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Kinetic and Thermodynamic Studies of Chromium Ion Adsorption Using Chitosan from Mussel Shell

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Abstract

A study was carried out to investigate the removal of chromium (VI) ion from chromate solution using deacetylated chitin extracted from mussel shell. Mussel shells were obtained from Gubi dam in Bauchi, Nigeria and chemical method was used to extract chitin and then chitosan from these shells. A batch adsorption study was used to generate data for kinetic modelling. Out of the four kinetic models tested, the adsorption process was found to follow the pseudo-second order kinetic model with an R^2-value of 0.9997; The process was physical with a free sorption energy of 0.224 kJ/mol. Also, the enthalpy of adsorption was -67.295 kJ/mol K and the Gibbs free energies were all negative, thus the process is spontaneous and exothermic.

Keywords: Kinetic, Chitosan, Mussel, Chromium, Adsorption, Thermodynamic

Introduction

Heavy metal contamination has been a critical problem mainly because metals tend to persist and accumulate in the environment therefore resulting in various diseases to man and wreaking havoc on the aquatic life (Queek*et al*, 1998; Sewvandi and Adikary, 2011). A wide range of physical and chemical processes are employed for the removal of these metals from such waters. Some of which are; precipitation, ultrafiltration, adsorption, ion exchange, reverse osmosis, oxidation, ozonation etc. Among these, the adsorption method has been proven to be an excellent method to remove heavy metals from contaminated water due to its advantages of being effective over the other processes mentioned (Kaushik and Sharma, 2005). Some of the adsorbent used for the purpose of heavy metal adsorption includes; chitosan, activated carbon, zeolites etc. (Razali *et al.*, 2010).

Chitosan is a natural polysaccharide comprising of copolymers of glucosamine and *N*-acetyl glucosamine, and can be obtained by the partial deacetylation of chitin, which is the main structural component of squid pens, cell walls of some fungi and also in shrimp and crab shells (Martino*et al.,* 2005; Aranaz *et al*., 2009).

A lot of works have been done on kinetics with respect to chitosan and adsorption. The equilibrium and kinetic studies on adsorption of metallic ions onto chitosan was carried out by Benavente (2008). Kinetics and equilibrium studies adsorption of Cu(II) and Cr(VI) ions by chitosan (Schuml *et al.,* 2001). Studies on removal of Cr(VI) and Cu(II) ions using Chitosangrafted- polyacrylonitrile (Shanmugapriya *et al*., 2011). Of all these, none has used the mussel shell chitosan for the purpose of kinetic and thermodynamic studies.Thus, this work will help enrich the available literature with the data from chromium ion adsorption using Mussel shell. The objective of this work is to study the kinetics of the adsorption process of chromium (IV) ion by chitosan synthesized from Mussel shell and also to determine the thermodynamic properties and parameters for the adsorption process.

Materials and Methods

Chitosan Extraction and Characterisation

The Chitosan used in this work was extracted by the process described by Abdulkarim *et al.* (2013), with a carbon nitrogen ratio of 5.9 and a degree of deacetylation of 60.69% and 60.66% calculated from the elemental analysis and the FTIR spectra of chitosan respectively. The FTIR spectra for chitosan gave a characteristic $-NH_2$ band of 3447 cm^{-1} and a carbonyl group band of 1477 cm^{-1}, also the surface area of the chitosan was determined to be 2.7225 ± 0.0741 m^2/g using the BET machine (Abdulkarim *et al*., 2013).

Kinetic studies

Using the optimum dosage of chitosan (2.5g) (Abdulkarim *et al.,* 2014) at room temperature (28^{o}C), sorption time was checked in succession of 20 minutes, from time $t = 20\ \text{min}$ to determine the optimum time for adsorption. The time study was terminated at $t = 120\ \text{min}$ when the adsorption process attained equilibrium.

Temperature Studies

The effect of temperature on the chromium uptake by the chitosan was studied. The temperature was varied from 28°C to 45°C keeping other parameters such as chitosan dosage (2.5 g) and contact time (80 min) constant.

