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Kinetics of the adsorption of hexavalent Chromium from aqueous solutions on low cost material

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This study proposes a Jordanian Pottery (Pot-Jo) as a low cost adsorbent for the removal of chromium from aqueous solutions. The effect of contact time, initial concentration of Cr(VI), temperature and ionic strength on the adsorption of Cr(VI) onto Pot-Jo were studied and discussed. The equilibrium (q_e) of adsorption of Cr(VI) onto pottery were found to be 20.287, 17.55, and 13.577 mg Cr(VI) per gram of pottery at temperatures 25, 35, and 45°C, respectively. Five kinetic models, the pseudo first-order equation, the pseudo second-order equation, the Elovich equation, the Ritchie's equation, and the intraparticle diffusion model were tested with respect to their adequacy to describe the adsorption process. The mechanism of adsorption was investigated by using the intraparticle diffusion model. It was found that there was no significant effect of the ionic strength on the removal of Cr(VI) from its solutions. Kinetic parameters, rate constants, equilibrium adsorption capacities and correlation coefficients, for each kinetic equation were calculated and discussed. Activation energy values were found to be between 13.85 and 33.10 kJ mol^{-1}. The Ritchie and pseudo-first order kinetic equation were found to correlate the experimental data well. The rate determining step is well described by intraparticle diffusion process. The k_{id} values ranging from 1.326 to 0.963 mgg^{-1}min$^{-1/2}$.

Key words: Chromium (VI), Sorption kinetics, Pseudo-second order, Lagergren, Tempkin.

INTRODUCTION

Water contamination with heavy metal ions is a very severe environmental problem all over the world. Chromium is a toxic pollutant that causes severe environmental and public health problems. For example, it was reported that $Cr_2O_7^{2-}$ can cause lung cancer (Sikaily et al., 2007; Li et al., 2008). In aqueous phase, Chromium mostly exists in two oxidation states, namely, trivalent Chromium [Cr^{3+}, $Cr(OH)_2^+$ or $Cr(OH)^{2+}$] and hexavalent Chromium ($HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$). Moreover, +6 state of Chromium has magnetic properties. Chromium in its compounds has many different colors, so it is widely used in many industrial fields such as plating, alloying, dyeing, tanning, finishing, wood preserving and refractory technologies. The maximum limit for Cr(VI) concentration in drinking water is 0.05 mg/L (Baral et al., 2006).

Conventional techniques for Cr(VI) removal from aqueous solution include precipitation, membrane filtration, solvent extraction with amines, ion exchange, activated carbon adsorption, electro-deposition, and various biological processes (Owlad et al., 2009; Wu et al., 2010; Tiravanti et al., 1997; Rengaraj et al., 2003; Kozlowski and Walkowiak, 2002; Gupta et al., 2001; Bhatti et al., 2010; Zubair et al., 2008; Shafqat et al., 2008; Gupta and Imran, 2004; Gupta and Rastogi, 2009; Gupta et al., 2010; 2012).

A survey of the literature has shown that only very small attempt has been made to use a pottery to remove heavy metals. Jordanian pottery (Pot-Jo) was chosen due to its low cost, its granular structure, insolubility in water, chemical stability, local availability and most importantly being an environment friendly natural material. The objective of this work is to investigate the applicability of Pot-Jo materials to remove Cr(VI) from aqueous solutions. A kinetic study was carried out investigating the pH, Cr(VI) concentration and the adsorbent particle size as parameters, pH, concentration and particle size as

Table 1. Chemical compositions (%wt) of Pot-Jo.

Raw pottery	SiO_2	Al_2O_3	TiO_2	K_2O	MgO	CaO	Fe_2O_3	Others
Pot-Jo	60.41	13.87	1.851	2.35	1.31	10.84	8.67	0.70

parameters. Thermodynamic data have been calculated in some cases to interpret the results. The effects of ionic strength, temperature and initial concentrations on Cr(VI) are particularly investigated. The kinetics on Cr(VI) adsorption on pottery materials was analyzed by various kinetic models. Five models were used in this study: (i) pseudo-first order kinetic model, (ii) pseudo-second order kinetic model, (iii) intraparticle diffusion model, (iv) Elovich equation, and (V) Ritchie's equation. Kinetic parameters such as the half-time, pre-exponential factor and activation energy are evaluated and discussed.

