Equilibrium, Kinetics and Thermodynamics of Hexavalent Chromium Adsorption onto Hen Eggshell from Aqueous Solution

[**1]Rabiu, T.O., [2]Folami, N.A., [2]Oso, A.O., [2]Jimoh, L.O., [1]Adigun, I.A.and[3]Sarumi, A.J.

[1]Department of Mechanical Engineering, Lagos State Polytechnic, Ikorodu Lagos, Nigeria
[2]Department of Chemical Engineering, Lagos State Polytechnic, Lagos, Nigeria
[3]Department of Computer Engineering, Lagos State Polytechnic, Ikorodu, Lagos, Nigeria

ABSTRACT: In this study, hen eggshell (HES) was employed as adsorbent for the removal of Hexavalent Chromium fromaqueous solution. The study applied batch methods to investigate the equilibrium, kinetics and thermodynamics of the Hexavalent Chromium adsorption using HES. The equilibrium data was best fitted to the Freundlich adsorption isotherm model (R^2=0.998) while the kinetic data was found to follow pseudo-second-order kinetic model ($R^2 = 0.999$).The results of ΔG^0 and ΔH^0 showed that the adsorption process was feasible, non-spontaneous, and endothermic.The negative value of ΔS^0 describes decreasing degree of freedom and randomness during theadsorption process at the solid-liquid interface with somestructural changes in the adsorbate and adsorbent.
Key words: Eggshell, Hexavalent Chromium, aqueous solution, equilibrium, kinetics, thermodynamics

I. INTRODUCTION

The textile industry is well-known globally for huge water consumption and as one of the largest generators of industrial wastewater with high colour and dissolved organic compounds (Ahmad et al., 2011). Water pollution is a menace whichmajor source is the indiscriminate discharge of untreated or poorly treated industrial effluents into the environment (Susu and Folami, 2014).In the textile industry, effluents from the dyeing and finishing processes are known to contain colour, a large amount of suspended organic solids and heavy metals such as Cr, Ni, and Cu (Ahmad et al., 2014).

Food wastes contain some valuable minerals which may be extracted so as to reducethe high cost of disposal of the environmental nuisance caused by such wastes (Ahmed et al., 2017).

Eggshell (ES) and eggshell membranes (ESM) are wastes produced in large quantities from sources such as poultries, homes, restaurants, bakeries and food manufacturing units.Each ES contains between 7000 and 17,000 pores (Zaman et al., 2018). Surface analysis of ES and ESM also revealed that they are porous materials and therefore can be employed as cost-effective adsorbents for the removal of hazardous chemicals thus, lessening the wastes going to landfill (Mopoung and Jitchaijaronekul, 2017).

Eggshell has been used for purification of hydrogen generated for fuel cells (Mittal et al., 2016), adsorption of dye (Tsai et al., 2008) or heavy metals from wastewater (Guo et al., 2011) and CO_2 from combustion gases in a fluidized bed (Botome et al., 2017; Mohammadi et al al., 2014). Other significant applications of eggshell include the production of thermoplastic materials such as high-density polyethylene to enhance rigidity, thermal stability and density of plastics. It is also being used to improve both physical and mechanical properties of soil, as well as renewable raw materials for catalyst synthesis in biodiesel production (Zaman etal., 2018; Tan et al., 2015).

Chromium and its compounds are toxic when introduced into natural water from a variety of industrial wastes. The major sources are from dyeing, electroplating, leather tanning, metal processing, paint and pigments, and the textile and steel fabrication industries (Al-Sou'od, 2013). These industries may release large quantities of toxic metal wastewater effluents above the permissible limit. The permissible limit for the discharge of Cr(VI) into inland surface water recommended byWorld Health Organization (WHO), Nigeria, India and US is 0.1mg/l and in potable water it is 0.05 mg/l (Mekonnen et al., 2015;www.epa.gov/sdwa;   www.nature.com).The

detrimental effects of Cr (VI) to biological systems and the environment had been well documented. Exposure to Hexavalent Chromium beyond the tolerance levels (0.05 mg/l) can have devastating effects on the human physiological, neurological and biological systems (Folami et al., 2019; Mishra and Gottipati, 2012).