Results and Discussion

The data used in investigating the kinetics of the adsorption process was obtained by checking the effect of variation of contact time on the final concentration. At a fixed dosage of 2.5g, and a temperature of 28°C, the equilibrium time for the process was investigated. Figure 1 shows how the reductions in the ion concentration became almost constant from 80 minutes contact time.

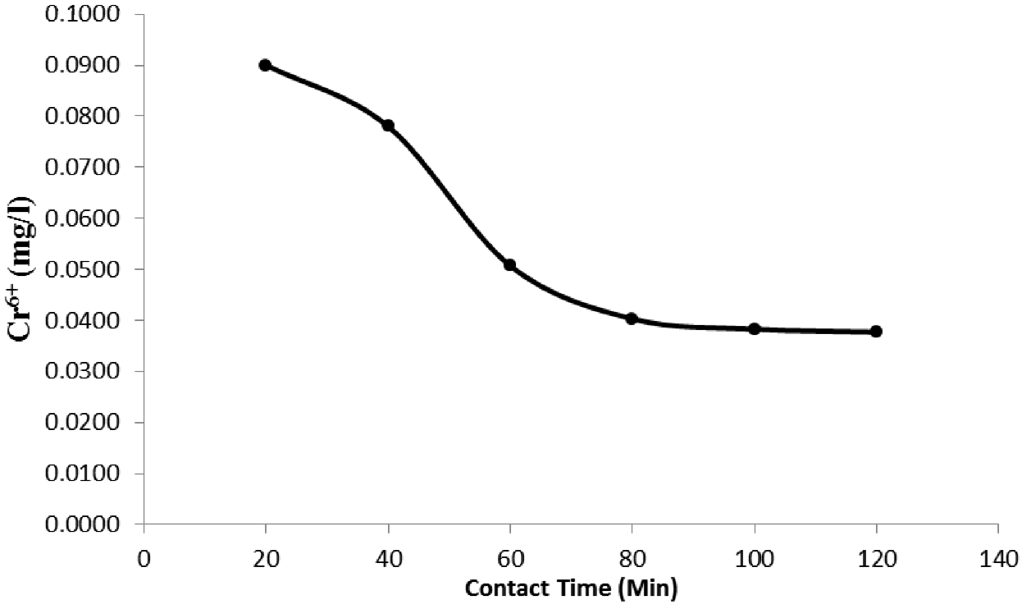

Figure 1: Effect of Contact Time on Cr^{6+} removal at 2.5g Chitosan Dosage

Determination of kinetic models for chromium (VI) removal using chitosan

Four kinetic models were tested to know the best model describing the kinetics of Chromium (VI) removal from waste water using chitosan. The essence of kinetic investigation is to find out the stage which plays a decisive role to the adsorption reaction rate. Therefore, the use of kinetic models to fit the time dependent experimental data is one of important steps for the adsorption study (Muhammad *et al*., 2012). Figure 2 shows the kinetic plot of chromium ion adsorption using chitosan as an adsorbent. In recent years, the pseudo-first order model has been widely used to describe the adsorption of pollutants from wastewater in different fields, such as the adsorption of methylene blue from aqueous solution by broad bean peels and the removal of malachite green from aqueous solutions using oil palm trunk fibre (Qiu *et al*., 2009). The integrated linear form of pseudo-first order kinetic model as proposed by Lagergren is presented as equation 1.

$$\ln(q_e - q_t) = \ln q_e - kt \qquad (1)$$

where, q_e is the amount of chromium (VI) ion adsorbed at equilibrium (mg/g), q_t is the amount of chromium (VI) ion adsorbed at time t (mg/g), k is the first order rate constant (min^{-1}) and t is the time (min). Hence, a linear trace is expected between the two parameters log (q_e - q_t) and t, provided the biosorption follows the pseudo-first order kinetics.

