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Equilibrium and Kinetics of Chromium Adsorption on Cement Kiln Dust

Mohamed Al-Meshragi, Hesham G. Ibrahim, and Mohamed M. Aboabboud

Abstract— **The adsorption of Chromium trivalent has been studied. Its equilibrium isotherm has been measured. The isotherm was determined by stirring 3 g of Cement Kiln Dust, with 250 ml of a chromium solution (from a tannery effluents wastewater) of initial concentrations 2336 and 4320 mg/L respectively. The stirring rate was used at constant rate of 1200 rpm and the temperature maintained at 25±2 ^{o}C. A contact time of around 60 min. was required to achieve equilibrium. The experimental isotherm results have been fitted using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equations. The monolayer adsorption capacity is 303 mg Cr(III) per g of Cement Kiln Dust. A comparison of kinetic models applied to the adsorption of Cr(III) ions on the adsorbent was evaluated for the first order, the pseudo first order, the pseudo second order, Elovich and intraparticle diffusion kinetic models, respectively. Kinetic parameters, rate constant, equilibrium sorption capacities and related correlation coefficients for each kinetic model were calculated and discussed. Results show that the pseudo second order kinetic model was found to correlate the experimental data well.**

Index Terms—**Isotherm and Kinetics, Intraparticle diffusion, Cement Kiln Dust, Tannery wastewater.**

I. INTRODUCTION

Chromium is an important toxic material because it does not undergo biodegradation. This pollutant is introduced into natural waters by a variety of industrial wastewaters including those from textile, leather tanning, electroplating, and metal finishing industries. When accumulated at high levels, chromium can generate serious problems and, when concentration reaches 0.1 mg/g body weight, it can ultimately become lethal [1]. Currently, the most common processes for elimination chromium are adsorption, reverse osmosis and chemical reactions that involve reduction and precipitation. Among them adsorption has been shown as a feasible alternative method for removing traces of chromium from wastewater. Although many different adsorbents were tried to remove chromium from wastewaters [1-3].

Adsorption is by far the most effective and widely used technique for the removal of toxic heavy metals from wastewater [4]. Owing to the high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low cost adsorbent materials. A variety of low cost materials like fly ash [5], wood charcoal[6], bituminous coal [7], bagasse and coconut jute [8], rice husk carbon [9], peat [10], red mud [11], Used black tea leaves [12], activated carbon from sugar industrial waste [13] and sugarcane bagasse [14] and have been tried.

As shown recently, research efforts have been directed towards the use of industrial waste as an adsorbent material in an attempt to minimize processing costs and with the protection of the environment and public health. Therefore, the present objective of this study is to evaluate the chromium trivalent removal potential and related kinetics of Cement Kiln Dust due to the fact that it is a very abundant as a byproduct from a cement manufacturing process an inexpensive material in The Great Jamahiriya and in the world. The adsorption ability of Cr(III) using CKD was investigated. The Lagnmuir, Freundlich, Temkin and Dubinin-Radushkevich equations were used to fit equilibrium isotherm. Finally, the rates and mechanism of the adsorption process were investigated. Various kinetic evaluations have been used to describe the adsorption process. Here we attempted to apply a simple first order kinetic model [15] for changing the bulk concentration, and pseudo first-order rate equation [16] and pseudo second-order [17], Elovich model [18,19] and intraparticle diffusion model [20,21] for the adsorbent phase concentration. These fundamental data will be useful for further applications in the treatment of particle waste or process effluents.

II. MATERIAL AND METHODS

The experiment was carried out to remove chromium (III) from tanning wastewater effluents by using by-pass cement kiln dust (CKD) as an adsorbent. The cement kiln dust was collected from the (Al-Mergheb Portland Cement Factory, Al-Khoms). The analysis of the sample of CKD was made by X-ray fluorescence, the composition of the constituents is shown in Table.1.

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Table.1 The chemical composition of CKD

Constituents	Composition*, (wt%)
SiO2	19.58
Al2O3	3.6
Fe2O3	2.97
CaO	54.89
MgO	2.12
K2O	2.32
SO3	0.83
Cl	0.54
Na2O	0.109
Other residues	13.041

* *Average values for four different batch samples.*

The wastewater obtained from national tanneries effluents, this wastewater obtained after the tanning operation was filtered to obtain a tanning solution, which is to be further treated for the chromium (III) removal.

