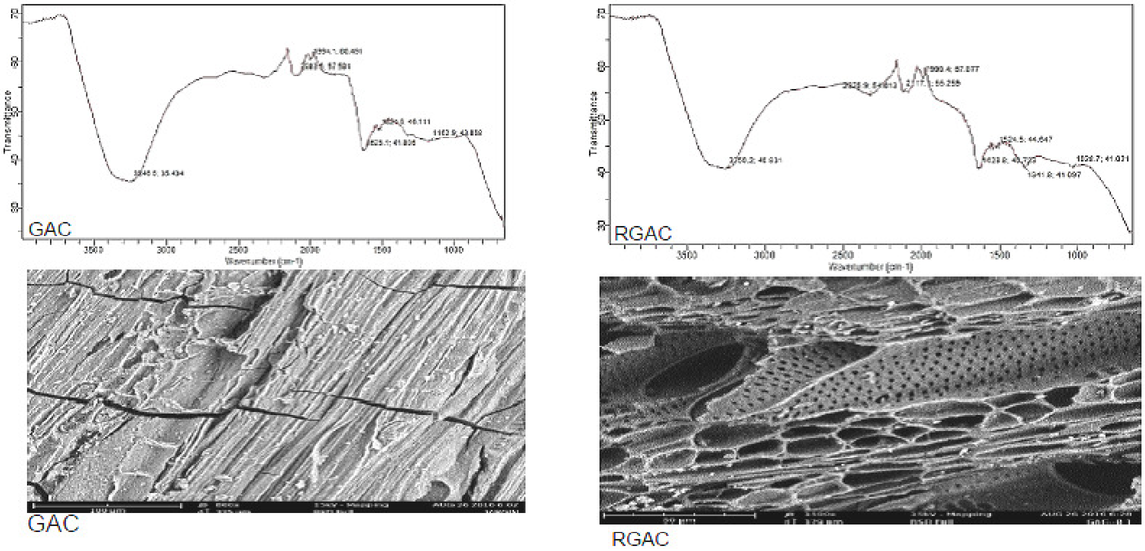

Fig. 3: SEM micrographs of virgin GCAC and Regenerated RGCAC with conspicuous pore size development with their respective FTIR spectrum

Table 1. **Comparative FTIR spectra characteristics of T_{Eff} and TT_{Eff}.**

Vib. Freq. (cm^{-1})	Observed Frequencies (cm^{-1})		Functional group
	T_{Eff}	TT_{Eff}	
1342-1000	1095.8	1341.8	C-C; C-H;
1680-1620	1636.3	1636.3	NH; C=C
3333-2000	2117.1 3306.1	2102.2 3295.0	O-H stretch; -NH stretch; ≡CH-H stretch; O-H Broad

3.3 Adsorption Studies (on Parametric factors)

3.3.1 Effect of pH

Highest % removal of Cr for T_{Eff} – GCAC was observed at pH 6 for GCAC and at pH 8 for T_{Eff} – RGAC. The results shown in Figure 4 indicate that maximum uptake of Cr ions takes place at pH 4 and decrease in adsorption capacity on either side of pH 4. The removal of Cr is pH dependent because the surfaces of activated carbons are negatively charged at certain pH [23]. The decrease in adsorption capacity in the low pH region is expected as the acidic medium leads to an increase in hydrogen ion concentration which then neutralizes the negatively charged carbon surface thereby decreasing the adsorption of the positively charged cation.

3.3.2 Effect of adsorbent dose

The removal of Cr was found to be highest with an adsorbent dosage of 2.5 g, achieving above 60 % Cr removal for GCAC and over 55 % removal for RGAC (Figure 5). The increase in removal of Cr with adsorbent dose can be attributed to the introduction of more binding sites for adsorption. Similar results have been reported [18, 24, 25]

3.3.3. Effect of initial concentration

The RE (%) of Cr in the sample is influenced by the initial adsorbate concentration. The highest percentage removal by GCAC was 67 % and 96 % with RGAC (Figure 6). Thus, at higher initial concentration, the percentage removal decreases. This could be linked to competition for attachment sites.