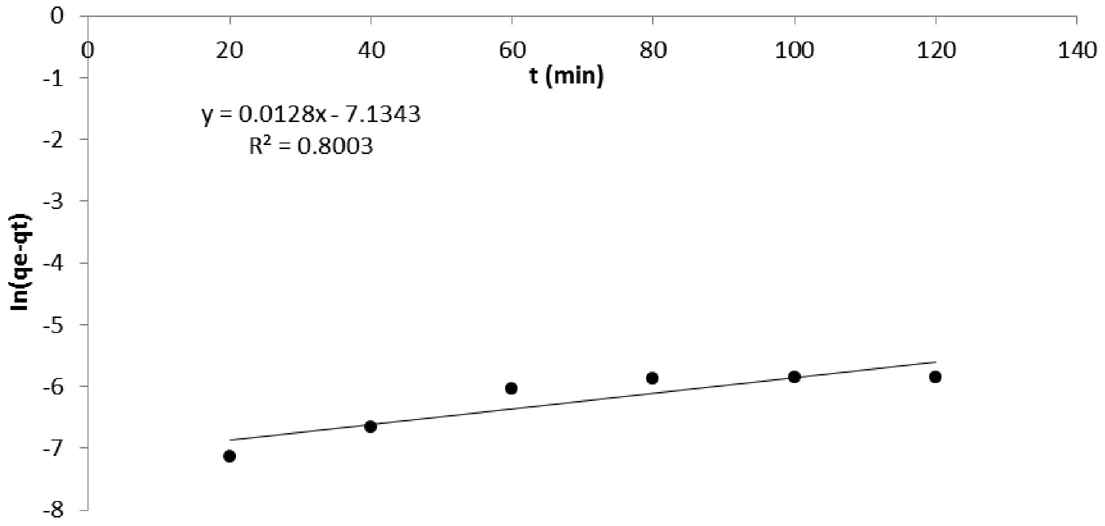

Figure 2: Testing the Pseudo First Order Kinetic model

Figure 2 is the plot obtained using the integrated form of pseudo-first order kinetic model with an R^2 value is 0.8003. The other constants in the equation are shown in Table 1.

The second order kinetic model was also tested to see its conformity with the generated experimental data. In earlier years, the second-order rate equations were reasonably applied to describe adsorption reactions occurring in soil and soil minerals. Recently, the equation has also been used to describe fluoride adsorption onto acid-treated spent bleaching earth and phosphamidon adsorption on an antimony (V) phosphate cation exchanger (Qiu *et al.*, 2009). The integrated form of the model (equation 2) is given as:

$$\frac{1}{C_e} = k_2 t + \frac{1}{C_o} \tag{2}$$

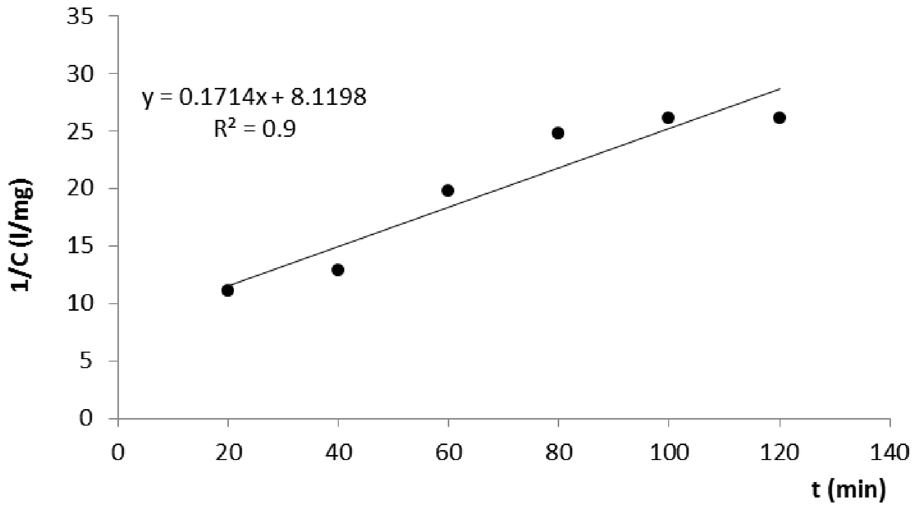

Figure 3: Testing the Second Order Kinetic Model

The plot obtained using equation 2 is presented as Figure 3. It is seen that the from the R^2 value, that the second order kinetic model fits better to the generated experimental data than the pseudo-first order kinetic model.