In order to minimize this menace, a wide range of processes have been reported to remove heavy metals including Hexavalent Chromium from water and wastewater such as chemical precipitation (Kanagaraj et al., 2008), ion-exchange (Cavaco et al., 2007) and electrochemical methods (Liu et al., 2011). The application of such methods is costly and often lead to toxic sludge generation (Gholipour et al., 2011).However, adsorption had been reported as the most preferred due to its high efficacy, cost-effectiveness, versatility and easy handling (Mittal et al., 2016; Mishra and Gottipati, 2012).

In the present study, adsorption isotherms, kinetics and thermodynamicsof Hexavalent Chromium removalfrom aqueous solution using hen eggshell as an adsorbent wereevaluated.

II. MATERIALS AND METHODS

2.1 Materials: The materials employed in this work include: Hen eggshell, de-ionized water, Chromium (VI)solution ($K_2Cr_2O_7$), 0.1 M HCl, 0.1 M NaOH, digital weighing balance, isothermal water bath shaker, measuring cylinder, oven, screen, stop clock, 250 ml Erlenmeyer flasks,Atomic AdsorptionSpectrophotometer (UNICAM 929, London).

2.2. Preparation of Adsorbent (Hen Eggshell, HES): The hen eggshell were collected from a local restaurant, washed thoroughly with de-ionized water to remove the dust and other stains and then dried in an oven at 85 ^{o}C for 30 minutes. The clean and dried HES were ground and screened to 120 – 150 μm particle sizes.

2.3. Preparation of Stock and $K_2Cr_2O_{7(aq)}$Solutions: A 5.0 g/l solution of chromium (VI) was prepared by dissolving 5.0 g of $K_2Cr_2O_7$ in 1000 ml of de-ionized water. The solution was then converted to various $K_2Cr_2O_{7(aq)}$concentrations required for this work by diluting the initial stock solution (5.0 g/l $K_2Cr_2O_{7(aq)}$) accordingly withde-ionized water.

2.4. Batch Equilibrium Studies: Different initial concentration (50, 100, 200, 300, 400 and 500 mg/l) $K_2Cr_2O_{7(aq)}$solutionwereinvestigated for the adsorption of Cr^{6+} ion onto HES in Batch equilibrium studies.In each case, 3.0 g of the HES

was added into100 mlof the adsorbate ($K_2Cr_2O_{7(aq)}$) in an Erlenmeyer flasks and pH adjusted to 2. Then,the flask was placed in an isothermal water bath shaker and subjected to the following process conditions: agitation speed 150 r.p.m., contact time 2 h and temperature 30 °C. After adsorption time was reached, the mixture was filtered to remove the adsorbent and the concentration of the Cr^{6+} ion in the filtrate in each case was determined using AA-Spectrophotometer.

The measure of the adsorption (Cr^{6+} removal) at equilibrium, q_e(mg/g), and Cr^{6+} percentage removal were evaluated using equation 2.1 and 2.2 respectively:

$$q_e = \frac{(C_o - C_e)V}{W} \qquad 2.1$$

$$Cr\ (VI)ion\ \%\ removal = \frac{(C_o - C_e)}{C_o} \times 100 \qquad 2.2$$

Where, $C_o$and C_e (mg/l) are the liquid-phase concentrationsof Cr^{6+} at initial and at equilibrium respectively. Vis the volume of the solution and Wis the mass of HESused.

2.5.Batch Kinetic Studies: In the batch kinetic studies, 3 g of HES was added to 100 ml of 200 mg/l initial concentration with other process parameter kept constant.But, the measurement of the Cr^{6+} ion concentration was taken at preset time interval (30, 60, 90, 120, 150 and 180mins). The quantity of Cr^{6+}ion uptake at any time, q_t (mg/g) was calculated using equation 2.3

$$q_t = \frac{(C_o - C_t)V}{W} \qquad 2.3$$

Where, C_t (mg/l) is the liquid-phase concentration of Cr^{6+} at any arbitrary time, t (mins).

2.6. Batch Thermodynamic Studies: In order to obtain thermodynamic parameters, the adsorption process was studied at various temperature 25, 30, 45 and55^{o}C through adjusting the temperature controller on the water bath shaker. Meanwhile, the concentration, adsorbent dose, contact time, solution pH and agitation speed used were 200 mg/l, 3 g, 2 h, 2 and 150 r.p.m. respectively in each case. The concentration of the Cr^{6+} ion left in the filtrate in each case was also determined using AA-Spectrophotometer.

