

ADSORPTION AND KINETIC BEHAVIOR OF FLY ASH USED FOR THE REMOVAL OF LEAD FROM AN AQUEOUS SOLUTION

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ABSTRACT

The removal of lead through adsorption by fly ash was investigated. Batch mode adsorption experiments using Atomic Absorption Spectroscopy (AAS) technique were performed. The results obtained were described by the Langmuir, Freundlich and Brunauer-Emmett-Teller (BET) adsorption isotherms using the least square fit method. The best fit was assessed by the linear coefficient of correlation (R^2) and the non-linear Chi-square test ($\sum \chi^2$). The experimental and theoretical values of the fly ash equilibrium capacity as an adsorbent were compared. It was found that the BET adsorption isotherm provides the best fit in view of the linear coefficient of correlation, while the Freundlich adsorption isotherm was found more appropriate in case of non linear Chi square test ($\sum \chi^2$) application. It was also found that the pseudo second order kinetic model provides the best description of fly ash adsorption behavior.

Keywords: fly ash, lead, water pollution, adsorption isotherms, kinetics study.

INTRODUCTION

The general body of literature on lead toxicity indicates that, depending on the dose, lead exposure can impact almost all the body's organs or systems. The most common systems affected are the nervous and reproductive systems, with brain and kidneys being the most affected organs [1 - 6].

Various methods such as chemical precipitation, flotation, ion exchange, adsorption, biological treatment, etc. are often used to remove heavy metals from waste water [7 - 10]. Adsorption is recognized as more useful and economical among the removing techniques applied. The application of low cost and easily available materials in wastewater treatment has recently attracted great inter-

est. Fly ash, a by-product of coal burning power plants, has been used as a potential adsorbent for removal of lead and other heavy metals for water pollution control or wastewater treatment [11 - 13].

A lot of investigations are reported in the literature on the utilization of fly ash for adsorption of individual pollutants in an aqueous solution. The results are encouraging for removal of heavy metals from industrial wastewater [14 - 18].

Therefore, the present study was undertaken to evaluate the effectiveness of fly ash for the removal of lead through adsorption. Laboratory batch kinetic and adsorption isotherm studies were conducted to determine the fly ash adsorption capacity.

With this point of view, the present study was under-

taken to evaluate the effectiveness of exhausted thermal power plant coal fly ash in the removal of lead ions from an aqueous solution. The effect of various experimental conditions such as the adsorbate amount and the contact time was studied at room temperature. To optimize the design of lead ions adsorption system, the results obtained from batch adsorption experiments were fitted to Langmuir, Freundlich and BET adsorption isotherms using least square fit method. The data obtained from the batch studies was used to study the kinetic behavior of fly ash.

EXPERIMENTAL

Materials and methods

Stock solution preparation

The stock solution of lead ions (500 mg l^{-1}) was prepared by dissolving 1.1598 g of $\text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 2 liters freshly distilled water. This stock solution of 500 mg l^{-1} was further diluted by adding distilled water to prepare solutions of different lead ions concentrations.

Fly ash

The fly ash used in the present study was collected from a coal fired thermal power plant located in central India. It was stored in an air tight container, and used for lead ions adsorption without any pretreatment. Variations in the fly ash properties may affect its ability to adsorb heavy metals. Therefore, its chemical composition was determined using standard methods. The fly ash collected for the study was sieved to study the size distribution. The latter was done by passing it over the standard size molecular sieves as per Indian Standard [19].

Scanning Electron Microscope (SEM) analysis was carried out to study the fly ash particles surface structure and morphology. Information about the surface area of the adsorbent used is an important requirement for modeling and simulation studies for any adsorption separation process. Therefore, the surface area of the fly ash used in the present study was determined by the BET method using liquid nitrogen gas. In this method, the amount of liquid nitrogen gas adsorbed can be measured by a volumetric or continuous flow procedure [20]. The BET equation can be written in a linear form as:

$$\left[\frac{1}{W \left(\frac{P}{P_0} \right) - 1} \right] = \frac{(C-1) \left(\frac{P}{P_0} \right)}{(W_m C) \left(\frac{P}{P_0} \right)} + \frac{1}{(W_m C)} \quad (1)$$

where P is the partial vapor pressure of the adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen), in Pa, P_0 is the saturated pressure of adsorbate gas, in Pa, W is the volume of the gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure ($1.013 \times 10^5 \text{ Pa}$)], in mL, W_m is the volume of the gas adsorbed at STP to produce an apparent monolayer on the sample surface, in mL, while C is a dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample. Thus, a linear plot can be obtained by plotting $1/[W(P/P_0)-1]$ versus P/P_0 . The values of slope and the intercept of the linear plot are used to calculate W_m and C . This plot should yield a straight line usually in the approximate relative pressure range 0.05 to 0.3.