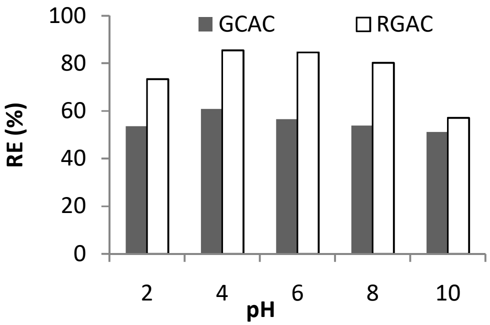

Fig. 4: Effect of pH on RE (%) of Cr by Adsorbents

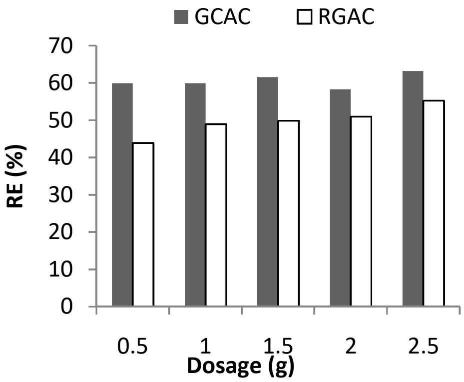

Fig. 5: Effect of Adsorbent Dosage on RE (%) of Cr

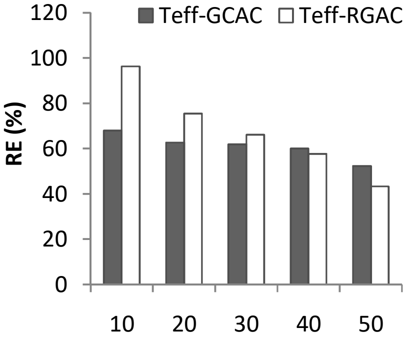

Fig. 6: Effect of Concentration on RE (%) of Cr

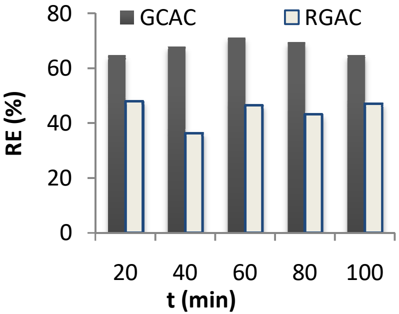

Fig. 7: Effect of Contact Time on RE (%) of Cr

Table 2 presents results on removal or adsorption or efficiency (%RE). This study indicated the suitability of using both adsorbents for the removal of Cr from chrome tan effluent via batch adsorption studies. Mean value > 47% and up to 80.2 % was reported for varying degree of pollutants.

Table 2. Equilibrium Phase Removal Efficiency (%) of Pollutants using Commercial and Regenerated Adsorbents.

Pollutant	**Experiment**	**Co (mg/L)**	**Ce (mg/L)**	**RE (%)**
Chloride Ion	T_{Eff} – GCAC	579.820	174.950	69.8
	T_{Eff} - RGAC	579.820	139.960	75.9
Sulphide Ion	T_{Eff} – GCAC	450.000	235.000	47.8
	T_{Eff} - RGAC	450.000	225.000	50.0
Nitrite Ion	T_{Eff} – GCAC	4.5	2.24	50.2
	T_{Eff} - RGAC	4.5	0.89	80.2
Chromium	T_{Eff}–GCAC	148.917	64.467	56.7
	T_{Eff} - RGAC	148.917	59.626	60.0

3.4 Kinetic models

R^2 for the **Elovich** model is 0.0049, this value is same as that for intra-particle diffusion model and indicates a high degree of unconformity to the expected model, and hence the active sites on the CAC are not heterogeneous. In reactions involving chemisorption of adsorbate on a solid surface without desorption of products, adsorption rate decreases with time due to an increased surface coverage. One of the most useful models for describing such 'activated' chemisorption is the Elovich's [26]. The general explanation for this form of kinetic model is that the active sites are heterogeneous in nature and therefore exhibit different activation energies for chemisorption [27].

