

## ADSORPTION OF LEAD (II) IONS ONTO DIATOMITE FROM AQUEOUS SOLUTIONS: MECHANISM, ISOTHERM AND KINETIC STUDIES

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### ABSTRACT

This study presents an evaluation of diatomite as a low cost adsorbent for Pb (II) removal from aqueous solutions under various conditions. The results demonstrate that adsorption of Pb (II) is strongly dependent on the pH of the solution. The effect of pH on adsorption of Pb (II) on diatomite was studied by varying pH from 2 to 12 at 20 °C. In the pH range of 2.0-4.0, the percentage of Pb (II) adsorbed increases slightly as the pH increases. At pH>4, the percentage of Pb (II) adsorbed decreases with increasing pH because hydrolysis and precipitation begin to play an important role in the sorption of Pb (II). At pH 4, the maximum adsorption capacity of diatomite was found to be 26 mg/g. The adsorption isotherms of Pb (II) on diatomite can be described well by the Freundlich model. The regression equation coefficients were calculated and the data fitted to a second-order kinetic equation for removal of Pb (II) ions. The high adsorption capacity of diatomite makes it a suitable low-cost material for the removal of Pb (II) from aqueous solutions.

**Keywords:** Adsorption, lead, low-cost adsorbent, isotherm, kinetic

### 1. Introduction

One of the most important environmental issues to be solved today is the presence of heavy metals from industrial wastewaters. Due to their toxicity and nonbiodegradable nature, heavy metals cause environmental and public health problems [1, 2]. Various techniques have been developed to remove heavy metals from aqueous solutions. These techniques include chemical precipitation, reverse osmosis, ion exchange, and adsorption [3-8]. Among them, adsorption is considered to be a particularly low-cost and effective process for the removal of heavy metals from aqueous solutions [9-11].

The most commonly used adsorbent is activated carbon and it generally has high metal adsorption capacity. Although activated carbon is effective in the removal of metal ions from wastewater, it is expensive and requires chelating agents to enhance its performance, thus increasing treatment cost [12]. For the past two decades, researchers have focused on using low-cost, efficient sorbents for heavy metal adsorption. Furthermore, the sorption behavior of several natural materials and waste products has also been investigated [13-15]. These include clay minerals [16, 17], agricultural by-products [18, 19], some aquatic plants [20, 21], and microorganisms [22, 23]. Most of these studies have shown that natural products can serve as good sorbents for heavy metals.

Diatomite is a siliceous sedimentary rock composed of an amorphous form of silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) containing a small amount of microcrystalline material. It has a unique combination of physical and chemical properties such as high porosity, high permeability, small particle size, large surface area, and low thermal conductivity. In addition, it is available in Turkey and in various locations around the world. Therefore, diatomite has been successfully used as adsorbent for the removal of heavy metals [24, 25].

The aim of this study is to investigate the adsorption properties of diatomite. The equilibrium adsorption data was applied to the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models. Adsorption experiments were performed in batch systems, using Pb (II) initial concentration, pH of solution, and contact time as variables.

## 2. Materials and methods

Diatomite samples were obtained from Çankırı-Çerkeş Basin of Turkey. The physicochemical properties of diatomite as reported by Aruntaş et al. (1998) are given in Table 1 [26]. For the experimental studies, the sample was washed with distilled water in order to remove any non-adhesive impurities and small particles, and then, dried at 70°C for 24 h to remove moisture. The dried samples were sieved and a range of 0.5-1.0 mm of particle size of diatomite was used in the remainder of the experiments.

**Table 1.** The physicochemical properties of diatomite

Parameters	Value
Moisture content, %	80
Water retention, %	182
Specific gravity, g mL <sup>-1</sup>	1.9
pH	7.3

All chemicals used in the experiments were purchased in analytical grade. The Pb (II) stock solution was prepared by dissolving  $\text{Pb}(\text{NO}_3)_2$  in distilled water.

The adsorption of Pb (II) onto diatomite was investigated by using batch systems. The adsorption capacity for diatomite was determined by adding 0.1-2.0 g of adsorbent to 100 mL of solutions of varying concentrations (1, 10, and 100 mg L<sup>-1</sup>). The system was adjusted to the desired pH varying from 2 to 8 by adding negligible volumes of NaOH or HCl. After the suspensions were shaken 24 h, the solid and liquid phases were separated by filtration. Pb (II) ions in the liquid phase were analysed using an atomic absorption spectroscopy. A UNICAM 929 model flame atomic absorption spectrophotometer with deuterium-lamp background correction was used for the determination of Pb (II). The measuring conditions were as follows: UNICAM hollow cathode lamp, 10 cm 1-slot burner, air-acetylene flame (fuel gas flow-rate 1.20 L min<sup>-1</sup>), 0.5 nm spectral bandwidth, and 7 mm burner height. The wavelength and the lamp current of Pb (II) was respectively 217 nm and 5 mA.