The total surface area (S_t) is defined by:

$$S_t = \frac{W_m N A_{CS}}{M} \quad (2)$$

where N is the Avogadro's number (6.023×10^{23}), M is the molecular mass of the adsorbate, while A_{CS} is the adsorbate cross sectional area (16.2 \AA^2 for Nitrogen). The specific surface area (S in $\text{m}^2 \text{g}^{-1}$) is then determined by the total surface area divided by the sample mass (w):

$$S = S_t / w \quad (3)$$

Equipment

Scanning electron microscope Philips SEM 515 was used to study the fly ash particles surface structure. Surface area analyzer Micromeritics ASAP 2020 V3.04 H was used to determine the fly ash surface area. Atomic absorption spectrophotometer GBC 932 AA was used to determine the concentration of lead ions present in a sample.

Adsorption isotherm studies

The results obtained from the batch adsorption experiments carried out in this study were fitted to the Langmuir, Freundlich and BET adsorption isotherms using the least square fit method.

The metal ions amount adsorbed by fly ash in mg/g was calculated using the following equation [21]:

$$q_e = \frac{(C_0 - C_e) \cdot V}{w} \quad (4)$$

where C_0 and C_e are the initial and the equilibrium concentrations, correspondingly, expressed in mg L^{-1} , V is the volume of the aqueous solution in L, while w is the mass of the adsorbent added to the solution in g.

The standard Langmuir equation [22] can be repre-

sented in its linear form as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a \cdot q_m} \quad (5)$$

where C_e is the equilibrium concentration of lead ions (mg l^{-1}), q_e is the solid phase concentration of lead ions (mg g^{-1}), while q_m (mg g^{-1}), and K_a (l mg^{-1}) are empirical constants, whose values can be estimated from the slope and the intercept of the linear plot of C_e/q_e vs. C_e .

The Freundlich equation [23] can be presented in its linear form as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

where K_f is the Freundlich characteristic constant [$(\text{mg g}^{-1})(\text{L g}^{-1})^{1/n}$], while $1/n$ is the heterogeneity factor of sorption.

The BET isotherm [24] is used in the present study in its linear form:

$$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{q_s C_{\text{BET}}} + \frac{(C_{\text{BET}} - 1)}{q_s C_{\text{BET}}} \left(\frac{C_e}{C_s} \right) \quad (7)$$

where C_e is the equilibrium concentration (mg L^{-1}), C_s is the adsorbate monolayer saturation concentration (mg L^{-1}), C_{BET} is the BET adsorption isotherm relating to the energy of surface interaction (L mg^{-1})

Chi-square test

Chi-square is a statistical test commonly used to compare observed data with data expected to be obtained on the ground of a specific hypothesis [25]. The Chi-square test statistics is basically the sum of the squares of the differences between the experimental data and the data obtained by modeling, with each squared difference divided by the corresponding data calculated using the models [26]. In this study, the Chi-square test was performed for all adsorption isotherms considered using the mathematical expression:

$$\chi^2 = \sum \frac{(q_{e,\text{calc}} - q_e)^2}{q_{e,\text{calc}}} \quad (8)$$

where $q_{e,\text{calc}}$ is the equilibrium (theoretical) capacity obtained from the adsorption model (mg g^{-1}) and q_e is the equilibrium capacity (mg g^{-1}) from the experimental data.

Kinetics studies

A number of experimental parameters are usually considered in the study of adsorption process kinetics.

Three well-known kinetic models, pseudo-first-order, pseudo-second-order and intra-particle diffusion model, were employed to describe the adsorption process. The pseudo-first order, proposed by Lagergren [27] for adsorption analysis, can be linearized in the form:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

where q_e and q_t are the sorption capacities (mg/g) of lead ions at equilibrium and at a time t , respectively, while k_1 is the corresponding pseudo first-order rate constant (l/min).

The pseudo second-order equation [28] can be written in its linear form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where k_2 is the rate constant for pseudo second-order sorption ($\text{g (mg}^{-1} \text{ min}^{-1})$).

The equation of the intra-particle diffusion model given by Weber Morris [29] can be used in the form:

$$q_t = k_{\text{id}} \cdot t^{1/2} \quad (11)$$

where k_{id} is the corresponding rate constant.