The rate constant of adsorption was determined from the first-order equation given by Langergren and Svenska [28]. The R^2 values for this model at studied are 0.003 and 0.062 for GCAC and RGAC, qe (exp) and qe(cal) tested didn't show any close agreement, the sum of error squares (% SSE) was higher for GCAC (1419.99) and RGAC (114.93) as shown in Table 3. The low correlation coefficient value obtained from the pseudo first-order kinetic model indicates that sorption is not occurring exclusively onto one site per ion [29]. This model is not applicable and does not explain the mechanism of adsorption kinetics.

The coefficient of regression for the pseudo-second order model suggested the applicability of the pseudo-second order kinetic model, 0.993 (GCAC) and 0.971 (RGAC) as best fit model which describes the adsorption kinetics process of Cr uptake on the adsorbents. This shows that the overall rate of the adsorption process was controlled by chemisorption and involves valence forces, through sharing or exchange of electrons between the sorbent and the sorbate [30]. The second-order kinetics is applicable to the system; since the plot of t/qt versus t (Figure 9), gave a linear relationship [31]. Low error function (18.3%) was recorded for RGAC and high (65.2%) for GCAC. A close agreement between the calculated and experimental qe values (292.4 and 333.3) was recorded for RGAC

Considering the Bhattacharya-Venkobachor kinetic model, Kinetic constants obtained from these plots (GCAC and RGAC) does not show good fits, given that their R^2 values are 0.4997 and 0.0412, likewise D_2 value for GCAC reads 0.001 while that of RGAC reads -0.021 [32].

Mode of Transport.

It was documented that the rate of sorption process is driven either by external, internal or by both types of diffusions [34]. The external diffusion sees to the transport of the Cr from the tan chrome solution to the boundary layer of the liquid phase. On the other hand, the internal diffusion directs the movement of the analyte, Cr from the external surface of the GCAC or RGAC to the internal surface of the cavities of the adsorbent. It is thus noteworthy, that during the adsorption of Cr over the porous GCAC or RGAC, three consecutive occurrence are inevitable: Film diffusion characterized by external transport < internal transport (R^2 value of 0.764-0.890, indicating a possible transport of the ingoing Cr ions to external surface of the GAC or RGAC); intraparticle diffusion where external transport > internal transport (R^2 value of 0.007-0.026, for transport of the Cr ions within the pores of the GAC and RGAC but for a slight adsorption, which takes place in the external surface) and Intraparticulate diffusivty where external transport is equivalent to internal transport with R^2 value of 0.764-0.890, Presumably an adsorption of the ingoing Cr ions on the interior surface of the adsorbents [34]. A comparison of the rate constant of these mode of transport shows that, the intra-particle diffusion is faster and is not the rate determining step in the uptake of chromium from tan chrome wastewater.

4.3.5 Adsorption Thermodynamic Studies

From results in Table 4, it has been observed that with increase in temperature, adsorption capacity decreases. This implies that for the initial dye concentration of each solution, the adsorption is exothermic in nature. Thermodynamic parameters; change in Gibb's free energy (ΔGº), change in enthalpy ΔHº and change in entropy ΔSº for the adsorption of Cr over GCAC and RGAC was estimated. The positive value for the enthalpy change, ΔH° for GCAC (2481 kJ/mol) and for RGAC (123.4 kJ/mol), indicates the endothermic nature of the adsorption, which explains the increase of Cr adsorption efficiency as the temperature increased until equilibrium is attained (Table 4). The positive value for the entropy change, ΔS° (9.969 KJ/mol and 3.738 KJ/mol), indicates that there is an increased disorder at the solid/liquid interface during Cr adsorption onto the GCAC and RGAC. Free energy change (ΔG°) shows that the adsorption process of Cr was exothermic and not spontaneous to maintain a favorable free-energy driving process (negative ΔG), the ΔH must be greater in magnitude than the ΔST, because adsorption leads to a loss of entropy (ΔS), as was similarly reported by Azraa *et* al. [33].

Table 3. Kinetic studies experimental constants for Cr adsorption onto adsorbents.