A. *Reduction of hexavalent chromium to trivalent chromium*

The most of chromium is discharged into aqueous solution from tannery effluents as Cr(III) and small content of Cr(VI). Also, CKD had no effect on the removal of hexavalent chromium, while it adsorbs trivalent chromium from solutions. Thus, before the addition of CKD to tanning solution, reduction of hexavalent chromium was carried out by using sodium bisulfite as a reducing agent and sulfuric acid (0.1 N). The sodium bisulfite was added in different amounts 0.5, 1 and 1.5 g to 50 ml of the tanning solutions sample, while sulfuric acid was gradually added [22]. The addition of sulfuric acid was continued until the reduction was completed as detected by oxidation reduction potential which was used as a sensor in the device titroprocessor (Type: Metrohm 682).

B. *Experimental Procedure*

The experimental was carried out by batch process for the tanning solution obtained from tanneries effluents. The Cr(III) content in the tanning solution was determined using UV visible spectrophotometer (Unicam 8700), at a wavelength of λ =540 nm. Each sample was digested by adding 5 ml of nitric acid to 50 ml of the sample before measuring its chromium content by the spectrophotometer. Then the solution was evaporated on a hot plate to its volume becomes 15 ml. Further, 5 ml of concentrate nitric acid and 10 ml of concentrate sulfuric acid (95% wt.) were added and the solution was evaporated until dense white fumes of SO_3 appeared. The solution was cooled and diluted to about 50 ml with distilled water. Then, the solution was heated top almost boiling to dissolve gradually salts and then cooled and diluted with distilled water to 100 ml after that, the solution was ready for chromium (III) measurement.

The initial concentrations of Cr(III) in tanning solutions were treated in an experimental were 2336 and 4320 mg/l respectively. These two tanneries batches are taking from two different national tanneries effluents wastewater.

In the determination of equilibrium adsorption isotherm 3 g CKD and 250 ml of the stock solution of Cr(III) (tanning solutions prepared above) were transferred a conical flask and agitated using an agitator operation at 1200 rpm for 60 min (the time required for equilibrium to be reached between trivalent chromium adsorbed and trivalent chromium in solution) at room temperature (25 ± 2 °C) and pH value 0.5. This pH was found to be the optimum for chromium trivalent adsorption onto CKD in the previous experiments (not shown). The pH of the test solutions was adjusted using reagent grade dilute sulfuric acid. A pH meter (Model: HI 8417, HANNA Instrument) was used to measure the pH of solutions.

The amount of adsorption at equilibrium, q_e (mg/g), was computed as follows:

$$q_e = \frac{(C_o - C_e)V}{m_s} \tag{1}$$

where C_o and C_e are the initial and equilibrium solution concentrations (mg/L), respectively, V the volume of the solution (L) and m_s the weight of CKD used (g). Each experiment was performed twice at least under identical conditions. Reproducibility of the measurements was mostly within 2%.

In the experiments of batch kinetic adsorption, 250 mL of the chosen desired concentration of the stock solution of Cr(III) were placed in a conical flask together with 3 g CKD and agitation by agitator at temperature (25 ± 2 °C) and pH value 0.5. At predicted intervals of time, samples were taken, and their concentrations were determined.

III. RESULTS AND DISCUSSION

A. *Equilibrium Studies*

Figure (1) shows the equilibrium adsorption of trivalent chromium (q_e vs. C_e) using by pass cement kiln dust. The isotherm rises sharply in the initial stages for low C_e and q_e values. This indicates that there are plenty of radially accessible sites. Eventually a plateau is reached, indicating that the adsorbent is saturated at this level. The decrease in the curvature of the isotherm, tending to a monolayer, considerably increasing the C_e values for a small increase in q_e, is possibly due to less active sites being available at the end of the adsorption process and/or the difficulty of the edge molecules in penetrating the adsorbent, Cr(III) molecules partially covering the surface sites.

In order to optimize the design of a sorption system to remove trivalent chromium fro tannery effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Four isotherm equations have been tested in the present study, namely; Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The goodness-of-fit between experimental data and the model predicted values was expressed by the correlation coefficient (r^2, values close or equal 1), it's not to ascribe more meaning to it than is warranted to obtaining the constants of the models from the best fitting. Just because r^2 is close to 1 does not mean that the fit is necessarily good [23]. So, the conformity between experimental data and the model predicted values was expressed by the total mean error, is the discrepancy between the experimental data and the predicted values [24]:

$$\in \% = \frac{\sum_{i=1}^{n} \left| \left(q_{e\,(Exper.)} - q_{e(Calc.)} \right) \right|}{\sum_{i=1}^{n} q_{e(Eper.)}} \qquad (2)$$

A relatively low (∈ %) value indicate that the model successfully describes the equilibrium kinetic of Cr(III) adsorption.