Figure 4 represents a plot for the pseudo-second order model. In 1995, Ho described a kinetic process of the adsorption of divalent metal ions onto peat (Qiu *et al.*, 2009), in which the chemical bonding among divalent metal ions and polar functional groups on peat, such as aldehydes, ketones, acids, and phenolics are responsible for the cation-exchange capacity of the peat.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

where, k_2 is the second order rate constant (g/mg min). A plot of $1/q_e$ against t and t/q_t against t should be linear if the adsorption follows second order (Figure 3) or pseudo-second order (Figure 4). q_e and $k_2$were calculated from the slopes and intercepts of the plots as shown in Table 1.

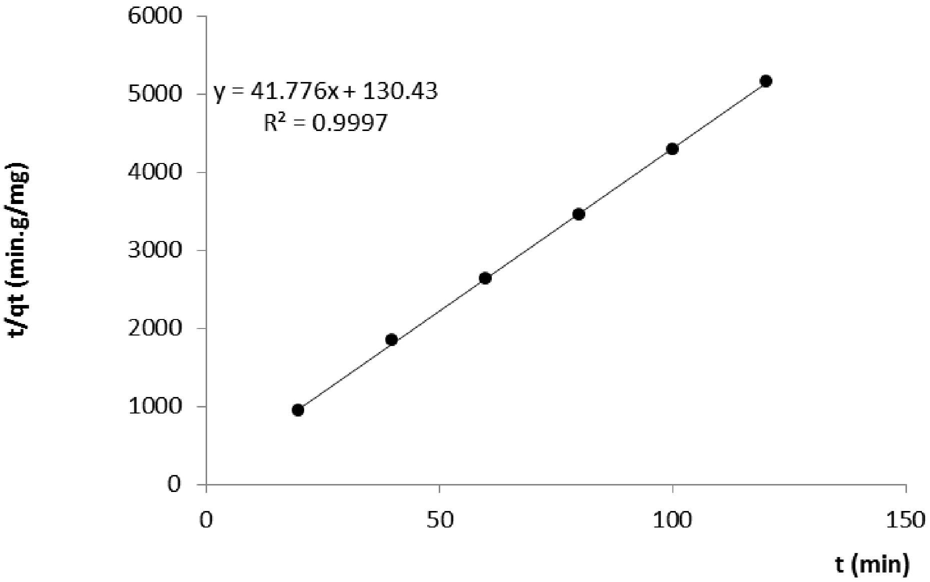

Figure 4 Testing the Pseudo Second Order Kinetic Model.

Figure 4 shows that the R^2 value (R^2=0.9997) is much higher than that from the second order model (0.90). This showed that the data generated from the use of chitosan on the removal of chromium (vi) ion fitted best into the pseudo-second order kinetic model.

Furthermore, another model (Elovich) of frequent application was also tested. The Elovich model which is a kinetic equation of chemisorption was established by Zeldowitsch (1934) and was used to describe the rate of adsorption of carbon monoxide on manganese dioxide that decreases exponentially with an increase in the amount of gas adsorbed (Ho, 2006). The Elovich model is generally expressed as

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \qquad (4)$$

where, 'a' is the initial adsorption rate (mg/g min) and b is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). A plot of q_t vs. $\ln t$ gives a straight line with a slope of l/b and an intercept of $\frac{1}{b}\ln(ab)$ with good correlation coefficients.