Kinetic Model	**Constants**	**Values**	
		T_{Eff}– GCAC	**T_{Eff} – RGAC**
First Order	R^2	0.003	0.062
	K_1 (min^{-1})	0.003	0.012
	qe-exp (mg/g)	1395.700	292.400
	qe-cal (mg/g)	4570.882	35.400
	SSE (%)	1419.985	114.934
Pseudo-Second Order	R^2	0.993	0.971
	K_2 (g/g min)	0.0008	5.2×10^{-4}
	qe-exp (mg/g)	1395.700	292.400
	qe-cal (mg/g)	1250.000	333.333
	SSE (%)	4245.698	18.29
Bhattacharya-Venkobachor	R^2	0.4997	0.0412
	D_2	0.001	-0.021
Elovich	R^2	0.007	0.033
	α (mg g^{-1} min^{-1})	1.574	0.024
	β (mg g^{-1})	6.353	3333.333

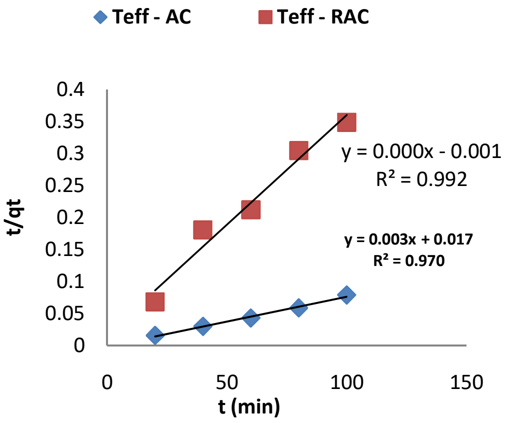

Fig.8: Pseudo Second Order Kinetic Plot for Adsorption of Cr onto Activated Carbon

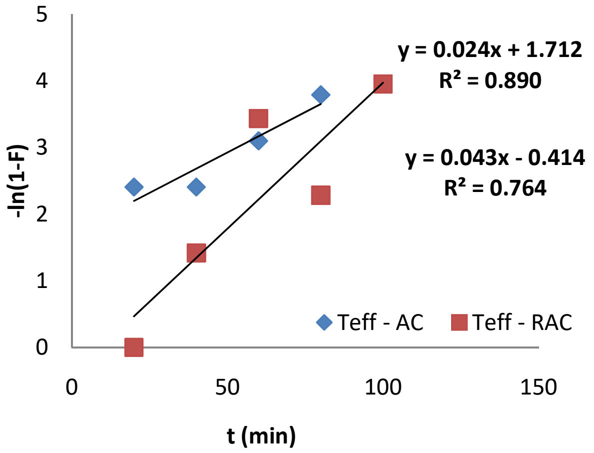

Fig. 9: Film Diffusion Plot for Adsorption of Cr onto Activated Carbon.

Table 4: Thermodynamic parameters for Cr adsorption onto activated carbon.

Thermodynamic parameters	Values	
	T_{Eff} – GCAC	T_{Eff}– RGAC
R^2	0.650	0.063
ΔS (KJ/mol)	9.969	3.738
ΔH (KJ/mol)	24810	123.4
ΔG(Kj/mol.K)	2471.031	119.662

3.6 Comparative studies

There was no significant statistical difference between T_{Eff} – GCAC and T_{Eff} – RGAC when the effect of contact time was tested (P>0.05, 0.003), the effect of temperature on percentage removal of Cr was also tested at 95% confidence interval for T_{Eff} – GCAC and T_{Eff} – RGAC. Result indicates that there was no statistically significant difference in values. Generally, the sorption phenomenon of Cr on regenerated adsorbent (RGAC) strongly agrees with those of Cr onto virgin Commercial adsorbent (GCAC) for the entire experimental runs.