MATERIALS AND METHODS

Sample collection

A pottery used in this study was supplied by a factory near Zarqa (40 km Eastern Amman). All reagents used were of AR grade (Sigma-Aldrich, Germany).

Sample preparation

Raw pottery material (Pot-Jo) was prepared and treated as in the literature (Khazali et al., 2007). The chemical compositions of the Pot-Jo (Table 1) were estimated by XRF (Philips Magix PW 2424) (Khazali et al., 2007).

Qualitative X-ray diffraction (XRD) analysis was performed on the Pot-Jo to determine a mineralogical composition. The XRD pattern was obtained on a Philips, PW 3040/60 X'PertPRO Console using Cu K_α radiator and RTMS detector X'celerator.

The stock solutions of test reagent are prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) in double distilled water to obtain total Chromium concentration levels ranging from 50 to 400 mg/L. The pH values of the initial solutions are adjusted by adding HCl (0.1 M) or NaOH (0.1 M). Ionic strength has been adjusted by adding potassium nitrate. The experimental runs have been carried out in batch mode at the different temperatures.

Experiments for studying adsorption kinetics

For adsorption kinetics, a different set of batch experiments was carried out to establish the effect of time and initial concentration of Cr(VI) on the adsorption and to investigate the parametric effects of initial adsorbate concentration on Cr(VI) adsorption. 100.0 ml Cr(VI) solution with different initial concentrations (50 to 400 ppm) at pH 3 was added to screw-cap conical flask already containing 1.0 g of Pot-Jo (particle size ≤250 μm). [It was found earlier that an initial pH of 3.0 is most favorable for Cr(VI) removal (Al-Sou'od, 2012)].

The mixture was mechanically shaken at a speed of 200 r·min^{-1} with a temperature-controlled water bath at constant pH value of 3. After 300 min, the final pH was measured and samples were filtered using a Whatman No. 1 filter paper. The adsorbents were separated, and the filtrate was analyzed spectrophotometrically (Marczenko, 1976) to determine Cr(VI) content. Cr(VI)

concentration was determined using an indirect UV-visible spectrophotometric method based on the reaction of Cr(VI) and diphenylcarbazide, which forms a red-violet colored complex. The absorbance of the colored complex was measured in a double beam spectrophotometer at 540 nm wavelength. All experiments were conducted in three replicates and the relative error between duplicates was less than 5%. The results were reported as mean values.

The controlling mechanism of the adsorption process was investigated by fitting the experimental data with Lagergren pseudo-first-order, pseudo-second-order kinetic models, Elovich equation, Ritchie's equation or the intraparticle diffusion model.

The adsorbed amount of Cr(VI) at equilibrium, q_e [in mg Cr(VI) per g adsorbent g[-1]] was calculated from the mass balance equation given in Equation 1 (Gode and Pehlivan, 2005):

$$q_e = \frac{C_i - C_e}{m} V \tag{1}$$

Where C_i and C_e are the initial and equilibrium concentrations (mg/L), m is the mass of pottery (g), and V is the volume of the solution (L). When t is equal to the equilibrium contact time, then the amount of metal ion sorbed at equilibrium, q_e, is calculated using Equation 1.

The percent Cr(VI) removal (%RE) was calculated for each equilibration by the expression presented as Equation 2.

$$\% \ RE = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

Where (%RE) is the percent of Cr(VI) adsorbed or removed.