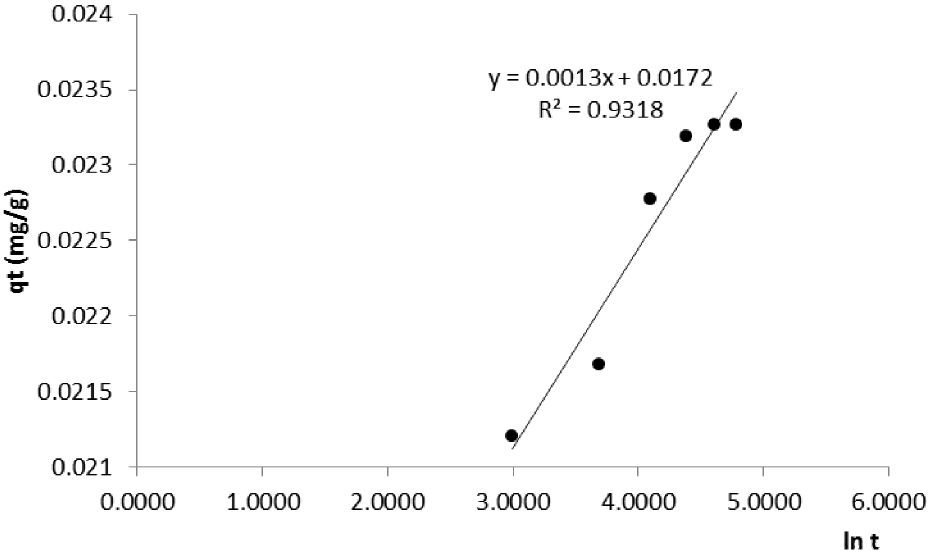

Figure 5: Testing the Elovich kinetic model

Figure 5 shows that the R^2(0.9318) value is less than that of the pseudo-second order plot but better than other models tested.

Table 1 shows the summary of the kinetic model and constants obtained from the test with the pseudo first order, second order, pseudo second order and the Elovich model. As discussed earlier, the data generated from the treatment fits best with the pseudo second order kinetics since it shows a highest R^2 Value of 0.9997.

Table 1: Evaluated constants obtained from kinetic models tested

Kinetic model	R^2	Slope	Intercept	Rate constant	Other constants
Pseudo-first order	0.8003	0.0128	7.1343	0.9881	q_e=-0.0204
Second order	0.885	0.1714	8.1198	0.1714	C_0=0.1232
Pseudo-second order	0.9997	41.776	130.43	403.7306	q_e=0.0077
Elovich	0.9318	0.0013	0.0172	b=769.231	a=724.4276

Determination of some thermodynamic parameters for Cr (VI) removal using chitosan

In order to characterise the adsorption process for this work, some basic thermodynamic parameters are needed. These parameters are discussed in the following sections.

The free sorption energy (E_s)

This is a parameter which tells whether the adsorption process is either physiosorption or chemisorption. The sorption energy (E_s) can easily be calculated using the Dubinin-Radishkevich (D-R) isotherm given as:

$$q_e = q_D \exp(-B_D [RT \ln(1+\frac{1}{C_e})]^2) \qquad (5)$$

Radushkevich (1949) and Dubinin (1965) have reported that the characteristic sorption curve is related to the porous structure of the sorbent (Ho *et al*, 2001).

The D-R isotherm can be written in a linear form as

$$\ln q_e = \ln q_D - 2B_D RT \ln(1 + {}^{1}\!/\!_{C_e}) \quad (6)$$

where q_D is the D-R isotherm constant, B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution. The relationship between the free energy of sorption (E_s) and B_D is given by equation 7

$$E_s = \frac{1}{\sqrt{(2B_D)}} \quad (7).$$

The mean free energy of sorption gives information about biosorption mechanism, physical or chemical. If E_s value is between 8 and 16 (kJ/mol), the sorption process follows chemisorption and if E_s<8 (kJ/mol), the sorption process is of a physiosorption (Kianfar *et al*, 2012).The sorption energy was calculated to be E_s= 0.224 kJ/mol, which implies that the adsorption process, was physical.

