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Kinetic Models on Chromium (VI) Adsorption onto Carbonized Oil Palm Kernel with Potassium Hydroxide Activation

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Abstract**—**Use of adsorption kinetic models for removal of chromium (VI) from aqueous solution by oil palm kernel with potassium hydroxide activation has been investigated. The adsorption capacity or amount of Cr(VI) adsorbed per unit mass of adsorbent was determined by the pseudo-zero order, pseudo-first order, pseudo-second order, intraparticle diffusion, Bangham pore diffusion, liquid film diffusion, modified Freundlich and Elovich models to describe the adsorption process. The kinetics data were marginally better fit with Elovich model as compared to other models. It is therefore suggest that the chemisorption was the rate controlling step for chromium (VI) adsorption onto the carbonized oil palm kernel with KOH activation as the adsorbent.

Keywords**—** chromium adsorption, kinetic model, oil palm kernel.

I. INTRODUCTION

The contamination of toxic heavy metal ions into the environment is a crucial problem to water quality. The water pollution is prevalent in majority countries and threatens the environment, the health of humans and wildlife. Chromium, one of the primary heavy metal pollutants, occurs in two stable oxidation states in aqueous solutions, Cr (III) and Cr (VI), and their properties are very different. Cr (III) has a limited hydroxide solubility and low toxicity. In contrast, Cr (VI), having mobile and strongly oxidant character, is known as mutagen and potential carcinogen. Common processes have been investigated for removing chromium from aqueous solutions. Principally, there are two types of treatment methods for Cr (VI) removal. One is to remove Cr (VI) directly, and the other is to reduce Cr (VI) to Cr (III).This is commonly considered due to its more impact on environment, owing to the reagents addition and cleaner produces with more settling production. The discharge limit of Cr (VI) into inland surface water is 0.1 ppm, and potable water is limited to 0.05 ppm. Most sources of water pollution with chromium are fertilizer, metal fabrication, electroplating plants, metal finishing, batteries, printing and mining. Due to the toxicity and non-biocompatibility, various treatment methods are considered such as chemical precipitation, electroflotation, membrane processes and oxidation [1-3].

However, these techniques have certain disadvantages such as less efficiency, high treatment and disposal costs. Adsorption is considered to be a more efficient and cost-effective technique for the removal of chromium from wastewater. Using suitable adsorbent to remove various toxic pollutants from industrial wastewater by adsorption is considered.

A review of Cr (VI) removal from aqueous solutions by raw and modified lignocellulosic materials [2-3] showed that oil palm waste has a few used as an adsorbent for Cr (VI) adsorption. Carbonized or activated carbon is produced from solid waste of palm oil processing mill (oil palm kernel or oil palm shell) in many tropical countries (e.g., India, Indonesia, Malaysia and Thailand). However, few facilities in Thailand produce adsorbents, and research is thus needed in order to obtain suitable product that meets to standards for environmental applications. As an initial part of the research, chemical activation using phosphoric acid (H_3PO_4) and potassium hydroxide (KOH) was employed to prepare carbonaceous materials as adsorbents from the oil palm kernel for Cr(VI) adsorption from aqueous solutions, and found that the potassium hydroxide was used to treat the oil palm kernel for carbonization at temperature 673 K for 2 h, and showed a high surface area and Cr (VI) removal [1], and in this part of research, the kinetic adsorption models such as, the pseudo-zero order, pseudo-first order, pseudo-second order, intraparticle diffusion, Bangham pore diffusion, liquid film diffuse on, modified Freundlich and Elovich models were investigated to describe the adsorption process.

II. MATERIAL AND METHODS

The oil palm kernels were washed with distilled water and dried. Dried oil palm kernels were immersed in 1 L of 1 M KOH for 1 h, and filtered with a stainless screen before being carbonized in a Muffle furnace at 673 K for 2 h, respectively. The carbonaceous material was cool and washed several times with hot water until pH 7 and dried in oven to use as adsorbent for Cr (VI) adsorption. The final material was referred to as carbonized oil palm kernel with KOH activation (KOH-COP). The properties of surface area, pore volume and pore diameter KOH-MSP C are 164 m2/g, 0.2411 cc/g and 58.81 °A, respectively. Adsorption studies were conducted using a batch adsorption technique. A number of stoppered Duran glass Erlenmeyer containing100 mL of chromium (VI) solution of at a desired concentration, pH and temperature was placed in a

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thermostatic shaker. In the studies, 1 g of the carbonaceous material was used to treat 100 mL of the Cr (VI) solution at a defined pH and temperature.