RESULTS AND DISCUSSION

Effect of contact time and initial concentration

Effect of contact time and initial pottery concentration on adsorption of Cr(VI) by Pot-Jo are shown in Figure 1. The concentrations selected for studies were 50, 100, 150, 200, 300, and 400 ppm. The results obtained have been plotted as %RE versus contact time (Figure 1). The graph shows that for all the concentrations, removal increases in initial stages, goes on increasing and acquires maximum value in 300 min. After 300 min, there is no further increase in removal. As shown in Figure 1, the removal of Cr(VI) increased from 42.2 to 78.1% by increasing the initial concentration of Chromium from 50 to 300 ppm at pH 3, 0.1 M ionic strength, temperature 25°C, 200 rpm and at a particle size of ≤250 μm. When these findings were compared with those reported for other low cost adsorbent materials for the removal of Cr(VI) like silica gel, polymer, carbon nanotubes, fly ash,
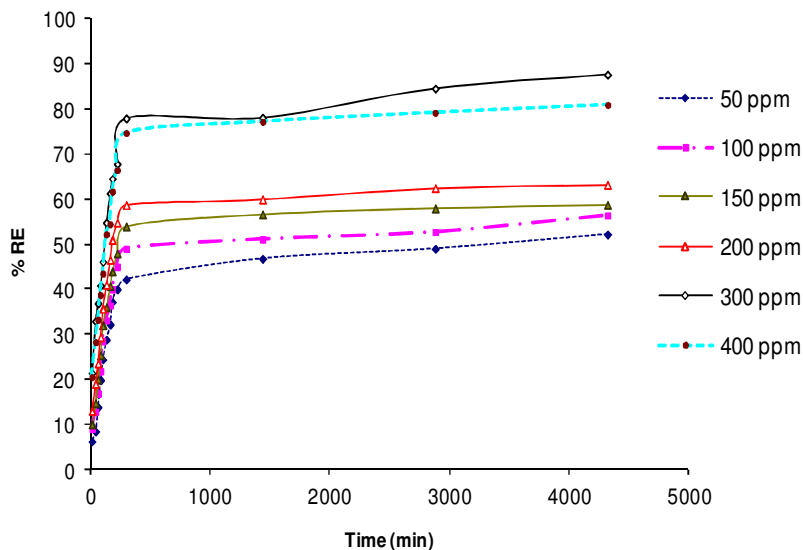
Figure 1. Effect of initial concentration and contact time on removal of Cr(VI) by Pot-Jo at 25°C and pH 3.

Table 2. Comparison between the pottery used and other reported values of %RE in the literature using low cost materials.

Adsorbent	% RE	References
Roots of *Typha latifolia*	45	Barrera-Díaz et al. (2004)
Ashes	60	Barrera-Díaz et al. (2004)
Green Algae spirogyra species	12 - 30	Gupta et al. (2001)
Green alga *Ulva lactuca*	92	El-Sikaily et al. (2007)
Almond Green Hull	94.14	Sahranavard et al. (2011)
Riverbed sand	74.3	Sharma and Weng (2007)
Natural zeolite	93	Campos et al. (2007)
Turkish fly ashes	25.46	Bayat (2002)
Afsin-Elbistan	30.91	Bayat (2002)
Fly ash	89.12	Sharma et al. (2008)
Walnut *(Juglans regia)*	85.32	Pehlivan and Altun (2008)
Hazelnut *(Corylus avellana)*	88.46	Pehlivan and Altun (2008)
Almond *(Prunus dulcis)*	55.00	Pehlivan and Altun (2008)
Coconut shell	80	Nameni et al. (2008)
Wheat bran	87.8	Nameni et al. (2008)
Pre-boiled sunflower stem	81.7	Jain et al. (2009)
Formaldehyde treated sunflower stem	76.5	Jain et al. (2009)
Pine needle	38	Park et al. (2007)
Walnut shell	24.6	Park et al. (2007)
Rice straw	26.3	Park et al. (2007)
Peanut shell	41.0	Park et al. (2007)
Sawdust	19.9	Park et al. (2007)
Jordanian pottery materials	78.1	Present work

clays, zeolites, chitosan, peat moss, biosorbent, food waste etc., it is appeared to act more efficiently than about most of these materials or at least comparable to those classified as very efficient (Table 2).

Effect of ionic strength

Ionic strength is one of the important factors influencing aqueous phase equilibrium. Generally, adsorption
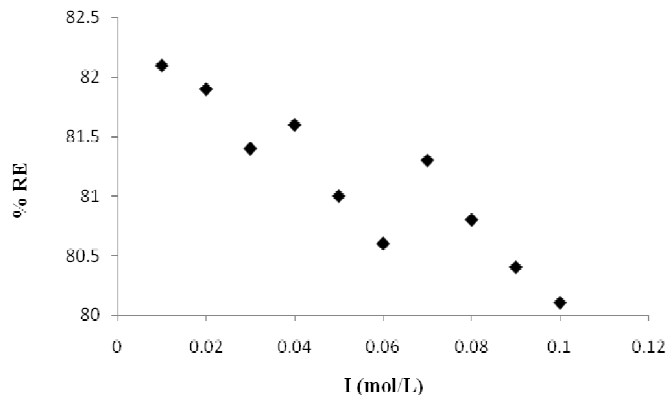
Figure 2. Effect of ionic strength for adsorption of Cr(VI) on Pot-Jo at 25°C and pH 3.