EXPERIMENTAL

A set of experiments was carried out using an aqueous solution of lead ions (of a concentration of 20 mg L^{-1} , 40 mg L^{-1} , 60 mg L^{-1} , 80 mg L^{-1} and 100 mg L^{-1}) aiming to investigate the effectiveness of the various adsorption isotherm models. The adsorbent quantity and the contact time were varied to determine the equilibrium time for lead ions removal. The fly ash amount was maintained at 1 g per 100 ml of a solution in each of the batch experiments carried out. Samples in different conical flasks were kept under constant stirring for three hours. It was experimentally verified that this was the time required for adsorption equilibrium establishment. The adsorbent was separated from the solution by centrifuging at a speed of 3000 rpm for 5 min. The residual solution was used to determine the quantity of lead adsorbed using AAS.

RESULTS AND DISCUSSION

Fly ash characterization

The chemical and mineral composition of fly ash varies widely, depending upon the minerals present in the coal and the burning condition. The chemical analysis of the fly ash used refers to: SiO_2 (62.6 %), Al_2O_3 (24.41 %),

Fe_2O_3 (4.04 %), TiO_2 (0.69 %), CaO (0.35 %), MgO (0.54 %), Na_2O (0.27 %), K_2O (0.21 %), SO_3 (0.84 %), P_2O_5 (0.037 %), MnO (0.28 %) and loss on ignition (1.27 %). According to chemical composition of the fly ash used the content of SiO_2 and Al_2O_3 corresponds to about 85 % of the total content, while Fe_2O_3 is the third largest constituent amounting to about 4 % of the total mass. All other constituents contribute to less than 3.5 %. It is also found that the fly ash contains less than 5 % of SO_3 . Furthermore, the loss on ignition is less than 6 %. Therefore, this fly ash can be classified as class 'F' according to ASTM C-618 [30].

The fly ash particle size distribution shows that the sample contains less than 8.88 % particles of a size above 75 μm , whereas approximately 91.12 % particles are of a size smaller than 75 μm .

Fig. 1 presents the SEM micrograph of a coal fly ash sample at 20000x magnification. It is evident that the fly ash particles are generally spherical in shape. However, some irregular shaped particles are also present.

To determine the surface area of the fly ash a graph of $1/[W(P/P_0) - 1]$ vs. P/P_0 is plotted. It is shown in Fig. 2. The BET surface area of the fly ash used, as determined from the Fig. 2, is found to be $10.5777 \pm 0.1429 \text{ m}^2 \text{ g}^{-1}$.

Effect of fly ash dose and contact time on its removal efficiency in respect to lead ions

To study the effect of fly ash dose and contact time on its removal efficiency in respect to lead ions from the aqueous solution, 100 ml of aqueous solutions of lead

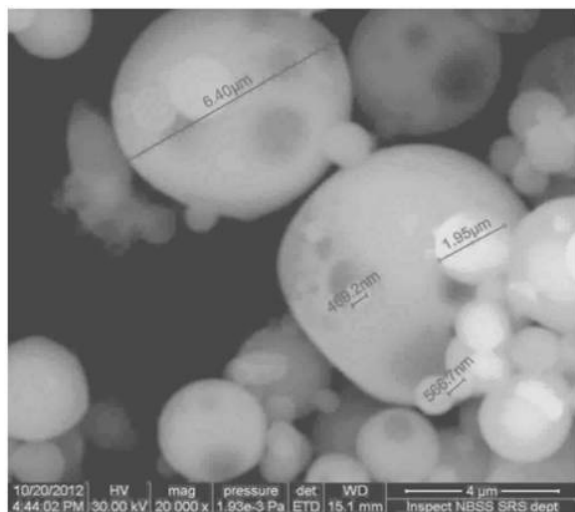


Fig. 1. A SEM image of a fly ash sample (magnification: 20000x).