The flasks were agitated at a shaking rate of 110 rpm for 2 h to ensure adsorption equilibrium. Samples were filtered with Whatman No.1 and No.42 filter papers and chromium (VI) content in the filtrate were analysed with an Atomic Adsorption Spectroscopy (model: Varian 640Z, 220). All experiments were carried out in duplicates and average values were reported.

III. RESULTS AND DISCUSSION

A. Adsorption Study

The impacts of changing the initial chromium (VI) concentration from 50 to 250 mg/L, temperature from 303 K to 323 K were studied for KOH-COP at a constant adsorbent dose 1 g/100 mL, pH 2.0, contact time 5, 10, 15, 30, 60, 120 min, stirring speed 110 rpm, on the chromium removal was obtained from the calculated with initial concentration and equilibrium concentration on the initial concentration as shown in Fig.1. When the initial Cr (VI) concentration in the solution increased from 50 to 100 ppm, the Cr (VI) removal increased. However, when the concentration increased from 100 to 250 ppm, the Cr (VI) removal decreased. Thus, the removal of Cr (VI) was dependent on the initial concentration. This is because at a low feed concentration, the ratio of available surface to the initial Cr (VI) concentration is high. However, in the case of higher concentrations, this ratio is low, and hence the percentage removal is also lower. The number of ions adsorbed from higher feed concentrations is more than that removed from less concentrated solutions. A higher metal concentration increased the mass transfer driving force, and thus increased the metal ions sorbed per unit weight of adsorbent at equilibrium. In addition, increasing metal ions and sorbent, which enhanced the sorption process. The same results were obtained with the temperature increased from 303 to 313 and 323 K, respectively.

B. Kinetic Adsorption Models

The kinetic of Cr (VI) adsorption on KOH-COP, some adsorption kinetic models, namely, pseudo-zero order adsorption kinetic model [4], pseudo-first-order adsorption kinetic model [4], pseudo-second order adsorption kinetic model [4], intraparticle diffusion model [5], Bangham's pore diffusion model [6], liquid film diffusion kinetic model [7], modified Freundlich kinetic model [8] and Elovich model [9] are investigated to describe the adsorbate uptake.

The traditional methods of determining the kinetic adsorption parameters by linear regression appear to give a good fit to experimental data. However, the R^2 is based on the linear forms of the kinetic equations, but does not represent the errors in the kinetic curves. To evaluate the fit of the kinetic equations to the experimental data, different error functions of non-linear regression were used here to determine the constants model parameters, and they were compared with those determined from the less accurate linearized data fitting. The residual root mean square error (RMSE) was used and defined as:

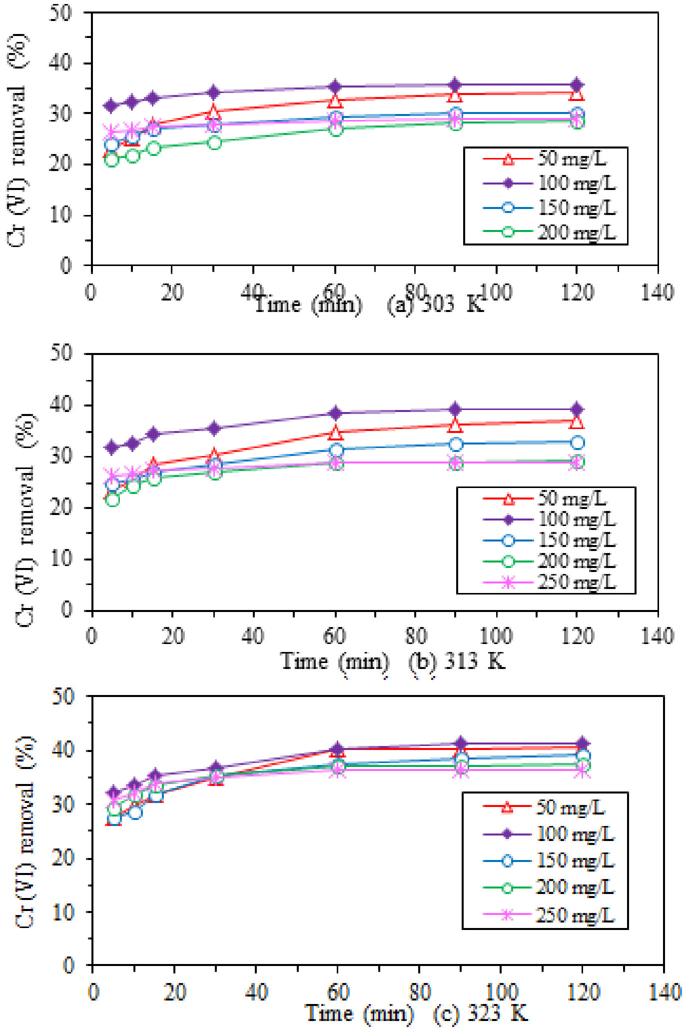

Fig.1: Effect of initial concentration 50, 100, 150, 200, 250 mg/L, pH 2.0 on the Cr (IV) removal at temperature 303, 313 and 323 K

$$\mathrm{RMSE} = \sqrt{\frac{1}{n-2}\sum_{i=1}^{n}(q_{e,exp} - q_{e,cal})^2} \qquad (1)$$

The subscripts "exp" and "cal" show the experimental and calculated values and n is the number of observations in the experimental data. The smaller the RMSE value, the better the curve fitting [10].

B.1. Pseudo-Zero Order Adsorption Kinetic Model

The chromium (VI) adsorption onto the KOH-COP, the adsorptions whose order is pseudo-zero are rare. The rate law of zero order is [4]:

$$\frac{dq}{dt} = k_{ad,0}[q_e - q_t]^0 = k_{ad,0} \qquad (2)$$

Where q_t, and q_e are amounts of Cr(VI) adsorbed at time t and at equilibrium, respectively, and $k_{ad,o}$ denote the adsorption rate constant. Thus, the rate of pseudo-zero order adsorption is a constant, independent of amounts of Cr (VI) adsorbed. Using the calculus with integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$, it can be showed:

$$(q_e - q_t) = q_e - k_{ad,0}\, t \tag{3}$$

The adsorption rate constant, $k_{ad,0}$ of zero-order adsorption can be calculated from the slope of linear plot of $(q_e - q_t)$ with t. Table 1 shows the adsorption kinetic parameters of pseudo-zero order adsorption kinetic model. It is observed that the correlation coefficients (R^2) were obtained from fit model moderately ($0.74 \le R^2 \le 0.91$). This is because this model depends on only rate constant.

TABLE I: Adsorption kinetic parameters of pseudo-zero order adsorption kinetic model

Concentration	303 K			313 K			323 K		
(mg/L)	$k_{ad,o}$	R^2	RMSE	$k_{ad,o}$	R^2	RMSE	$k_{ad,o}$	R^2	RMSE
50	0.0058	0.8162	0.7855	0.0073	0.8996	0.8070	0.0075	0.8798	0.6869
100	0.0067	0.8645	2.2076	0.0085	0.9100	2.2320	0.0103	0.9132	0.9580
150	0.0091	0.8500	2.5718	0.0140	0.9492	2.5750	0.0189	0.8344	1.9692
200	0.0165	0.9313	2.9249	0.0141	0.7390	3.0965	0.0160	0.7483	1.6235
250	0.0216	0.9125	3.4575	0.0072	0.7974	4.6037	0.0154	0.7728	1.5103

B.2. Pseudo-first Order Adsorption Kinetic Model

A pseudo-first order adsorption is a adsorption whose rate depends on the amounts of Cr(VI) adsorption raised to the first power. The chemical rate is [4]:

$$\ln(q_e - q_t) = \ln q_e - k_{ad,1}\, t \tag{4}$$

After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$. The adsorption rate constant $k_{ad,1}$ of pseudo-first order adsorption can be calculated from the plot of $\ln(q_e - q_t)$ against t. Table 2 shows the adsorption kinetic data fit model well ($0.93 \le R^2 \le 0.95$) and RMSE values are 0.6 – 4.98.