III. RESULTS AND DISCUSSION

3.1. Adsorption Isotherm

The adsorption isotherms are used to show how the adsorption molecules distribute between the solid phase and liquid phase at equilibrium

state. The Langmuir and Freundlich isotherms were considered in this work. The linear regression was used to determine the best-fitting isotherm and the significance of isotherm models compared by evaluating the correlation coefficients, R^2.

Langmuir's isotherm model is based on the theory that adsorption energy is constant and occurs on homogeneous surface by monolayer adsorption process. When the surface is covered by a monolayer of adsorbate, the adsorption goes on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs (Ahmad, et al., 2014). The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e \qquad\qquad 3.1$$

Where C_e(mg/l) is the Cr^{6+} ion equilibrium concentration and q_e(mg/g) is the amount of Cr^{6+} ionadsorbed per unit mass of HES. Q_o(mg/g) is the Langmuir constant related to adsorption capacity and K_L(l/mg) is rate of adsorption. The values of Q_o, and $K_L$were calculated from the intercept and slope of linear plot of C_e/q_e against $C_e$as depicted by Figure 3.1 and are presented in Table 3.1.
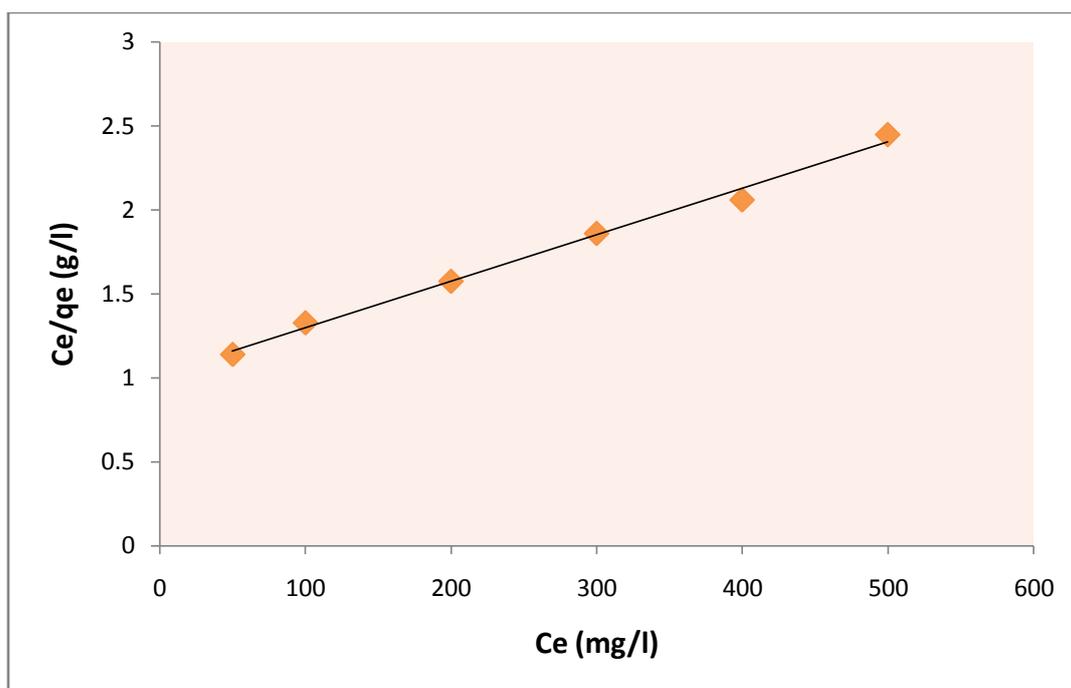
Figure 3.1: Plot of Langmuir Isotherm Model for Cr^{6+} ion Adsorption onto HES

Table 3.1: Langmuir and Freundlich Isotherm Parameters and Correlation Coefficient for the Adsorption of Cr^{6+} ion onto Hen Eggshell at 30 ^{o}C

Adsorbent	Langmuir Isotherm Parameters			Freundlich Isotherm Parameters		
	Q_o (mg/g)	K_L (l/mg)	R^2	K_F (mg/g)	n	R^2
HES	228.53	0.322	0.931	3.96	2.619	0.998