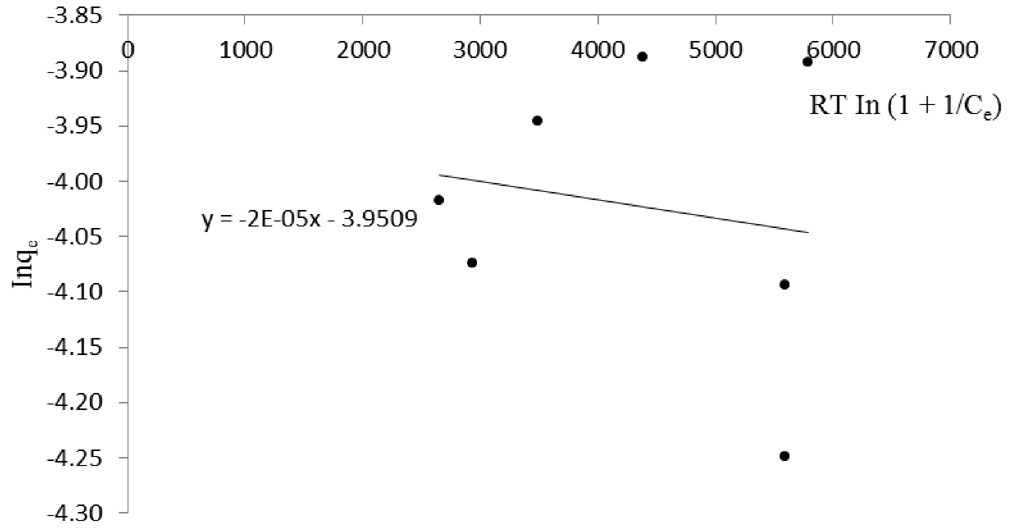

Figure 6: Dubinin-Radishkevich (D-R) isotherm

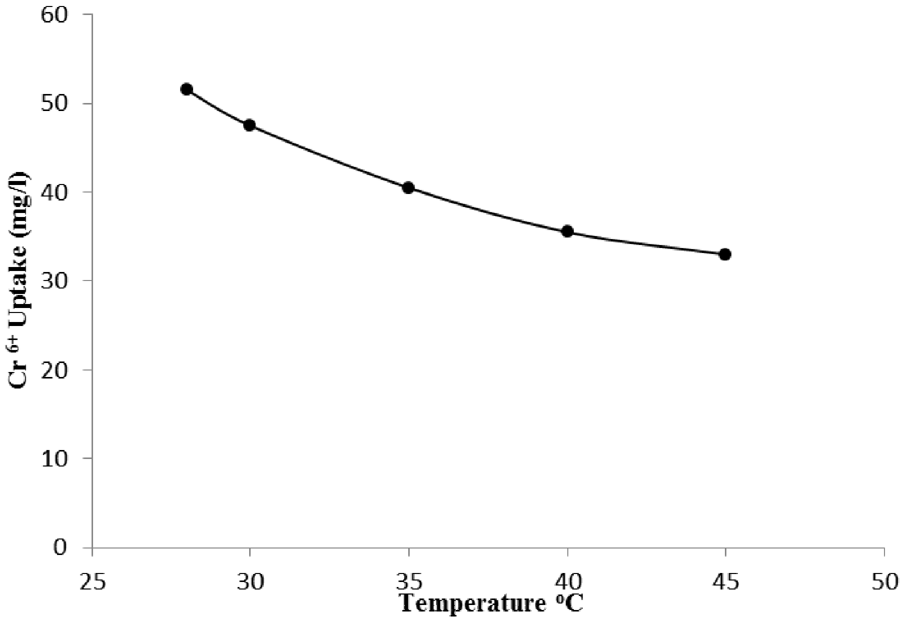

Figure 7: Effect of solution temperature on Chromium ion uptake

Calculation of enthalpy (ΔH_{ads}), Gibbs free energy (ΔG_{ads}) andentropy (ΔS_{ads}).

Thermodynamic parameters can be calculated using the relations used by Kumal and Gayathri (2009), Ren*et al.* (2012) and Kianfar*et al.* (2012).

$$K_c = \frac{C_o - C_e}{C_e}$$

$$(8) \ln K_c = \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{RT}$$

$$(9) \Delta G_{ads} = -RT \ln K_c \qquad (10)$$

Where K_c is the distribution coefficient, R= 8.314 mol/J/K and T is the absolute temperature and ΔG_{ads} is the Gibbs free energy for adsorption.