decreases with increasing ionic strength of the aqueous solution. The effect of the interfering ion KNO_3 was evaluated. The electrostatic attraction at low ionic strengths applied in this work (0.01 to 0.1 M KNO_3) appears to play a negligible role in the removal of Cr(VI) as indicated by the fact that no significant decrease in the removal of Cr(VI) ion was observed for the interval of (0.01 to 0.1 M) KNO_3 ionic concentration (Figure 2).

Adsorption kinetics

In order to investigate the adsorption mechanism of Cr(VI) onto clay's pottery, the experimental data were modeled using the first-order rate equation of Lagergren (Lagergren, 1898), the pseudo second-order rate equation (Ho and McKay, 1999), Elovich model (Güzel et al., 2008), Ritchie's equation (Viswanathan, 1979) and intraparticle (Weber and Morris, 1963) kinetic models.

In order to understand the kinetics of removal of Cr(VI) by adsorption, many models were tried. The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of the interactions were studied by determining the amount adsorbed at different agitation times for various amounts of the adsorbent at constant Cr(VI) concentration. The order of adsorbate-adsorbent interactions has been described by using various kinetic models. Traditionally, the pseudo-first order model derived by Lagergren (1898) has found wide application. On the other hand, several authors (Weber and Morris, 1963; Zacar and Engil, 2004; Zacar, 2003) have shown that second-order kinetics can also very well describe these interactions in certain specific cases.

The pseudo first-order equation

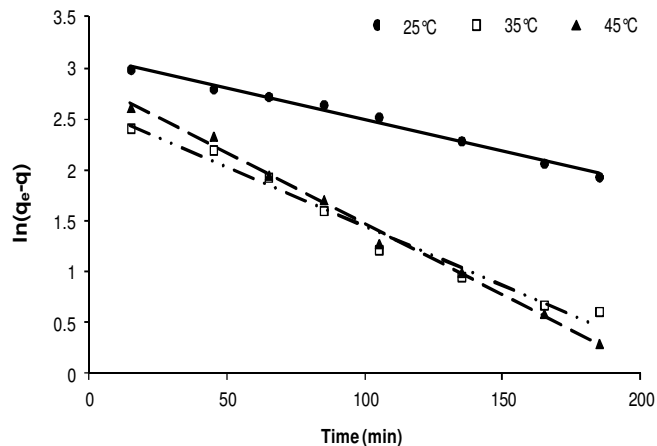When adsorption is preceded by diffusion through a boundary, the kinetics in most cases follow the pseudo-first-order rate equation of Lagergren (Equation 3).

$$\frac{dq_t}{dt} = k_{ads}(q_e - q_t) \tag{3}$$

Where q_e and q_t (mg/g) are the amounts of Cr(VI) adsorbed at equilibrium and at any time t (min), and k_{ads} (min^{-1}) is the first-order adsorption rate constant. The integrated rate law, after applying the initial condition of $q_t = 0$ at t = 0 is given by Equation 4.

$$\ln(q_e-q_t) = \ln q_e - k_{ads}.t \tag{4}$$

The linear plot of $\log(q_e\_q_t)$ versus t at three different temperatures (25, 35, and 45°C) shows the applicability of the Lagergren equation (Figure 3).

The values of the Lagergren constants, q_e and k_{ads}, and the correlation coefficients are calculated from linear pseudo first-order equation at all concentration studied and are presented in Table 3. The correlation coefficients for the pseudo first-order kinetic model obtained at all the studied concentrations were high. The R^2 values for the plots were in the range of 0.994 to 0.999 (Table 4).