Freundlich model is an empirical expression that is well-known relationship describing the sorption equation. It takes into account a heterogeneous surface and multilayer adsorption to the binding sites located on the surface of the sorbent (Mishra and Gottipati, 2012). The Freundlich model is expressed as:

$$Logq_e = LogK_f + \frac{1}{n}LogC_e \qquad\qquad 3.2$$

Where K_f and n are indicative parameters of adsorption capacity and adsorption intensity respectively. As shown in Figure 3.2, the values of K_f and n were evaluated from the intercept and slope of the plot of $Logq_e$ against $LogC_e$ respectively. If n is greater than one, it implies that the adsorbate is favourably adsorbed on the adsorbent. The higher the value of n, the more favourable the adsorption and the stronger adsorption intensity (Ahmad and Alrozi, 2011).
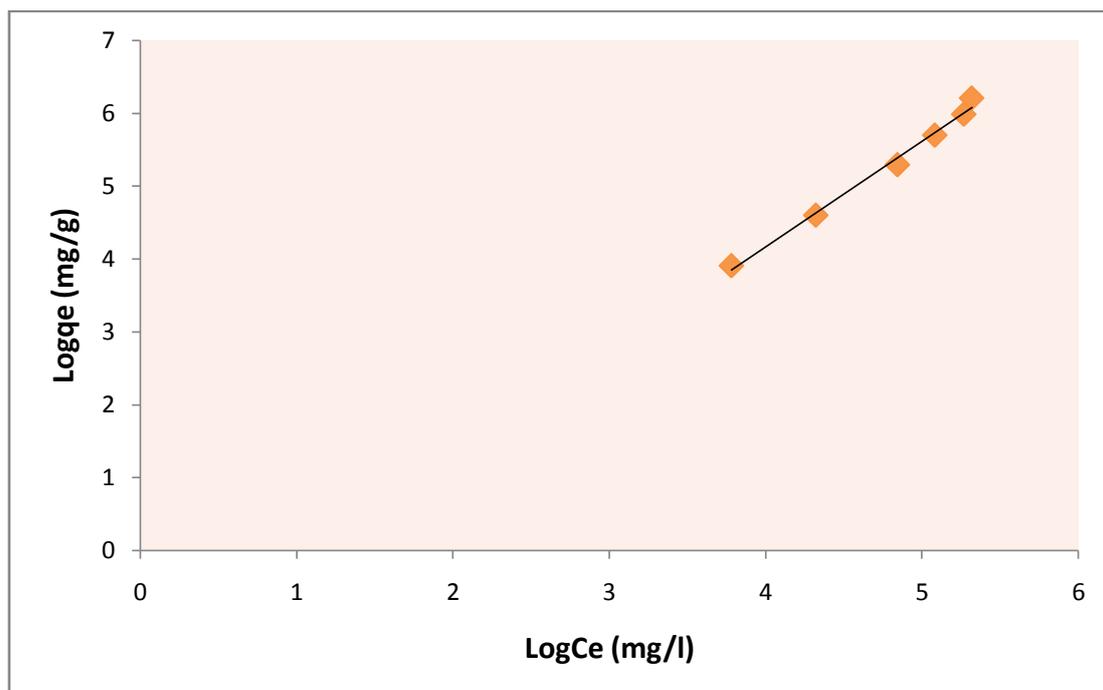
Figure 3.2: Plot of Freunlich Isotherm Model for Cr^{6+} ion Adsorption onto HES

As provided in Table 3.1, Freundlich model gave higher R^2 value(0.998) than Langmuir model (0.931), which indicate that HES adsorption of Cr^{6+} ion was made up of heterogeneoussurface and multilayer adsorption (Gao et al., 2013). This outcome agreed with previous works on adsorption by activated carbonprepared from pinang frond (Ahmad et al., 2014), tea seed shells (Gao et al., 2013),mango nut (Kwaghger et al., 2012) and potato peel waste (Abdullah and Prasad, 2009).