Table 2: Values for Calculation of Thermodynamic Parameters

Temp(^{0}C)	Ce (mg/l)	kc=(Co-Ce)/Ce	In Kc	1/T (K^{-1})	ΔG_{ads}
28	0.1050	4.9048	1.5902	0.00332	-3.98159
30	0.1450	3.2759	1.1866	0.00330	-2.99072
35	0.2150	1.8837	0.6332	0.00325	-1.62240
40	0.2650	1.3396	0.2924	0.00319	-0.76126
45	0.2900	1.1379	0.1292	0.00314	-0.34179

Using equation 9 and Table 2, Figure 8 was plotted.

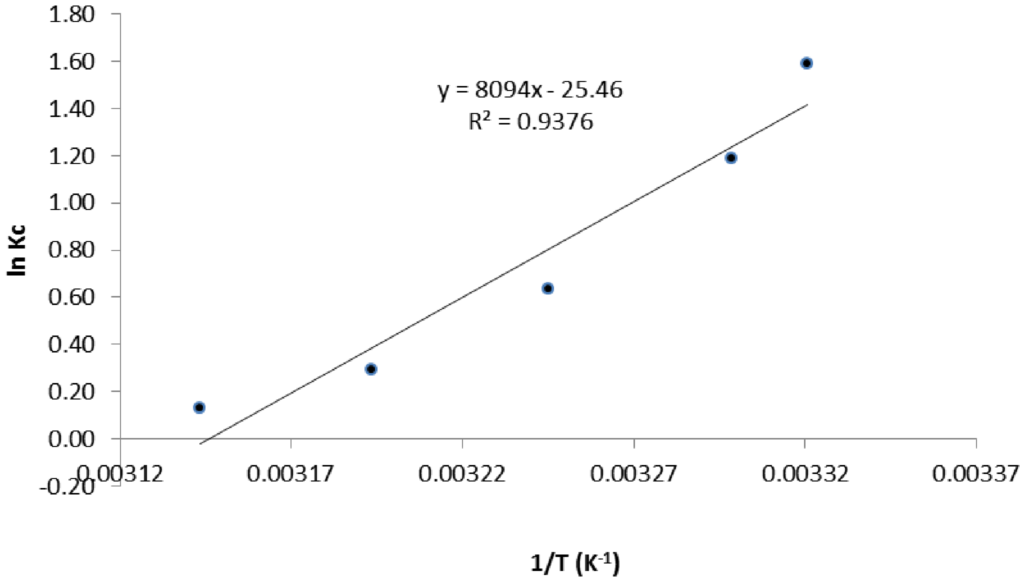

Figure 8: Plot for calculation of thermodynamic parameters.

Using equations 8 and 9, the following parameters were calculated

$$\Delta H_{ads} = -67.295\, kJ\, /\, mol$$

$$\Delta S_{ads} = -0.212\, kJ\, /\, mol\ K$$

Equation 10 was used to calculate the Gibbs free energy as shown in Table 2

The thermodynamic parameters as shown above gave an insight on the type of adsorption and the enthalpy of the adsorption process. The enthalpy of the process was determined to be -67 kJ/mol, the negative sign in the value indicates that the adsorption is exothermic i.e., the adsorption takes place with the release of energy. On the other hand, the entropy value which is -0.212 kJ/molK indicates that there is decrease in the degree of disorderliness of the sorbates as they approach the adsorption layer. Furthermore, the negative values of the Gibbs free energy as shown in Table 2 indicate that the adsorption process was completely spontaneous.

Conclusion

The adsorption process was not favoured by increase in temperature as the adsorption decreases with increase in temperature within the temperature range of 28^{o}C to 45^{o}C. The pseudo second order kinetic model with an R^2-value of 0.9997 was the best fitted kinetic model among the four models tested.

The negative values of enthalpy (-67 kJ/mol) and Gibbs free energy obtained from the thermodynamic studies indicate clearly that the adsorption process was exothermic and spontaneous.

The value of the free sorption energy E_s(0.224 kJ/mol) determined using the Dubinin-Radishkevich model is also an evident that the adsorption is physical as the value was less than 8 kJ/mol which is a range for only physiosorption.