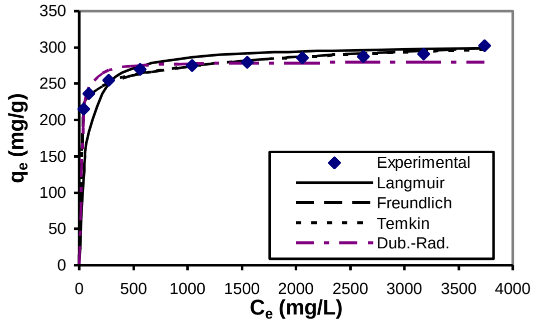

Fig.1 Equilibrium isotherms of Cr(III) on CKD. Conditions: 3 g/250 mL dose, 25 °C temperature and pH 0.5.

i) The Langmuir Isotherm

The widely used Langmuir isotherm has found successfully application in many real sorption processes [25-31] and is expressed as:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \qquad (3)$$

A linear form of this expression is:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \qquad (4)$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed Cr(III) per unit weight of adsorbent and unabsorbed Cr(III) concentration in solution at equilibrium, respectively. The constant K_L is the Langmuir equilibrium constant and the K_L/a_L gives the theoretical monolayer solution capacity, Q_o. Therefore a plot of C_e/q_e versus gives a straight line of slope a_L/K_L and intercept $1/K_L$. The values of the Langmuir constants a_L, K_L and Q_o with the correlation coefficient are listed in Table(2) for the Cr(III)-CKD system and the Langmuir isotherm is plotted in Figure (1) together with the experimental data points. The mean total error (∈ %) between this models with the experimental data was 8.870 %. We note that the monolayer saturation capacity (Q_o) is 303.149 mg/g. the value of the total mean error is higher than other three isotherms values. In all cases, the Langmuir equation represents the poorest fit of experimental data than other isotherm models (Figure.1).

ii) The Freundlich Isotherm

The well known Freundlich isotherm is often used for heterogeneous surface energy systems [1,25,27,2,33]. The Freundlich equation is given as:

$$q_e = K_F C_e^{1/n} \qquad (5)$$

A linear form of this expression is:

$$\log q_e = \log\ K_F + \frac{1}{n}\ \log\ C_e \qquad (6)$$

where K_F is he Freundlich constant and n the Freundlich exponent. K_F and n can be determined from the linear plot of log q_e versus log C_e. The values of the Freundlich constants together with the correlation coefficient are presented in Table (2) and the theoretical Freundlich equation is shown in Figure (1). Value of the mean total error (∈ %) is much lower than values of the other three isotherm models, which is reach up to 1.102519%. In all cases, the Freundlich equation represents the best fit of experimental data than other isotherm equations (Figure. 1). This trend is due to the high surface area of the adsorbent, and multilayer of adsorption on the CKD. This trend was investigated also by Schneider, et al. [1] of adsorption Cr(III) onto activated carbon, in which Freundlish isotherm gives a best fits.

iii) The Temkin Isotherm

The Temkin isotherm [25,34] have been used in the following form:

$$q_e = \frac{RT}{b} \ln (A\ C_e) \qquad (7)$$

A linear form of the Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b}\ \ln\ A\ +\ \frac{RT}{b}\ \ln\ C_e \qquad (8)$$

where; $\frac{RT}{b} = B$.

The sorption data can be analyzed according to equation (8). Therefore a plot of q_e versus ln C_e enables one to determine the constants A and b. the values of the Temkin constants A and B are listed in Table (2) and the theoretical plot of this isotherm is shown in Figure (1). The correlation coefficient is also listed in Table (2). Value of the mean total error (∈ %) is equal to 1.315%, it's lower than the Langmuir value but higher than Freundlich Value. Therefore, the Temkin equation represents a better fit of experimental data than of both Langmuir and Dubini-Radushkavich equations, but not in the case of Freundlich equation (Figure.1).