3.2. Adsorption Kinetics

Kinetics adsorption data of Cr^{6+} ion onto HES was analyzed using pseudo-first-order and pseudo-second-order. The pseudo first- order kinetic model is given by the equation 3.3 (Abdullah and Prasad, 2009):

$$In(q_e - q_t) = Inq_e - k_1 t \qquad 3.3$$

Where q_e and q_t(mg/g) are the amount of adsorbate adsorbed at equilibrium and at any time, t(min) respectively, and k_1 (1/min) is the adsorption rate constant. Figure 3.3 shows that the linear plot of ln $(q_e - q_t)$ versus tgives a gradient of k_1 and intercept at lnq_e. Table 3.2 shows the values of k_1 and R^2 obtained from the plots at 30 ^{o}C, where the R^2 value of pseudo-first-order model did not fit well with the range of contact time. In addition, the experimental q_e value did not match with the calculated value obtained from the linear plots. Thus, the adsorption of Cr^{6+} ion onto HES was not following pseudo-first-order model and the kinetic data were further treated with the pseudo-second order kinetic model.
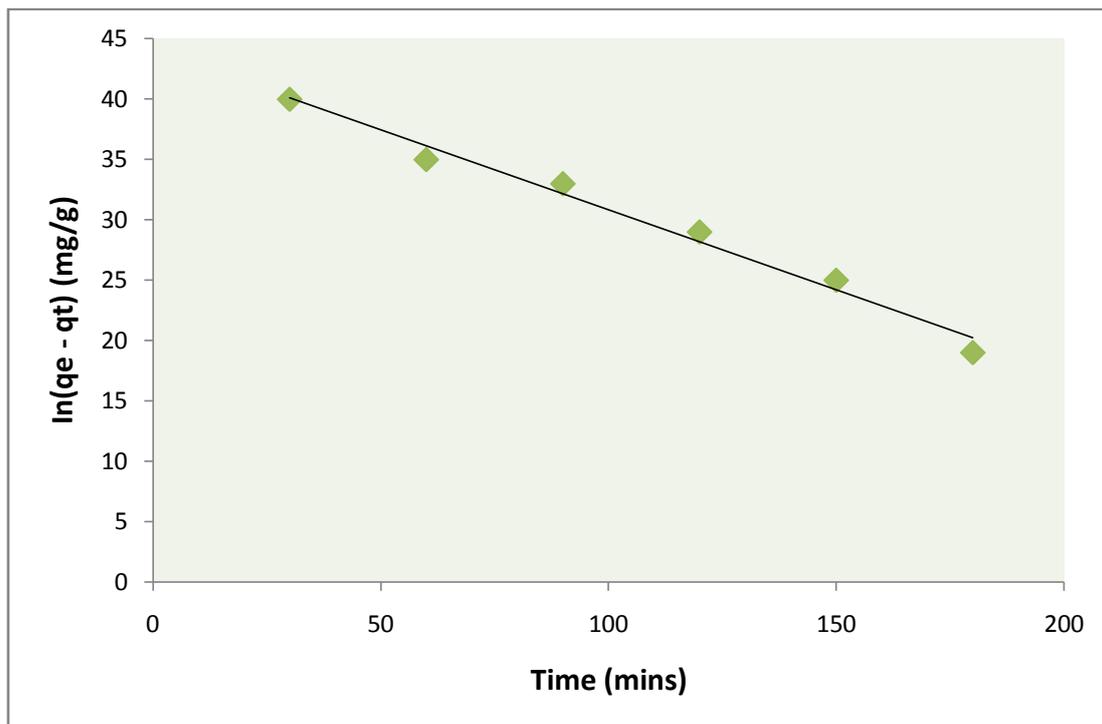
Figure 3.3: Plot of Pseudo-First Order Kinetic Model for Cr^{6+} ion Adsorption onto HES

Table 3.2: Pseudo-First Order and Pseudo-Second Order Kinetic Parameters and Correlation Coefficients for the Adsorption of Cr^{6+} ion onto Hen Eggshell at 30 ^{o}C

q_e (exp.) (mg/g)	First Order Kinetic Parameters			Second Order Kinetic Parameters		
	q_e (mg/g)	k_1 (l/min)	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2
121.50	97.771	0.714	0.963	126.60	0.016	0.999

The pseudo-second-order model predicts the performance over the total range adsorption and is expressed as given by equation 3.4 (Mekonnen et al., 2015):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad\qquad 3.4$$