TABLE II: Adsorption kinetic parameters of pseudo-first order adsorption kinetic model

Concentration	303 K			313 K			323 K		
(mg/L)	$k_{ad,1}$	R^2	RMSE	$k_{ad,1}$	R^2	RMSE	$k_{ad,1}$	R^2	RMSE
50	0.0379	0.9960	0.7678	0.0384	0.9895	0.6981	0.0620	0.9329	0.7209
100	0.0492	0.9955	2.1198	0.0428	0.9882	2.0566	0.0416	0.9896	2.0490
150	0.0438	0.9786	2.4132	0.0373	0.9822	2.3044	0.0353	0.9920	2.7272
200	0.0387	0.9775	2.6000	0.0415	0.9660	3.1118	0.0516	0.9748	4.0345
250	0.0321	0.9360	3.1650	0.0424	0.9550	4.5802	0.0649	0.9867	4.9859

B.3. Pseudo-Second Order Adsorption Kinetic Model

A pseudo-second order adsorption is a adsorption whose rate depends on the concentration of one reactant raised to the second power. Using calculus, we can obtain the following expressions for the second order adsorptions [4]:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_{ad}t \tag{5}$$

The adsorption rate constant k_{ad} of first order adsorption can be calculated from the slope of linear plot of $1/(q_e - q_t)$ against t. Table 3 shows that the adsorption kinetic rate constants, $k_{ad,2}$ were presented from fit model moderately and the correlation $0.75 \le R^2 \le 0.94$.

TABLE III: Adsorption kinetic parameters of pseudo-second order adsorption kinetic model

Concentration	303 K			313 K			323 K		
(ppm)	$k_{ad,2}$	R^2	RMSE	$k_{ad,2}$	R^2	RMSE	$k_{ad,2}$	R^2	RMSE
50	0.5008	0.8774	0.4656	0.4279	0.8202	0.7175	2.1049	0.9395	0.7682
100	1.5239	0.8388	0.5191	0.5220	0.8228	0.6686	0.3874	0.8323	1.1845
150	0.5959	0.7619	1.4370	0.2073	0.8026	2.1179	0.1235	0.8793	3.2524
200	0.2024	0.7856	2.7675	0.2604	0.9634	3.0757	0.5055	0.9400	4.4395
250	0.0914	0.7537	3.9510	0.5283	0.9588	3.4225	1.5420	0.8301	5.4665

B.4. Intraparticle Diffusion Model

The initial rate of intraparticle diffusion is calculated as follows [5]:

$$q_t = k_{id}\, t^{0.5} + C \tag{6}$$

Where k_{id} is intraparticle diffusion rate constant (mg/g min$^{0.5}$) and obtained from the slope of linear plot of q_t and $t^{0.5}$. According to this model, the linear plot of q_t and square root of time ($t^{0.5}$) should be linear if intraparticle diffusion is involved in adsorption process and if line pass through the origin then intraparticle diffusion is the rate controlling step. Table 5 shows that the intraparticle diffusion rate constants, k_{in} values were obtained from slope and R^2 for intraprticle diffusion model are between 0.94-0.98. When the plots did not pass through the origin, these are indicated that the intraparticle diffusion is not the only rate-limiting step, but other kinetic model may control the rate of adsorption.

TABLE IV: Adsorption kinetic parameters of intraparticle diffusion adsorption kinetic model

Concentration (mg/L)	303 K			313 K			323 K		
	k_{in}	R^2	RMSE	k_{id}	R^2	RMSE	k_{id}	R^2	RMSE
50	0.3143	0.9485	1.7405	0.0793	0.9490	0.0558	0.0786	0.9155	0.0752
100	0.2471	0.9591	1.3714	0.0907	0.9453	0.0680	0.1104	0.9494	0.0814
150	0.4838	0.9582	2.6751	0.1518	0.9727	0.0915	0.2057	0.9116	0.1588
200	0.8740	0.9839	4.7963	0.1512	0.8362	0.1486	0.1686	0.8339	0.1819
250	1.1858	0.9778	6.4575	0.0766	0.8752	0.0719	0.1612	0.8468	0.1745

B.5. Bangham Pore Diffusion Model

The Bangham equation is presented to limit by the pore diffusion at different adsorption time by following [6]:

$$\log\log\left[\frac{C_i}{C_i - mq_t}\right] = \log\left[\frac{mK_B}{2.303\,V}\right] + a_B\log t \qquad (7)$$

Where m is weight of adsorbent used in solution (g/L) C_i is initial concentration of adsorbate in solution (mg/L), a_B and K_B constants were calculated from the intercept and slope of the linear plots of log log[C_i/ (C_i – mq_t] against log t. This model can be used to check whether the pore diffusion is only rate-controlling step or not. Table 5 shows that the most of adsorption kinetic data fit model well ($0.93 \le R^2 \le 0.95$) and RMSE values are high in range 2-11. This may indicate that the diffusion of Cr (VI) into pores of the COP-KOH is not only rate controlling step.