iv) The Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich isotherm and the Langmuir isotherm equations have been used for the sorption of metal ions on surfactant-modified montmorillonite and sorption of acid dyes on activated carbon [34,35] or sorption of phosphorus on calcined alunite [25]. The Dubinin-Radushkevich equation has the following form:

$$q_e = q_m \ e^{-\beta\varepsilon^2} \tag{9}$$

A linear form of Dubinin-Radushkevich isotherm is:

$$\ln q_e = \ln \ q_m - \beta\varepsilon^2 \tag{10}$$

Where q_m is the Dubinin-Radushkevich monolayer capacity (*mg/g*), β a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = \frac{RT}{M} \ln \ (1 + \frac{1}{C_e}) \tag{11}$$

where R is the gas constant (8.314 J/mol.K), T is the absolute temperature and M is the molecular weight of the adsorbed. The Constant β gives the mean free energy (E) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship [34,35]:

$$E = \frac{1}{\sqrt{2\beta}} \tag{12}$$

The Dubinin-Radushkevich constants are calculated and given in Table (2) and the theoretical Dubinin-Radushkevich isotherm is plotted in Figure (1) together with experimental data points.

The value of mean total error has been determined and the value is higher than both Freundlich and Temkin values but lower than Langmuir value. Therefore, the Dubinin-Radushkevich equation represents a better fit of experimental data than Langmuir model but is not in the both cases of Freundlich and Temkin models (Figure 1).

B. *Kinetic Studies*

Figure (2) shows that the amount of Cr(III) adsorption increases with time and it remains constant after a contact time of about 60 min. (i.e. equilibrium time). The equilibrium time is independent of initial Cr(III) concentration. The time profile of chromium uptake is a single, smooth and continuous curve leading to saturation, suggesting the possible multilayer coverage of chromium on the surface of the adsorbent.

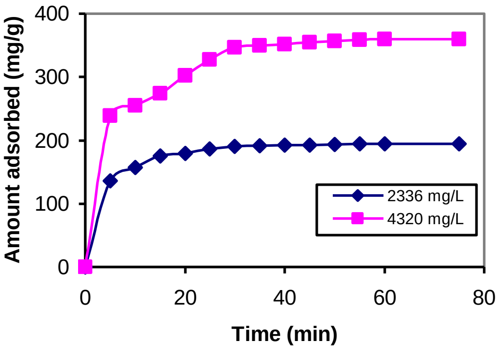

Fig.2 Adsorption kinetics of Cr(III) on CKD at different initial concentrations. Conditions 3 g/250 mL dose, 25 °C temperature and pH 0.5.

In order to examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data. Many models such as homogeneous surface diffusion model and heterogeneous diffusion model (also known as pore and diffusion model) have been extensively applied in batch reactors to describe the transport of adsorbate inside the adsorbent particles [36-38]. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (r^2, values close or equal to 1). A relatively high r^2 value indicates that the model successfully describes the kinetics of Cr(III) adsorption.

i) *Simple First Order Model*

The sorption kinetics may be described by a simple first order equation [12,15]. The change in bulk concentration of the system using the following simple first order rate Equation (13):

$$C_t = C_o \ e^{k_1 t} \tag{13}$$

Equation 13 can be rearrangement to obtain a linear form:

$$\log C_t = \frac{k_1}{2.303} t + \log C_o \tag{14}$$

Where C_t and C_o are the concentration of Chromium at time t and initially (mg/L), respectively, and k_1 is the first order rate constant, (1/min.).

The experimental results showed that the log C_t versus log t (Figure.3) for different initial concentrations of Cr(III) were deviated considerably from the theoretical data. A comparison of the results with the correlation coefficient is shown in Table.3, which indicates the failure in expressing this adsorption process by the simple first order kinetics. On the other hand, the literature review Sparks [39] has proposed that the simple kinetic models such as first- or second order rate equations are not applicable to the adsorption system with solid surfaces, which are rarely homogeneous like our CKD, because the effect of transport phenomena and chemical reactions are often experimentally inseparable. This trend was investigated also by Hossain, et al. [12] .

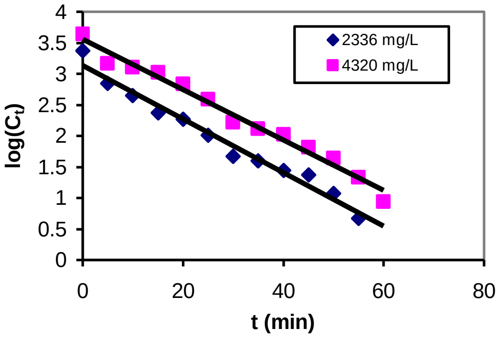

Fig.3 Plot of the simple first order adsorption kinetics of Cr(III) on CKD at different initial concentration.