Where k_2(g/mg.min) is the rate constant of second-order adsorption. Figure 3.4 showed that the linear plot of t/q_t versus t gave $1/k_2 q_e^2$ as the intercept and $1/q_e$ as the slope. In Table 3.2, the R^2 for the pseudo-second-order adsorption gave the higher value (0.999) which indicates that this kinetic model has a good relation and is consistent between the experimental and the calculated q_e value. It also showed that the pseudo-second-order model adsorption is predominant.
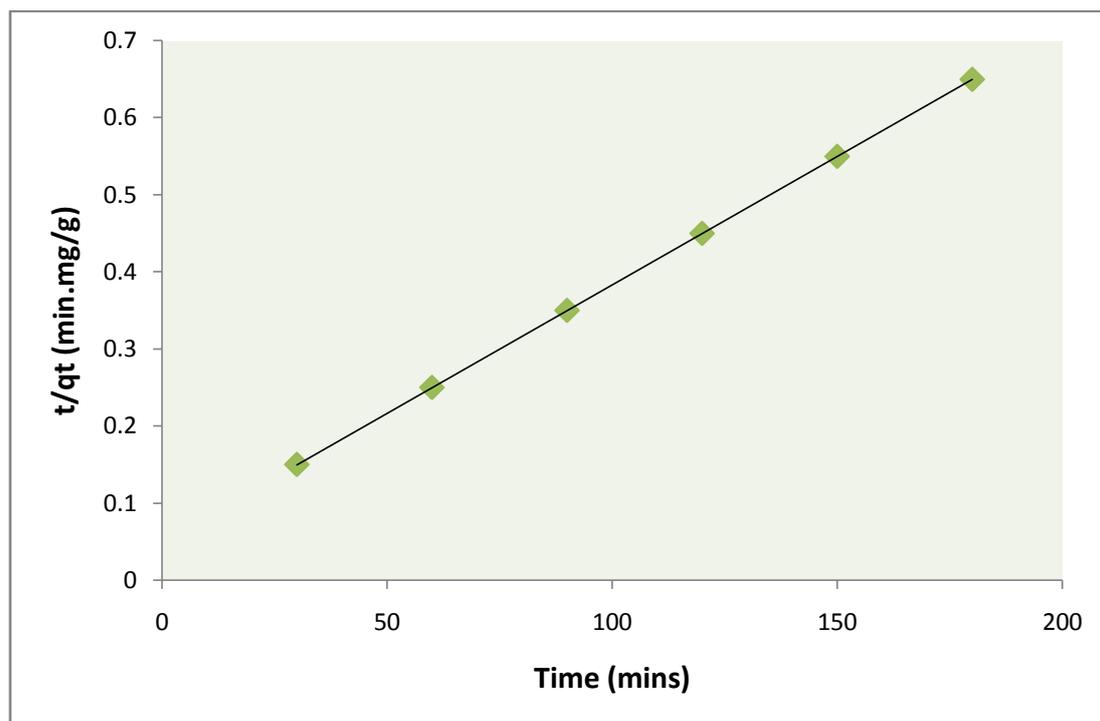
Figure 3.4: Plot of Pseudo-Second Order Kinetic Model for Cr^{6+} ion Adsorption onto HES

3.3. Adsorption Thermodynamics

Thermodynamic parameters provide information of inherent energy changes associated with the adsorption process. The thermodynamic adsorption parameters determined were standard enthalpy change (ΔH^0), standard free energy change (ΔG^0), and standard entropy change (ΔS^0). The parameters are evaluated from the following equations (Mekonnen et al., 2015):

$$InK_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad 3.5$$

$$\Delta G^0 = -RTInK_L \qquad 3.6$$

Where R(8.314 J/mol.K) is the universal gas constant, T (K) is the absolute solution temperature, and K_L(l/mg) is theLangmuir isotherm constant. ΔH^0 and ΔS^0 were evaluated from the slope and intercept of the linear plot of lnK_Lversus 1/T respectively. To obtain the activation energy of adsorption, Arrhenius equation was employed:

$$Ink_2 = InA - \frac{E_a}{RT} \qquad 3.7$$

Where k_2(g/mg h) is the rate constant obtained from the pseudo-second-order kinetic model, E_a(kJ/mol) is the Arrhenius activation energy of adsorption and Ais the Arrhenius factor. When $lnk_2$was plotted against 1/T, a straight line with gradient of $-E_a$/Rwas obtained.