TABLE V: Adsorption kinetic parameters of Bangham pore diffusion adsorption kinetic model

Concentration (mg/L)	303 K				313 K				323 K			
	k_b	a_b	R^2	RMSE	k_b	a_b	R^2	RMSE	k_b	a_b	R^2	RMSE
50	2.0790	0.1538	0.9721	2.3271	1.9819	0.1821	0.9886	2.2302	2.4590	0.1648	0.9716	2.1058
100	3.4742	0.0530	0.9815	4.5446	3.2871	0.0909	0.9758	4.2829	3.2283	0.1083	0.9814	4.1451
150	2.4706	0.0813	0.9805	7.4091	2.2990	0.1176	0.9828	7.1043	2.5109	0.1478	0.9684	6.4630
200	1.9205	0.1183	0.9860	10.1208	2.1785	0.1024	0.9376	10.0247	3.0899	0.0928	0.9433	8.8749
250	1.7787	0.1314	0.9766	12.6657	2.8664	0.0385	0.9604	12.5684	3.3239	0.0703	0.9502	11.2267

B.6. Liquid Film Diffusion Kinetic Model

The liquid film diffusion equation is presented by following [7]:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -K_{lf}\,t$$

$$q_t = q_e - q_e e^{-k_{lf}\,t} \qquad (8)$$

Where k_{lf} is the external mass transfer coefficient (1/min).

The linear plot of ln(1-q_t/q_e) against t, the zero intercept may expect that the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbent. k_{lf} can be calculated from the slope of plot of q_t against e^{-t}. Table 6 shows the external mass transfer coefficients obtained from the plot of q_t against e^{-t}, k_{lf}. The experimental data have given the poor correlations ($R^2 < 0.6$), this is confirmed that the kinetic of adsorption process is not controlled by diffusion through the liquid film surrounding the solid adsorbent.

TABLE VI: Adsorption kinetic parameters of liquid film diffusion adsorption kinetic model

Concentration (mg/L)	303 K			313 K			323 K		
	k_{fd}	R^2	RMSE	k_{fd}	R^2	RMSE	k_{fd}	R^2	RMSE
50	3.6515	0.4619	1.0870	3.7254	0.3905	1.1363	3.5714	0.3589	1.2813
100	2.5281	0.3999	2.4317	2.9549	0.3324	2.5952	3.1340	0.3470	2.6911
150	3.0655	0.4666	3.0064	3.2213	0.3070	3.1529	3.4750	0.3620	3.7177
200	3.3019	0.3420	3.6223	3.4182	0.5929	3.8650	3.2213	0.5358	4.9957
250	3.4136	0.3439	4.4213	2.3137	0.4386	4.9683	2.9320	0.5118	6.1884

B.7. Modified Freundlich Kinetic Model

The modified Freundlich equation is expressed by the following [8]:

$$q_t = K_{mf}\,C_i\,t^{1/m_{mf}} \qquad (9)$$

$$\ln q_t = \ln\left[K_{mf}\,C_i\right] + \frac{1}{m_{mf}}\ln t$$

where k_{mf} is the apparent adsorption rate constant (L/g min), m_{mf} is a constant, Ci is the initial Cr(VI) concentration (mg/L). The values of k_{mf} and m_{mf} are used empirically to evaluate the effect of surface loading and ionic strength on the adsorption process and also can be obtained from intercept and slope of linear of ln q_t and ln t, respectively. From the results, the modified Freundlich model fit the experimental data well, according to R^2 values listed in Table 7 ($0.93 \le R^2 \le 0.98$). The RMSE values are between 0.04 – 0.14.