4. CONCLUSION

Kinetics, Thermodynamics and Mode of Transport were successfully utilized for the interpretation of the Adsorptive detoxification of chrome tan liquor via chromium uptake on virgin and regenerated adsorbents. The Kinetic equilibrium study shows that the adsorption of Cr from tannery effluent is best modeled using pseudo-second order kinetics, and this proves to be true using both GCAC and RGAC. The correlation coefficients, R^2 which favours the pseudo-second-order model is an indication of a chemisorption mechanism as also indicated by high Gibb's free energy value. Intraparticle transport is not the rate limiting step, probably because the external transport of the Cr ions within the pores of the GAC and RGAC is greater than the internal transport, but for a slight adsorption, which takes place in the external surface. The positive value for the enthalpy change, ΔH° for GCAC and for RGAC shows that the adsorption reaction is endothermic. We concluded that the RGAC compares favorably to GCAC in removal of Cr from tannery effluent.

REFERENCES

1. Hassan Z, Abdorrahman H, and Vahdat J. Studies of the adsorption thermodynamics and kinetics of Cr(III) and Ni(II) removal by polyacrylamide; J. Serbia. Chem. Soc. 2012; 77 (3): 393–405).
2. Krishnamoorthy A, Joseph CJ. Adsorption of chromium (vi) ion onto activated amla dust: Adsorption inotherms and kinetics. Indian Journal of Chemistry. 2004; 42: 45-50.
3. Ghosh M, Singh SP. Comparative uptake and phytoextraction study of soil induced chromium by accumulator and high biomass weed species. Appl Ecol Environ. 2005; 3:67–79.
4. Jahan MA, Akhtar NM, Khan CK, Roy R, Islam N. Characterization of tannery wastewater and its treatment by aquatic macrophytes and algae .Bangladesh Journal of Science and Industrial Research. 2014; 49(4): 233-242.
5. Krishanamoorthi SV, Sivakumar K, Saravanan V, Sriram P. Treatment and Reuse of Tannery Waste Water by Embedded System; Journal of Modern Applied Science. 2009; 3(1):129.
6. Malek A, Hachemi M, Didier V. New approach of depollution of solid chromium leather waste by the use of organic chelates.Economical and environmental impacts.Journal of Hazardous Materials 2009. 170: 156–162.
7. Bosnic MJ, Buljan R, Daniels P. Pollutants In Tannery Effluents; United Nations Industrial Development Organization (UNIDO), 2000; US/RAS/92/120 Regional Programme for Pollution Control in the Tanning Industry in South-East Asia.
8. Mandi L, Souad T, Abderrahim J. Depuration of tannery efluent by phytoremediation and iniltration percolation under arid climate. Options Méditerranéennes. 2009; A 88: 199- 205
9. Vassiliki GP , Dimitris K, Ersi V. A Method for the Removal of Chromium from Tanned Leather Wastes. Journal of the Air & Waste Management Association. 1998;48:9, 846-852, DOI: 10.1080/10473289.1998.10463735
10. Huiyan J, Junsheng L, Wei H. The status and developments of leather solid waste treatment: A mini-review. Waste Management & Research. 2016; 1–10 DOI: 10.1177/0734242X16633772
11. Pati A, Chaudhary R. Studies on the Generation of Biogas from Collagen Hydrolysate obtained from Chrome Shavings by Alkaline Hydrolysis: A Greener Disposal Method. Research Journal of Recent Sciences. 2013; 2: 234-240
12. Paul H, Antunes APM, Covington AD, Evans P, Phillips PS. Towards zero solid waste: utilising tannery waste as a protein source for poultry feed. Paper presented to: 28th International Conference on Solid Waste Technology and Management, Philadelphia, PA, USA, 10-13 March 2013; Philadelphia USA

13. Kawser AM, Monika D. Monirul I, Mosammat SA, Shahidul I, Muhammad AA. Physico-Chemical Properties of Tannery and Textile Effluents and Surface Water of River Buriganga and Karnatoli, BangladeshWorld Applied Sciences Journal. 2011; 12 (2): 152-159.

14. Islam BI, Musa, E, Salma A, Babiker ME. Evaluation and Characterization of Tannery Wastewater Journal Of Forest Products & Industries. 2014; 3(3).

15. Abbas HS, Waleed MA. Estimation of efficiency of regenerated granular activated carbon by different methods.Indian Academy of Science Journal. 2008; (14): 2678.
16. Martine RL, Ng WJ. Chemical Regeneration of Exhausted Activated Carbon.Journal of water research. 1984; (18)1: 59-73.