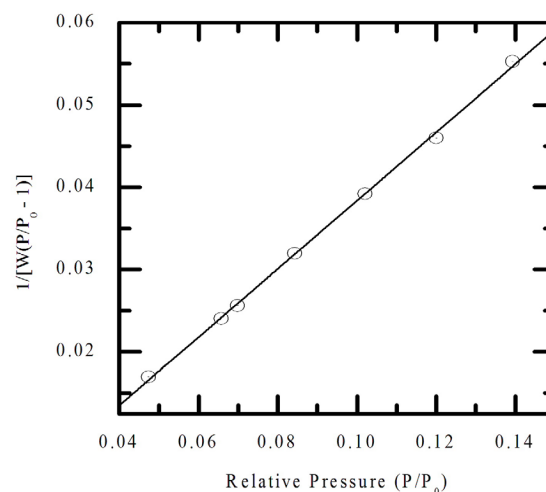


Fig. 2. A plot of $1/[W(P/P_0 - 1)]$ vs. (P/P_0) .

ions (20 mg L^{-1} , initial pH of 5.82) were taken in a conical flask and 1 g of fly ash was added. The mixture was stirred from 10 min to 180 min using a magnetic stirrer at 150 rpm. The solution was then centrifuged for 5 min at a speed of 3000 rpm. The resultant solution was used to determine the lead ions concentration in the sample. A graph between the percentages of the lead ions removed vs. the contact time is plotted. It is illustrated in Fig. 3.

It is seen from the Fig. 3 that the removal efficiency in respect to the lead ions increases with the contact time increase. Furthermore, it is very high at the beginning of the adsorption. Then it continues to increase but at a slower rate. The removal efficiency reaches 53.2 % in just 10 min and increases to about 95.95 % when the contact time is increased to 3 h. After that, the contact time increase does not affect the removal efficiency. Therefore, the equilibrium time of contact required for lead ions removal from the solution is found in this study equal to 3 h, while the value of q_e is estimated to 1.9 mg g^{-1} .

Adsorption isotherms study and Chi square test

To optimize the design of an adsorption system for lead ions sorption from an aqueous solution, it is important to establish the most appropriate equilibrium curves. The values of C_0 and C_e and respective value of q_e as obtained from batch adsorption studies are listed in Table 1. The various parameters required to plot the graphs of the Langmuir, Freundlich and BET adsorption isotherm are calculated on the ground of the experimental data.

The results obtained in the batch adsorption experiments are fitted to the Langmuir adsorption isotherm by plotting C_e/q_e vs. C_e using the least square fit method as

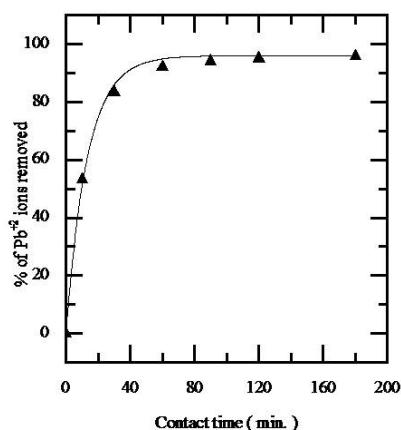


Fig. 3. Effect of the contact time on the removal efficiency of fly ash in respect to lead ions.

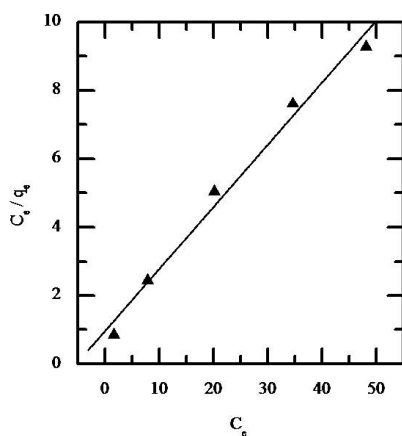


Fig. 4. Langmuir isotherm referring to lead ions adsorption on fly ash.

shown in Fig. 4. The coefficient of correlation (R^2) is found equal to 0.986. The values of q_m is estimated to be equal to 5.52 mg g⁻¹, the value of K_a is found equal to 0.186 l mg⁻¹.

The adsorption data are also fitted to the Freundlich adsorption isotherm by plotting $\ln q_e$ versus $\ln C_e$ using the least square fit method. The isotherm graph is shown in Fig. 5. The coefficient of correlation (R^2) is found equal to 0.992. The value of n , i.e. the reciprocal of the heterogeneity factor of adsorption is estimated equal to 3.401, whereas that of K_p i.e. the Freundlich characteristic constant equals 1.653.