Numerical values for activation energy (E_a) of adsorption process were determined using the Arrhenius equation (Equation 5) (Srivastava et al., 1995).

$$\ln k_{ads} = \ln A - \frac{E_a}{RT} \tag{5}$$

The plots of ln k_{ads} versus $1/T$ were found to be linear. Numerical values for activation energy (E_a) were determined from slopes of Arrhenius graphs related to adsorption process of Cr(VI) onto pottery materials.

The activation energy for the adsorption of Cr(VI) was found to be between 13.85 and 33.19 $kJmol^{-1}$. From the value of activation energy, it appears that the adsorption

Figure 3. Lagergren plot for adsorption of Cr (VI) on Pot-Jo at 25, 35 and 45°C

Table 3. Adsorption kinetic parameters by Lagergren equation at different temperatures and pH 3 [Cr(VI)] = 300 ppm.

Clay's type	T/°C	K_{ads} (min^{-1})	q_e (mgg^{-1})	$t_{1/2}$ (min)	E_a (kJmol^{-1})
	25	0.00602	22.287	115.14	
Pot-Jo	35	0.0116	17.55	59.75	33.19
	45	0.0139	13.577	49.87	

Table 4. Comparison of rate constants calculated based on respective pseudo-first-order, pseudo-second-order, Elovich, Ritchie and Intraparticle diffusion kinetic models.

Temperature 25°C	Pseudo First order			Pseudo-second order			Elovich model			Ritchie model			Intraparticle diffusion		
	K_{ads} (min^{-1})	q_e (mgg^{-1})	R^2	k_2 (gmg^{-1}min^{-1})	q_e (mgg^{-1})	R^2	α (mgg^{-1}min^{-1})	B (gmg^{-1})	R^2	q_∞ (mgg^{-1})	α	R	k_{id} (mgg^{-1}min$^{-1/2}$)	C	R
25	0.00602	22.29	0.999	0.00058	33.47	0.964	5.398	0.0289	0.923	25.97	0.0147	0.977	1.326	0.792	0.988
35	0.0116	13.58	0.977	0.00056	29.39	0.943	8.295	0.0113	0.955	26.18	0.0451	0.984	1.228	7.373	0.957
45	0.0139	17.55	0.994	0.00800	29.33	0.915	2.987	0.0212	0.911	27.25	0.036	0.969	0.963	10.593	0.947

of Cr(VI) on pottery is a chemical adsorption process. This is confirmed from the fact that the activation energy for chemical adsorption is usually more than 4 to 6 kJ mol^{-1} (Tewaria et al., 2005).

The half-adsorption time ($t_{1/2}$) is the time required to uptake half of the maximal amount of Cr(VI) adsorbed at equilibrium. It characterizes the adsorption rate well. In the case of a pseudo-first-order process, its value is given by the following relationship:

$$t_{1/2} = \frac{\ln 2}{k_1} \tag{6}$$

Values of $t_{1/2}$ are reported in Table 3.

The pseudo second-order equation

The pseudo second-order adsorption kinetic rate equation is expressed as (Srivastava et al., 1995):

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right) \tag{7}$$

Where: k_2 is the rate constant of pseudo second-order adsorption (g·mg^{-1}·min^{-1}).

The linear form of the equation is given by equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \tag{8}$$

If the initial adsorption rate, h (mg·g^{-1}·min^{-1}) is:

$$h = k_2 q_e^2 \tag{9}$$

Then Equations 8 and 9 become:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}(t) \tag{10}$$

The plot of (t/q_t) and t of Equation 10 should give a linear relationship (Figure 4) from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