References

Abdulkarim, A., Isa, M.T., Ameh, A.O. and Muhammed, J. A. (2014) ‘Chromium Ion adsorption Using Chitosan from Mussel', *IOSR Journal of Applied Chemistry*, vol. 7(1), pp. 24-28.

Abdulkarim, A., Isa, M.T., Surajudeen, A., Muhammad, J. A. and Ameh, A.O. (2013) 'Extraction and Characterisation of Chitin and Chitosan from Mussel Shell', *Civil and Environmental Research (IISTE)*, vol. 3, no. 2, pp. 108-114.

Aranaz, I., Mengíbar, M., Harris, R., Paños, I., Miralles, B., Acosta, N., Galed, G. and Heras, Á. (2009) 'Functional Characterization of Chitin and Chitosan', *Current Chemical Biology*, pp. 203-230.

Benavente, M. (2008) 'Adsorption of Metallic Ions onto Chitosan: Equilibrium and Kinetic Studies', *Licentiate Thesis*, vol. 1, May, pp. 5-16.

Ho, Y.S. (2006) 'Review of second-order models for adsorption systems', *Journal of Hazardous Materials*, vol. B136, February, p. 681–689.

Kaushik, N. and Sharma, J.K. (2005) 'Studies on the role of adsorbents in removal of direct dyes from textile effluent.', *National Environmental Pollution Technology*, vol. 4, no. 2, pp. 163-166.

Kianfar, S., Moheb, A. and Ghaforian, H. (2012) 'Equilibrium, Kinetiic and Thermodynamic Studies on Solution Using a Spore Forming Bacillus Issolated from Waste Water of a Leather Factory.', *World Academy of Science, Engineering and Technology*, vol. 69, January, pp. 481-485.

Martino, A.D., Sittinger, M. and Risbud, M.V. (2005) 'Chitosan: A versatile biopolymer for orthopaedic tissue-engineering', *Biomaterials*, pp. 5983-5990.

Muhammad, I.M., El-Nafaty, U.A., Abdulsalam, S. and Makarfi, a.Y.I. (2012) 'Removal of oil from produced water using eggshell', *Civil and Environmental Research*, vol. 2, no. 8, September, pp. 52-63.

Qiu, H., Lv, L., Pan, B.C., Zhang, Q.J., Zhang, W.M. and Zhang, Q.X. (2009) 'Critical review in adsorption kinetic models', *Journal of Zhejiang University SCIENCE A*, vol. 10, no. 5, April, pp. 716-724.

Quek, S.Y., Wase, D.A. and Forster, C.F. (1998) 'The use of sago waste for the sorption of lead and copper.', *Water South Africa*, vol. 24, no. 3, pp. 251-256.

Razali, M.N., Yunus, R.M., Jemaat, Z. and Alias, S. (2010) 'Monoethanolamine Waste Water Treatment Via Adsorption Method; A study on comparison of Chitosan, Activated Carbon, Alum snd Zeolite', *Journal of Applied Science*, vol. 10, no. 21, pp. 2544-2550.

Schmuhl, R., Krieg, H.M. and Keizer, K. (2001) *Adsorption of Cu(II) and Cr(VI) ions by chitosan: Kinetics and equilibrium studies*, January, [Online], Available: HYPERLINK "http://www.wrc.org.za" http://www.wrc.org.za [16 January 2014].

Sewvandi, G.A. and Adikary, S.U. (2011) *Removal of Heavy Metals From Wastewater Using Chitosan*, 10 March, [Online], Available: HYPERLINK "http://management.kochi-tech.ac.jp/ssms_papers/sms11-5519_f7ef9ac7c0fc35b5704c4fdba8c7e34a.pdf [29 July 2012].

Shanmugapriya, A., Ramya, R., Ramasubramaniam, S. and Sudha P, N. (2011) 'Studies on removal of Cr(VI) and Cu(II) ions using Chitosan grafted-polyacrylonitrile', *Archives of Applied Science Research*, vol. 3, no. 3, pp. 424-435.