The BET adsorption isotherm model is also investigated by plotting $C_e / q_e (C_s - C_e)$ versus C_e / C_s using the least square fit method. The results obtained are visualized in Fig. 6. The coefficient of correlation (R^2) is found to be 0.996. The value of q_s (mg g⁻¹) equals 4.545, whereas those of C_s (mg l⁻¹) and C_{BET} (l mg⁻¹) equal 312

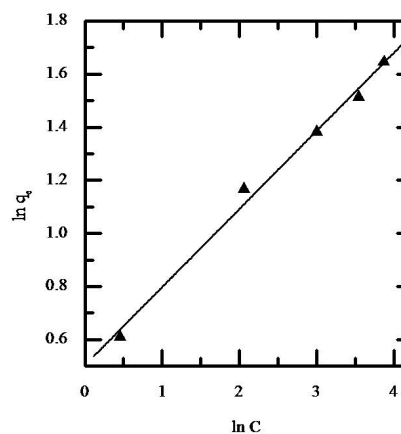


Fig. 5. Freundlich isotherm referring to lead ions adsorption on fly ash.

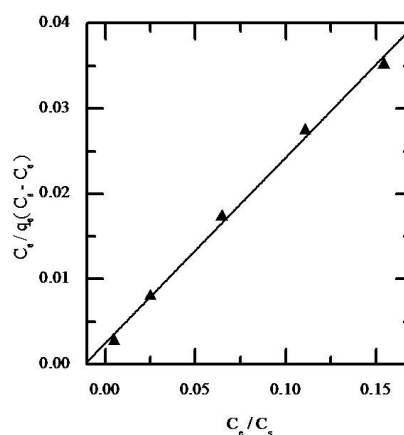


Fig. 6. BET isotherm referring to lead ions adsorption on fly ash.

and 110, respectively.

The experimental values of q_e and those calculated (theoretical value) on the ground of the best fit linear equations are compared in Table 1.

The various adsorption isotherm constants and values of $\sum \chi^2$ referring to the Chi square test obtained for the different adsorption isotherms are summarized in Table 2.

The adsorption data analysis is important to optimize the design of the adsorption system for adsorptive removal of lead ions from an aqueous solution. The best fit isotherm must have the minimum value of Chi square ($\sum \chi^2$) and the maximum value of the coefficient of correlation (R^2). It is evident from Table 2 that the value of $\sum \chi^2$ is minimal for the Freundlich adsorption isotherm and maximal for the Langmuir adsorption isotherm. It is also seen from the Table 2 that the value of the coefficient of correlation (R^2) is maximal for the

Table 1. Juxtaposition of experimental and theoretical (calculated) values of q_e .

Sr. No.	C_0 (mg l ⁻¹)	C_e (mg l ⁻¹)	Experimental value of q_e (mg g ⁻¹)	q_e (mg g ⁻¹)calculated on the ground of the adsorption isotherm used		
				Langmuir	Freundlich	BET
1	20	1.58	1.842	1.257982	1.89171	1.6398
2	40	7.84	3.216	3.281653	3.02956	3.4469
3	60	20.14	3.986	4.363709	3.99801	4.2935
4	80	34.58	4.542	4.783524	4.68667	4.7645
5	100	48.12	5.188	4.971218	5.16480	5.1191

Table 2. Langmuir, Freundlich and BET adsorption isotherm constants referring to lead ions.

Langmuir Adsorption Isotherm Constants				
q_m (mg g ⁻¹)	k_a (l mg ⁻¹)	R^2	$\sum \chi^2$	
5.524861878	0.186598	0.986	0.32678528	
Freundlich Adsorption Isotherm Constants				
n	K_f (mg g ⁻¹)	R^2	$\sum \chi^2$	
3.401361	1.653674861	0.992	0.017386628	
BET Adsorption Isotherm Constants				
q_s	C_s (mg l ⁻¹)	C_{BET} (l mg ⁻¹)	R^2	$\sum \chi^2$
4.54545	312	110	0.996	0.0737474

Table 3. Values of various parameters referring to the kinetics of lead ions adsorption on fly ash.

Sr. No.	t (min)	$t^{1/2}$	q_t (mg g ⁻¹)	$\ln (q_e - q_t)$	t/q_t
1	10	3.162278	1.064	-0.15665	9.398496
2	30	5.477226	1.669	-1.38629	17.97484
3	60	7.745967	1.844	-2.59027	32.53796
4	90	9.486833	1.884	-3.35241	47.7707
5	120	10.95445	1.901	-4.01738	63.12467

Table 4. Values of constants referring to different models describing the kinetics of lead ions adsorption on fly ash.