Table .2 Langmuir, Freundlich, Temkin and Dubinin-Radushkevich constants

Langmuir					**Freundlich**			
K_L (L/g)	**a_L (L/mg)**	**Q_o (mg/g)**	**r^2**	**$\in$%**	**K_F (L/g)**	**n**	**r^2**	**$\in$%**
5.102	**0.01683**	**303.149**	**0.998**	**8.870**	**173.38**	**15.12**	**0.9831**	**1.102519**

Temkin				**Dubinin-Radushkevich**				
B	**A (L/g)**	**r^2**	**$\in$%**	**q_m (mg/g)**	**β (mg^2/J^2)**	**E (J/mg)**	**r^2**	**$\in$%**
16.999	**$1.0348*10^4$**	**0.9779**	**1.315**	**$1.0201*10^5$**	**0.0026**	**9.805**	**0.849**	**3.349**

ii) Pseudo Firs-order Model

The sorption kinetics may be described by a pseudo first order equation [12,25,40,41,42]. The differential equation is the following:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (15)$$

After integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Equation (15) becomes:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303}t \qquad (16)$$

Equation (16) can be rearrangement to obtain a linear form:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \qquad (17)$$

where q_e and q_t are amounts of chromium adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the equilibrium rate constant of pseudo first-order adsorption, (1/min).

Figure (4) shows a plot of linearization form of pseudo first-order model at all concentrations studied. The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t were used to determine the pseudo first-order constant k_1 and equilibrium adsorption density q_e . However, the experimental data deviated considerably from the theoretical data. A comparison of the results with the correlation coefficients is shown in Table 3. The correlation coefficients for the pseudo first order kinetic model obtained at all the studies concentrations were low. Also the theoretical q_e values found from the pseudo first-order kinetic model did not give reasonable values. This suggests that this adsorption system is not a pseudo first-order reaction.

iii)Pseudo Second-order Model

The adsorption kinetics may also be described by a pseudo second-order equation [25,37,42,43,44,45,46]. The differential equation is the following:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (18)$$

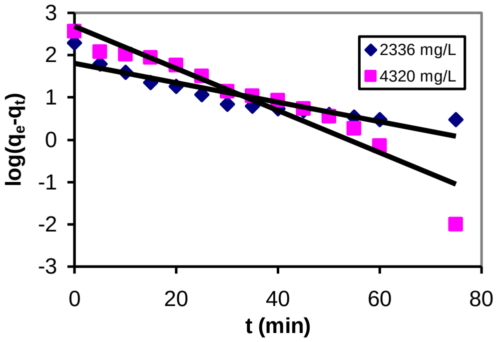

Fig.4 Plot of the pseudo first-order adsorption kinetics of Cr(III) on CKD at different initial concentration.
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Integrating Equation (18) and applying the boundary conditions, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (19)$$

Equation (19) can e rearranged to obtain a linear form:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (20)$$

where k_2 is the equilibrium rate constant of pseudo second-order adsorption (g/mg.min).

The slopes and intercepts of plots t/q_t versus t were used to calculate the pseudo second-order rate constants k_2 and q_e. The straight lines in plot of t/q_t versus t Figure (5) show good agreement of experimental data with the pseudo second-order kinetic model for different initial chromium concentrations. Table 3 lists the computed results obtained from the pseudo second-order kinetic model. The correlation coefficients for pseudo second-order kinetic model obtained were greater than 0.998 for all concentrations. The calculated q_e values also agree very well with the experimental data. These indicate that the adsorption system studied belongs to the second order kinetic model. The similar phenomena are also observed in adsorption of dye RR189 on cross-linked chitosan beads [43], in adsorption of dye BB69 and DR227 on activated clay [44] and in adsorption of AB9 on mixed sorbents (activated clay and activated carbon) [42] and in adsorption of Chromium hexavalent on used black tea leaves [12].