Table 3.4: Thermodynamic Parameters for the Adsorption of Cr^{6+} ion onto HES

ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)	E_a (kJ/mol)	ΔG^0(kJ/mol)			
			298 K	303 K	318 K	328 K
7.85	-10.92	8.98	8.75	9.90	10.85	11.50

ΔH^0, ΔS^0, ΔG^0 and E_a for the adsorption of Cr^{6+} ion onto HES are reported in Table 3.4. The positive value of ΔH^0showed that the adsorption of Cr^{6+} ion onto HES wasendothermic in nature, which supported the observation made during batch thermodynamic studies where the Cr^{6+} ion removal increase with increasein solution temperature. The negative value of ΔS^0describes decreasing degree of freedom and randomness during theadsorption process at the solid-liquid interface with somestructural changes in the adsorbate and adsorbent. Similar trends had also been reported in the adsorption of Zinc by walnut shell (Olafadehan et al., 2018), Hexavalent Chromium by potato peel waste (Abdullah and Prasad, 2009) and direct dyesby carbon nanotubes (Kuo et al., 2008).

ΔG^0 value was positive which depicted the condition ofnon-spontaneous nature of the process at therange of temperature studied. The E_a value was positive andlower than 40 kJ/mol indicating the feasibility of theadsorption process and that the adsorption was physicallycontrolled respectively (Ahmad et al., 2014).

IV. CONCLUSION

In the textile industry, effluents from the dyeing and finishing processes are known to contain colour, a large amount of suspended organic solids and heavy metals such as Cr, Ni, and Cu. It has been widely reported that the exposure to Hexavalent Chromium beyond the tolerance levels (0.05 mg/l) can have damaging effects on the human physiological, neurological and biological systems.In this study, batch methods were used to investigate the equilibrium, kinetics and thermodynamics of the Hexavalent Chromium adsorption using hen eggshell. The equilibrium data was best fitted to the Freundlich adsorption isotherm model. The results of kinetic models showed that the pseudo-second-order kinetic model correlate well to the experimental data. The results of the thermodynamic parametersshowed that the adsorption process was feasible, non-spontaneous, and endothermic.The negative value of entropydescribes decreasing degree of freedom and randomness during theadsorption process at the solid-liquid interface with somestructural changes in the adsorbate and adsorbent.

REFERENCES

[1]. Abdullah, M.A. and Prasad, A.G.D. (2009): Kinetic and equilibrium studies for the biosorption of Cr (VI) from aqueous solutions by potato peel waste, Int. J. Chem. Eng. Res. 1, 51–62.

[2]. Ahmad, M.A. and Alrozi, R. (2011): Removal of malachite green dye from aqueous solution using rambutan peel-based activated carbon: equilibrium, kinetic and thermodynamic studies. Chemical Engineering Journal. 171 (2) 510–516, 2011.

[3]. Ahmad, M.A., Herawan, S.G. and Yusof, A.A. (2014): Equilibrium, Kinetics, and Thermodynamics of Remazol Brilliant Blue R Dye Adsorption onto Activated Carbon Prepared from Pinang Frond, ISRN Mechanical Engineering, Vol. 14: 184-265.

[4]. Ahmad, M.A., Yun, E.T.C., Abustan, I., Ahmad, N. and Sulaiman, S.K. (2011): Optimization of Preparation Conditions for Corn Cob Based Activated Carbons for the Removal of Remazol Brilliant Blue R dye,

[5]. Ahmed, T.A.E., Suso, H.P. and Hincke, M.T. (2017): Indepth comparative analysis of the chicken eggshell membrane proteome. J. Proteomics, 155: 49-62.

[6]. Al-Sou'od, K. (2013): Adsorption kinetics for the removal of hexavalent chromium using low cost materials. Res. J. Chem. Environ., 17, 25–30.

[7]. Botomé, M.L., Poletto, P., Junges, J., Perondi, D. and Dettmer, A. et al., (2017): Preparation and characterization of a metal-rich activated carbon from CCA-treated wood for CO_2 capture. Chem. Eng. J., 321: 614-621.

[8]. Cavaco, S.A., Fernandes, S., Quina, M.M. and Ferreira, L.M. (2007): Removal of chromium from electroplating industry effluents by ion exchange resins. J. Hazardous Materials.144, 634–638.

[9]. Folami, N.A., Oyebola, M.O., Dare, B.T. and Edafeshebure, O. (2019): Comparative evaluation of the potentials of exotic and indigenous breed hen eggshell powder as an adsorbent for the removal of Hexavalent Chromium fromaqueous solution. An article accepted for publication (July 8, 2019) – African Journal of Environmental Science and Technology (AJEST-03.06.19-2718).