Pseudo first order kinetic model		
k_1 (min ⁻¹)	q_e (mg g ⁻¹)	R^2
0.034	0.834	0.960
Pseudo second order kinetic model		
k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
0.065	2.04	0.999
Intra-particle Diffusion model		
K_{id} (mg g ⁻¹ min ^{-1/2})		R^2
0.10		0.789

BET adsorption isotherm, while it is minimal for the Langmuir adsorption isotherm.

Adsorption kinetics study

The values of the current adsorption capacity of the fly ash sample in respect to lead ions at time t, q_t , are esti-

mated in the course of the batch experiments carried out. They are listed in Table 3 and further used to determine the various kinetic parameters considered. The pseudo first-order kinetic model is been verified by plotting $\ln (q_e - q_t)$ vs. t. It is presented in Fig. 7. The value of the correlation coefficient (R^2) is found to 0.96. The values

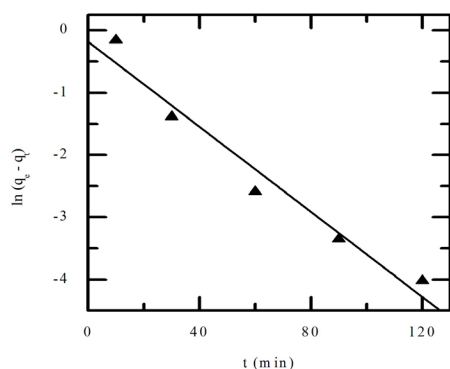


Fig. 7. Pseudo-first order model applied to the kinetics of lead ions adsorption on fly ash.

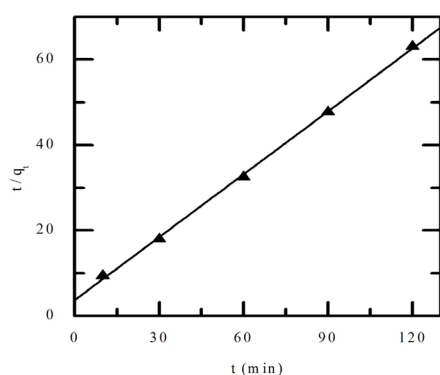


Fig. 8. Pseudo-second order model applied to the kinetics of lead ions adsorption on fly ash.

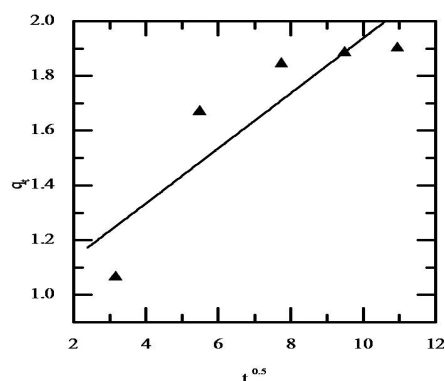


Fig. 9. Intra-particle diffusion model applied to the kinetics of lead ions adsorption on fly ash.

of t/q_t vs. t are plotted in correspondence with the pseudo second-order kinetic model examined. The visualization is presented in Fig. 8. The validation of the intra particle diffusion model is verified by plotting $t^{1/2}$ vs. q_t as shown in Fig. 9. The values of the coefficient of correlation (R^2) and other parameters concerning the different kinetic models considered are summarized in Table 4. The value of R^2 is expected to have a maximal value in case of a best fit.

It is seen from the Table 4 that the first order rate ex-

pression and the intra-particle diffusion model can not fit well to the experiment data. In contrast, the pseudo second-order kinetics shows a much better correlation coefficients ($R^2 = 0.999$), suggesting that this model is applicable to the adsorption kinetics description. The experimental values are fitted to the corresponding equations by the least square fit method and the values of q_e , i.e. the sorption capacity of fly ash in respect to lead ions at equilibrium are calculated. The value of 2.04 thus estimated is very close the experimental one, which equals 1.90.

CONCLUSIONS

The study reveals that coal fly ash used in the present work can be used effectively for the adsorption of lead ions from an aqueous solution. The fly ash used can be classified as class F. The adsorption studies carried out show that the BET isotherm model fits well in view of the values of the linear dependences correlation coefficient R^2 obtained. However, the Freundlich adsorption isotherm is found the most suitable based on the non linear Chi square test. It can also be concluded that the Langmuir adsorption isotherm is the least preferred model studied based on the value of the linear dependences regression coefficient and that of the Chi square $\sum \chi^2$. The study of the kinetics of lead ions adsorption on fly ash shows that the best fit of the value of the adsorbent capacity is obtained in case the kinetics is described by a pseudo-second model – the theoretical value is 2.04 compared to the experimental one of 1.90.

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