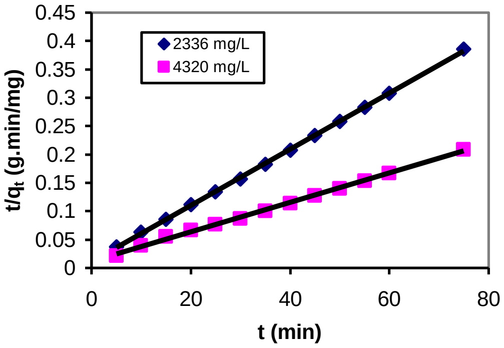

Fig.5 Plot of the pseudo second-order adsorption kinetics of Cr(III) on CKD at different initial concentration.

iv) Elovich Model

The Elovich model equation is generally expressed as [18,19]:

$$\frac{dq_t}{dt} = \alpha \ exp(-\beta q_t) \qquad (21)$$

where α is the initial adsorption rate (mg/g.min) and β is the adsorption constant (g/mg) during any experiment.

To simplify the Elovich equation, Chien and Clayton [18] assumed $\alpha\beta >> t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ equation (21) become:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (22)$$

If Cr(III) adsorption fits the Elovih model, a plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$.

Figure (6) shows a plot of linearization form of Elovich model at all concentrations studied. The slopes and intercepts of plots of q_t versus $\ln(t)$ were used to determine the constant β and the initial adsorption rate α. However, the experimental data deviated considerably from the theoretical data. A comparison of the results with the correlation coefficients is shown in Table 3. The correlation coefficients for the Elovich kinetic model obtained at all the studies concentrations were low. This suggests that this adsorption system is not an acceptable for this system.

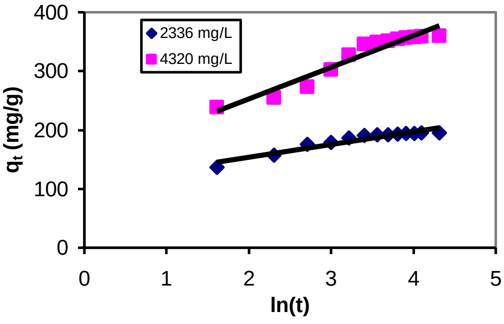

Fig.6 Plot of the Elovich model for adsorption kinetics of Cr(III) on CKD at different initial concentration.

v) The Intra-particle Diffusion Model

The intra-particle diffusion model is expressed as [20,21,47]:

$$R = k_{id}\,(t)^a \qquad (23)$$

A linearization form of the equation is followed by:

$$\log R = \log k_{id} + a\log(t) \qquad (24)$$

where R is the percent of Cr(III) adsorbed, k_{id} is a rate factor (percent Cr(III) adsorbed per minute) and a depicts the adsorption mechanism.

Such plots may present a multilinearity [37,40], indicating that two or more steps take place. The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution.

Figure (7) show a plot of the linearized form of the intraparticle diffusion model at all concentrations studied. As shown in Figure (7), the external surface adsorption (stage 1) is completed before 5 min., and then the stage of intraparticle diffusion control (stage 2) is attained and continuous from 5 min to 30 min. Finally, final equilibrium adsorption (stage 3) starts after 30 min. the chromium (III) is slowly transported via intraparticle diffusion into the particles and is finally retained in the micropores. In general, the slope of the line in stage 2 is called as intraparticle diffusion rate constant, k_{id}. The rate parameters k_{id}, together with the correlation coefficients are also listed in Table 3.

A comparison of calculated and measurement results for 4320 mg/L and 2336 mg/L concentrations are shown in Figures (8) and (9) respectively. As can be seen from these figures, the pseudo second-order kinetic model provides the best correlation for all of the adsorption process, whereas the Elovich model fits the experimental data well for an initial period of the adsorption process only. Hence it was concluded that the pseudo second-order kinetic model was found to be rate limiting, followed by the Elovich kinetic model. Similar phenomena are also observed in adsorption of chrome dye (OCRME) on mixed adsorbents-fly ash and coal [48], in adsorption of phenols on fly ash [49], in adsorption of lead (II) on cypress leaves [50], in adsorption of phosphorus on calcined alunite [25], and in adsorption of chromium (VI) on the activated carbon prepared from agricultural wastes [47].