[10]. Gao, J.J., Qin, Y., Zhou, T., Cao, D., Xu, P., Hochtetir, D. and Wang, Y. (2013): Adsorption of methylene blue onto activated carbon produced from tea (Camellia sinensis L.) seed shells: kinetics, equilibrium, and thermodynamics studies. Journal of Zhejiang Univ-Sci B (Biomed & Biotechnol). 14 (7) 650-658

[11]. Gholipour, M., Hashemipour, H. and Mollashahi, M. (2011): Hexavalent chromium removal from aqueous solution via adsorption on granular activated carbon: adsorption, desorption, modeling and simulation studies, J. Engineering and Applied Science. 6, 10–18.

[12]. Guo, X., Zhang, F., Peng, Q., Xu, S. and Lei, X. et al. (2011): Layered double hydroxide/eggshell membrane: An inorganic biocomposite membrane as an efficient adsorbent for Cr (VI) removal. Chem. Eng. J., 166: 81-87.

[13]. Kanagaraj, J., Babu, N.K.C. and Mandal, A.B. (2008): Recovery and reuse of chromium from chrome tanning waste water

aiming towards zero discharge of pollution, J. Cleaner Prod., 16, 1807–1813.

[14]. Kuo, C.Y., Wu, C.H. and Wu, J.Y. (2008): Adsorption of direct dyes from aqueous solutions by carbon nanotubes: determination of equilibrium, kinetics and thermodynamics parameters," Journalof Colloid and Interface Science. 327 (2) 308–315.

[15]. Kwaghger, A., Kucha, E.I. and Iortyer, H.A. (2012):Optimization of Conditions for the Preparation of Activated Carbon from Mango Nuts Using $CaCl_2$, International Journal of Environment and Bioenergy, Vol. 1(3): 146 – 161.

[16]. Mekonnen, E., Yitbarek, M. and Soreta, T.R. (2015): Kinetic and Thermodynamic Studies of the Adsorption of Cr (VI) onto Some Selected Local Adsorbents. South Africa J. Chem., 68, 45–52

[17]. Mittal, A., Teotia, M., Soni, R.K. and Mittal, J. (2016): Applications of egg shell and egg shell membrane as adsorbents: A review. J. Mol. Liq., 223: 376-387. DOI: 10.1016/j.molliq.2016.08.065

[18]. Mishra, S. and Gottipati, R. (2012): Preparation and Characterization of Microporous Activated Carbon from Biomass and its Application in the Removal of Chromium(VI) from Aqueous Phase, PhD Thesis, Department of Chemical Engineering, National Institute of Technology, Rourkela, Odisha – 769008

[19]. Mohammadi, M., Lahijani, P. and Mohamed, A.R. (2014): Refractory dopant-incorporated CaO from waste eggshell as sustainable sorbent for CO_2 capture: Experimental and kinetic studies. Chem. Eng. Journal, 243: 455-464. DOI: 10.1016/j.cej.2014.01.018

[20]. Mopoung, S. and Jitchaijaroenkul, K. (2017): 'Characterization of Activated Carbon from Eggshell Membranes Prepared Using Sodium Acetate and Zinc Metal Activation' American Journal of Applied Sciences, 14 (8): 737.747

[21]. Olafadehan, O.A., Akpo, O.Y., Enumuo, O., et al. (2018): Equilibrium, kinetics and thermodynamic studies of biosorption of zinc ions from industrial wastewater using derived composite biosorbent from walnut shell. African Journal of Environmental Science and Technology, 12 (9) 335 – 356.

[22]. Susu, A.A. and Folami, N.A. (2014): Recycling of Polyethylene Therephthalate Bottles/Containers and Nylon Water Sachets collected from Dumpsites in Lagos State, Nigeria, J. Environ. Sciences and Water Resources, Vol. 3 (4): 069 – 079.

[23]. Tsai, W.T., Hsien, K.J., Hsu, H.C., Lin, C.M. and Lin, K.Y. et al., (2008): Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution. Bioresource Technol., 99: 1623-1629.

[24]. www.epa.gov/sdwa(visited March 14, 2021 at 18:25 Hour)

[25]. www.nature.com (visited March 14, 2021 at 18:05 Hour)

[26]. Zaman, T., Mostari, S., Al-Mahmood, A. and Rahman, S. (2018): Evolution and characterization of eggshell as a potential candidate of raw material, Ceramica, Vol. 64 (37): 1 – 12.

IJAEM