17. Ang H, Lee K. Analysis of mercury in Malaysian herbal preparations: a peer-review. Journal of Biomedical Science. 2005; 4: 31–6.
18. Verma VK, Mishra AK. Kinetic and Isotherm Modeling of Adsorption of Dyes Onto Rice Husk Carbon; Global NEST Journal. 2010; (12) 2 : 190-196.
19. Vijayakumar G, Tamilarasan R, Dharmendirakumar. M. Adsorption, Kinetic, Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite; Journal of Material and Environmental Sciences. 2012; 3 (1) :157-170.
20. Parimalam R, Raj V, Sivakumar P. Adsorption Isotherms, Kinetics, Thermodynamics and Desorption Studies of Reactive Orange16 on Activated Carbon Derived from Ananascomosus(L.),Journal of Engineering and Applied Sciences. 2011; 6(11):

21. Tarawou T, Young E. Intraparticl and liquid film diffusion studies of Cu^{2+} and Pb^{2+} ions from aqueous solution using powdered Cacao pod (Theobroma cacao). International Research Journal of Engineering and Technology. 2015 ; (02) :08.

22. Nwabanne JT, Igbokwe PK. Copper (II) uptake by adsorption using Palmyra palm nut; Advances in Applied Science Research, 2011; 2(6):166-175.

23. Suguna M, Siva N, Kumar M, Venkata S, Krishnaiah A. Removal of divalent manganese from aqueous solution using Tamarindusindica Fruit Nut Shell M. Journal of Chemical and Pharmaceutical. Research . 2010; 2(1): 7-20.

24. Namasivayam C, Yamuna RT. Utilizing biogas residual slurry for dye adsorption; American .Dyestuff Reporter.1994;235-239.

25. Sarioglu M, Atay UA. Removal of methylene blue by using biosolid, Global NEST Journal, 2006; (8) 2: 113-120.

26. Gunay A, Arslankaya E, Tosun I. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. Journal of Hazardous Material 2007; (146) :362-371.
27. Masood A, Mohd A, Sumbul R. Adsorption of zinc (ii) and nickel (ii) from Aqueous solution using syzygiumaromaticum (cloves): kinetic and isotherm studies. RASAYAN Journal of Chemistry. 2009 ;(2)4: 791-806
28. Olugbenga SB, Oladipo MA, Misbaudeen AH, Olalekan AM. Kinetic and equilibrium studies of methylene blue removal from aqueous solution by adsorption on treated sawdust; Macedonian Journal of Chemistry and Chemical Engineering. 2010; (29)1: 77–85
29. Nuhoglu Y, Malkoc E. Thermodynamic and kinetic studies for environmentally friendly Ni(II) biosorption using waste pomace of olive oil factory. Bioresource Technol. 2009. 100(8): 2375-2380
30. Ho YS, and McKay G. Pseudo-Second Order Model for Sorption Processes.Process Biochemistry, 1999;(34):735-742.

31. Itodo AU, Itodo HU. Application Of Isotherm Studies On The Evaluation Of Sorption Energies For Dyestuff Removal Onto Derived Thermo-Cracked Shea Nut Shells; Electronic Journal of Eenvironmental, Agricultural and Food Chemistry. 2011; 10 (3).

32. Ejikeme PM, Okoye AI, Onukwuli OD. Kinetics and isother studies of Cu^{2+} and Pb^{2+}ionx removal from simulatd waste water by Gambeya seed shell activated carbon. The African review of Physics. 2011; 6:17.
33. Azraa A, Jain K, Tong S, Rozaini C, Tan LS. Equilibrium, Kinetic and Thermodynamic Studies on the Adsorption of Direct Dye onto a Novel Green Adsorbent Developed from UncariaGambir.Extract.Journal of Physical Science. 2012; 23(1), 1–13, 2012.
34. Karthikeyan S, Sivakumar B, Sivakumar N. Film and Pore Diffusion Modeling for Adsorption of Reactive Red 2 from Aqueous Solution on to Activated Carbon Prepared from Bio-Diesel Industrial Waste. E-Journal of Chemistry. 2010; 7(1): 175-S184