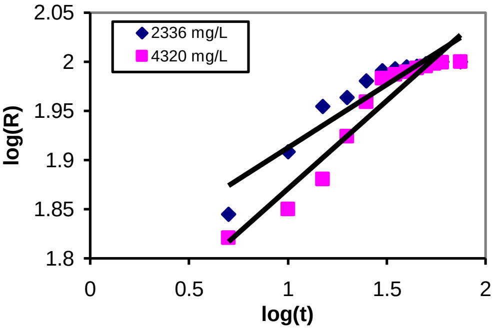

Fig.7 Plot of the intra-particle diffusion model for adsorption kinetics of Cr(III) on CKD at different initial concentration

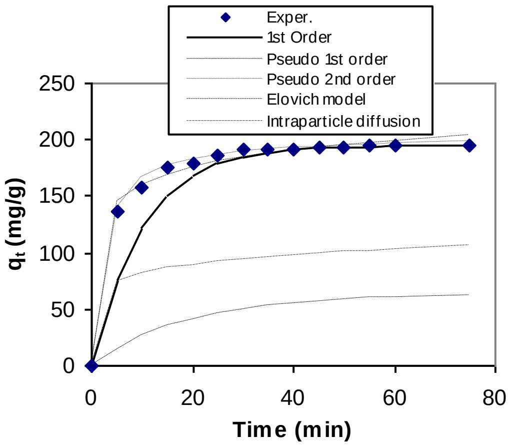

Fig.8 Comparison between the measured and modeled time profiles for adsorption of Cr(III) (for initial concentration 2336 mg/L).

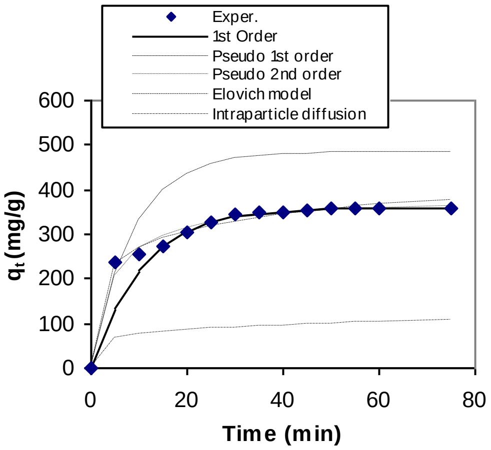

Fig.9 Comparison between the measured and modeled time profiles for adsorption of Cr(III) (for initial concentration 4320 mg/L).

Table.3 Comparison of the simple first order, pseudo first- and second-order adsorption, Elovich model and intraparticle diffusion rate constants, and calculated experimental q_e values for different initial Cr(III) concentrations

		Simple 1st order		**Pseudo 1st order**			**Pseudo 2nd order**		
C_o	**$q_{e\,exp.}$**	**k_1**	**r^2**	**k_1**	**$q_{e\,cal.}$**	**r^2**	**k_2**	**$q_{e\,cal.}$**	**r^2**
(mg/L)	**(mg/g)**	**(1/min)**		**(1/min)**	**(mg/g)**		**(g/mg.min)**	**(mg/g)**	
2336	**194.667**	**0.09925**	**0.976**	**0.05297**	**63.1865**	**0.848**	**2.12×10^{-3}**	**204.08**	**0.999**
4320	**360.01**	**0.0935**	**0.982**	**0.11492**	**483.931**	**0.914**	**5.87×10^{-3}**	**384.615**	**0.998**

Elovich Model			**Intra-particle diffusion**		
β	**α**	**r^2**	**k_{id}**	**a**	**r^2**
(g/mg)	**(mg/g.min)**				
0.0464	**3680.849**	**0.904**	**60.956**	**0.1279**	**0.884**
0.01858	**794.596**	**0.931**	**49.2045**	**0.1789**	**0.929**

IV. CONCLUSION

Equilibrium and kinetic studies were made for the adsorption of chromium trivalent from aqueous solutions onto cement kiln dust (CKD) in the concentration range 2336 – 4320 mg/L at pH 0.5 and 298 K. the equilibrium data have been analyzed using Lanmguir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Freundlich isotherm was demonstrated to provide the best correlation and the lowest total error for sorption of Cr(III) onto CKD.

The suitability of the fist and pseudo first- and second- order equations, Elovich kinetic model and intraparticle diffusion kinetic model for the sorption of Cr(III) onto CKD is also discussed. The pseudo second-order kinetic model agrees very well with the dynamical behavior for the adsorption of Cr(III) onto CKD for different initial Cr(III) concentrations over the whole range studied.

It may be concluded hat CKD may be used as low-cost, natural and abundant source for the removal of Cr(III) and it may be an alternative to more costly materials. It may also be effective in removing as well other harmful or undesirable species such as dyes, present in the waste effluents.

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