The applicability of two models (pseudo-first-order model and pseudo-second-order) can be tested by linear fitting of ln(q_e - q) versus t, and (t/q) versus t, respectively. To quantify the applicability of each model, the correlation coefficient, R^2, was calculated from these plots. A comparison of the correlation coefficients, R^2, showed that the pseudo-first-order model fits better the experimental data ($R^2 \approx 0.999$) than the pseudo-second-order model (R^2 is in the range of 0.964 to 0.915) (Table 4). This confirms that it was not appropriate to use the pseudo-second-order kinetic model to predict the absorption kinetics of Cr(VI) onto clay's pottery for
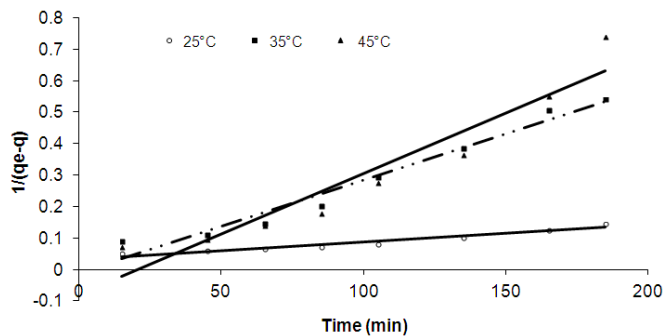
Figure 4. The pseudo second-order adsorption kinetics of Cr (VI) on Pot-Jo at 25, 35 and 45°C.
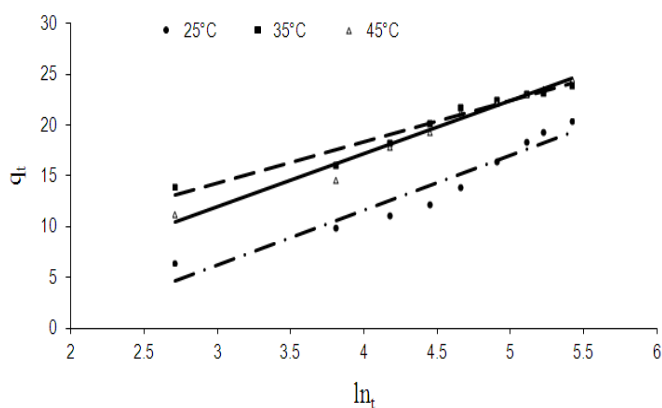

Figure 6. The Ritchie's kinetics of Cr(VI) on Pot-Jo at 25, 35 and 45°C.

Figure 5. The evaluation of Elovich adsorption kinetics for Cr (VI) adsorption on Pot-Jo at 25, 35 and 45°C.

$$q_t = \alpha \ln(\alpha\beta) + \alpha \ln t \qquad (12)$$

If Cr(VI) adsorption fits the Elovich model, a plot of q_t versus ln(t) should yield a linear relationship with a slope of α and an intercept of $\alpha\ln(\alpha\beta)$ (Figure 5).

Ritchie's equation

Ritchie's equation can be written using the following equation (Ritchie, 1977):

$$\frac{q_\infty}{q_\infty - q_t} = \alpha t + 1 \qquad (13)$$

Where q_∞ is the amount of adsorption after an infinite time, α the initial adsorption rate.

The value for q_∞ is obtained from the intercept at $(1/t) = 0$ on a plot of $(1/q)$ against $(1/t)$ (Figure 6). Ritchie found a good linear relationship between t and $q_\infty/(q_\infty - q)$, according to Richie's equation as observed by Austin et al. (1971), Bansal et al. (1971), Deitz and Turner (1971), and Samuel and Yeddanapalli (1974). In recent years, the Ritchie equation has also been applied to solution/solid adsorption systems, for example, the adsorption of cadmium ions onto bone char (Inbaraj and Sulochana, 2004), and the adsorption of Cd(II) onto acid-treated jackfruit peel (Cheung et al., 2001).

for the entire adsorption period.

The Elovich equation

Elovich equation is another expression based on the adsorptive capacity of adsorbents and was initially developed to describe the kinetics of gas chemisorption on solids. The Elovich or Roginsky-Zeldovich equation is generally expressed as follows:

$$\frac{dq_t}{dt} = \beta \exp(-\alpha q_t) \qquad (11)$$

Where q_t is the amount of Cr(VI) sorbed by pottery at a time t, α is the initial Cr(VI) sorption rate [mmol/(g min)] and β is the desorption constant (g/mmol) during any one experiment.