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TABLE VII: Adsorption kinetic parameters of modified Freundlich adsorption kinetic model

Concentration (mg/L)	303 K				313 K				323 K			
	k_{mf}	m_{mf}	R^2	RMSE	k_{mf}	m_{mf}	R^2	RMSE	k_{mf}	m_{mf}	R^2	RMSE
50	0.0190	7.7364	0.9690	0.0400	0.0203	6.6084	0.9875	0.0332	0.0222	7.5445	0.9720	0.0523
100	0.0294	23.3566	0.9813	0.0260	0.0282	13.8489	0.9762	0.0296	0.0279	11.7303	0.9819	0.0367
150	0.0220	14.4897	0.9794	0.0454	0.0207	10.1262	0.9838	0.0244	0.0225	8.3361	0.9660	0.1011
200	0.0176	9.7792	0.9864	0.0409	0.0197	11.3747	0.9342	0.1203	0.0267	13.3328	0.9403	0.1455
250	0.0164	8.7590	0.9767	0.0079	0.0249	30.6816	0.9599	0.0445	0.0284	17.6163	0.9483	0.1306

B.8. Elovich Adsorption Kinetic Model

Elovich equation is presented to describe the actual adsorbent surfaces are energetically heterogeneous by the following Aroua et. al [9]. This reaction also involves chemisorption of the adsorbate on a solid surface without desorption. The adsorption rate decreases with time due to and increased surface coverage. The mechanism of adsorbent and adsorbate does not consider in the equation (10).

$$q_t = \frac{1}{B}\ln AB - \frac{1}{B}\ln t \qquad (10)$$

Where A is the initial adsorption rate (mg/g min) and B is related to extent of surface coverage and activation energy for chemisorption (g/mg) and calculated from the intercept and slope of the plots q_t and ln t. Table 8 shows the adsorption kinetic parameters of Elovich adsorption kinetic model. It is observed that the adsorption kinetic data fit model very well ($R^2 > 0.95$) and RMSE values are 0.4-0.6.

TABLE VIII: Adsorption kinetic parameters of Elovich adsorption kinetic model

Concentration (mg/L)	303 K				313 K				323 K			
	A	B	R^2	RMSE	A	B	R^2	RMSE	A	B	R^2	RMSE
50	5.75×10^2	5.4128	**0.9818**	0.4679	1.39×10^2	4.4048	**0.9893**	0.4932	3.52×10^2	4.4141	**0.9690**	0.5144
100	3.99×10^9	6.9224	**0.9821**	0.4184	1.57×10^5	3.8740	**0.9744**	0.5168	1.57×10^4	3.1829	**0.9795**	0.5405
150	3.01×10^5	3.5299	**0.9842**	0.5410	2.22×10^3	2.3439	**0.9779**	0.5237	3.06×10^2	1.6784	**0.9736**	0.5024
200	1.37×10^3	1.9817	**0.9827**	0.5091	9.73×10^3	2.2119	**0.9517**	0.6025	5.99×10^4	1.9816	**0.9509**	0.6106
250	3.69×10^2	1.4623	**0.9742**	0.3450	4.12×10^{12}	4.4412	**0.9625**	0.5155	4.39×10^6	2.0837	**0.9550**	0.6133

Since the pseudo-zero order, pseudo-first order and pseudo-second order adsorption kinetic models concerned with speed, or rates, at which a chemical reaction occurs. The kinetic is the movement or change in concentration of reactant or product with time; therefore, kinetic refers to the rate of the reaction, or the reaction rate and could not identify the diffusion mechanism; the kinetic results have to analyze by using intraparticle diffusion model, Bangham pore diffusion and liquid film diffusion kinetic models. The modified Freundlich model has been used to analyze about the effect of temperature to nature of the adsorption process. The Elovich model is involved the chemisorption of the adsorbate on a solid surface without desorption of product, adsorption rate decreased with time due to an increased surface coverage.

Several kinetic models have been used to predict the variation of adsorbed Cr (VI) with time. The RMSE and the kinetic parameters are given in Table 1 – Table 8 to representation that the Elovich adsorption model has the high R^2 for all condition and RMSE value has very low. When the initial Cr (VI) concentration increased from 50 mg/L to 100 mg/L to A higher, the adsorption rate increased, when concentration increased from 100 - 250 mg/L, the adsorption rate decreased to A lower, according to the Cr (VI) removal for at temperatures 303 K, 313 K and 323 K, respectively.

IV. CONCLUSION

The kinetics data were marginally better fit with Elovich model as compared to other models. It is therefore suggest that the chemisorption was the rate controlling step for chromium (VI) adsorption onto the KOH-COP.

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