To simplify the Elovich equation, Chien and Clayton (Zacar and Engil, 2004) assumed $\alpha\beta t \gg 1$, and on applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Equation (11) then becomes:
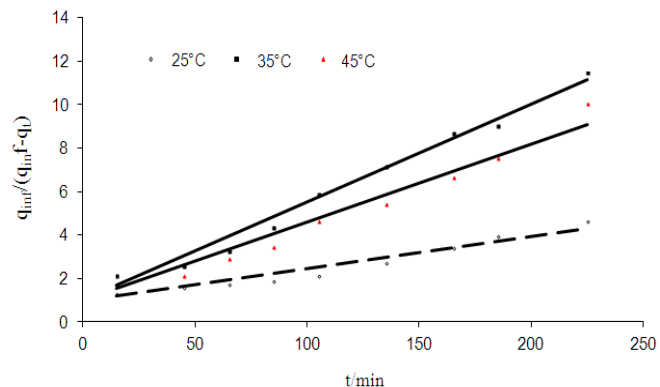
Intraparticle diffusion

The mechanism of sorption is either film diffusion controlled or particle diffusion controlled. Before adsorption takes place, several diffusion processes known to affect the adsorption process takes place. The sorbate will have to diffuse through the bulk of the
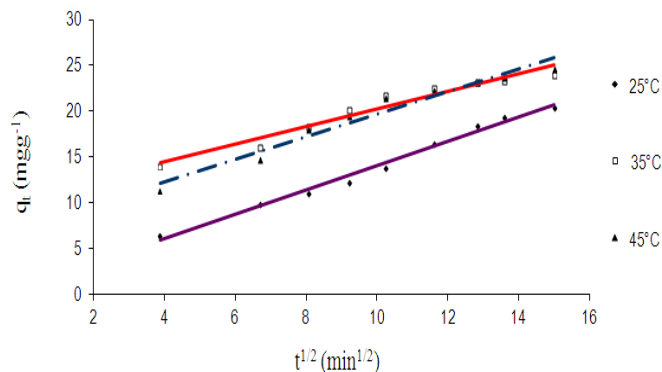
Figure 7. The intraparticle diffusion adsorption kinetics of Cr (VI) on Pot-Jo at 25, 35 and 45°C.

solution to the film surrounding the adsorbent and then into the micropores and macropores of the adsorbent.

The intraparticle diffusion model is expressed (Furusawa and Smith, 1974) as follows:

$$q_t = k_{id} (t)^{1/2} + C \qquad (14)$$

Where: q_t is the amount of Cr(VI) sorbed by pottery at a time t, C is the intercept of linear plots, k_{id} is the intraparticle diffusion rate constant ($mgg^{-1}min^{-1/2}$). The k_{id} values under different conditions were calculated from the slopes of the straight line portions of the respective plots (Figure 7). Higher values of the intraparticle rate constants (K_{id}) illustrate an enhancement in the rate of adsorption, whereas larger values illustrate a better adsorption mechanism. The values of intercept C (Table 4) provides information about the thickness of the boundary layer, the resistance to the external mass transfer increases as the intercept increases. The constant C was found to increase with increasing the temperature, corresponding to an increase of thickness in the boundary layer and to a decrease of the chance of external mass transfer to dominate. The high values of R^2 indicate the application of this model.

If intraparticle diffusion is rate-limited, then plots of adsorbate uptake q_t versus the $t^{1/2}$ would result in a linear relationship. Values of k_{id} were found to be between 1.326 and 0.963 mg/g $min^{1/2}$ with a R^2 value of 0.988 to 0.947 (Table 4). If the plot of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step (Ho, 2004). However, the linear plot in our study did not pass through the origin. This indicates some degree of boundary layer control and also that the intraparticle diffusion was not the only rate controlling step (Ho, 2004).

Conclusions

The finding of this study demonstrate the good ability of

the naturally occurring Pot-Jo materials in removing heavy metals of interest [Cr(VI) ions in this work]. Therefore, it might be considered as good adsorbent material that could work efficiently to replace the high cost activated carbon. The adsorption kinetics can be well described by the Ritchie and pseudo-first order kinetic equation with intraparticle diffusion as one of the rate determining steps. Both the Ritchie and pseudo-first order models were considered the most appropriate due to their high correlation coefficients relative to other kinetic models. The first-order adsorption rate constant, K_{ads} values were found to be decreased from 0.00602 to 0.0139 with increasing temperature from 25 to 45°C. The results indicate that there was no significant decrease in the removal of Cr(VI) ion for the interval of (0.01 to 0.1 M) KNO_3 ionic concentration. The activation energy of sorption was evaluated for the sorption of Cr(VI) on Pot-Jo. The activation energy (33.19 $kJmol^{-1}$) was determined to be same order of magnitude as the activation energy of chemisorptions.

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