## 3. Results and discussion

### 3.1. Effect of pH

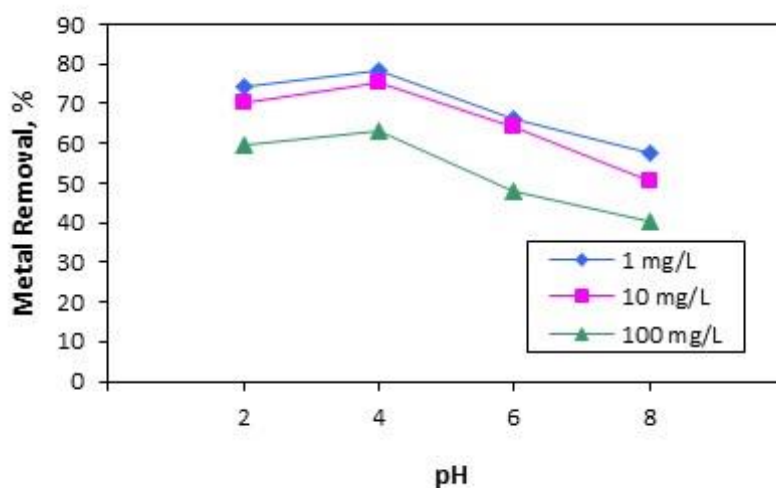
The pH of the solution is an important controlling parameter for the adsorption of heavy metals on the sorbents and influences the metal speciation and surface metal binding sites. The effect of pH on the adsorption of Pb (II) at different initial Pb (II) concentrations (1, 10, and 100 mg L<sup>-1</sup>) at 25 °C is shown in Fig. 1.

The results show that adsorption of Pb (II) onto diatomite is affected by pH. This is partly due to the fact that hydrogen ion ( $\text{H}^+$ ) themselves are strong competing ions and partly that the solution pH influence the chemical groups on to the adsorbent surfaces [26]. The process involved for Pb (II) adsorption are the following [26]:





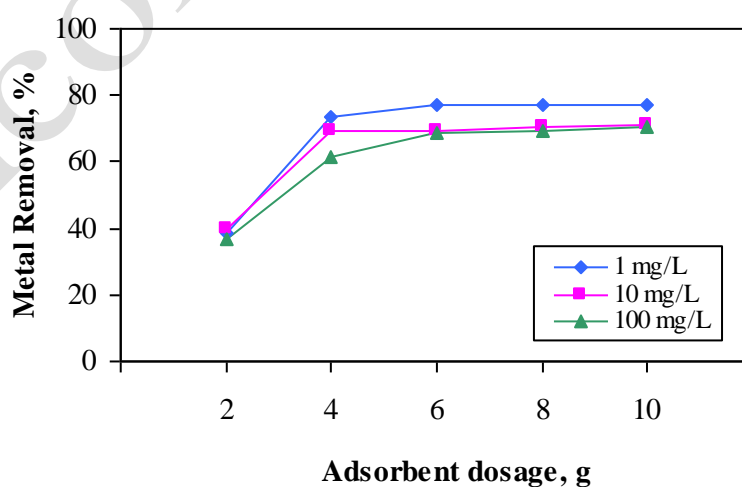
The maximum percent removal of Pb (II) was observed at pH 4 and significantly decreased at higher pH values. Above pH 4, the sorption yield decreases with increasing pH because hydrolysis and precipitation begin to play an important role in the sorption of Pb (II) [27].



**Figure 1.** Effect of pH for the removal of Pb (II) onto diatomite

### 3.2. Effect of adsorbent dosage

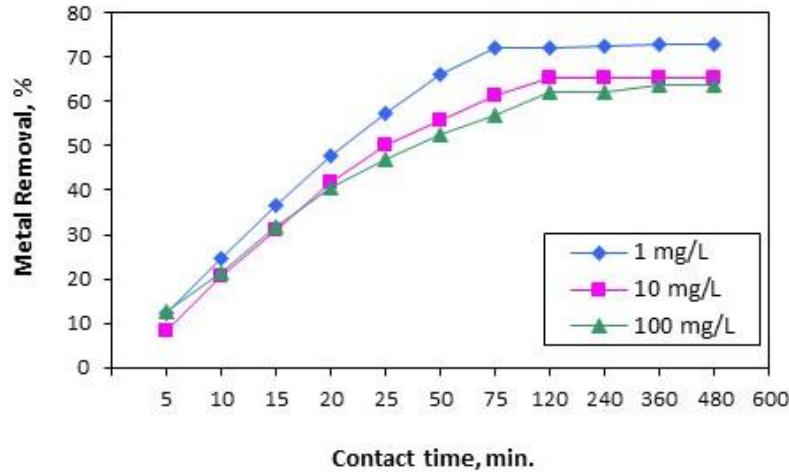
The adsorbent dosage was varied from 2 to 10 g L<sup>-1</sup>. The effect of the amount of diatomite on Pb (II) removal is presented in Fig. 2 and the removal of Pb (II) increases with increasing diatomite dosage. The Pb (II) removal was not changed significantly for 4 g L<sup>-1</sup> adsorbent dosage and higher. For this reason, the adsorbent dosage of diatomite for Pb (II) removal was determined to be 4 g L<sup>-1</sup> for further adsorption experiments. Similar observations were found Pb (II) removal using mineral adsorbents by Varank et al. (2014) and Rashed (2001) [28-29].



**Figure 2.** Effect of adsorbent dosage for the removal of Pb (II) onto diatomite

### 3.3. Effect of contact time

The influence of contact time on the adsorption of Pb (II) ions onto diatomite was also investigated. In the experiments, optimum values of pH (4) and diatomite dosage (4 g L<sup>-1</sup>) were used for Pb (II) removal. The effect of contact time is shown in Fig. 3. The results reveal that the metal removal is higher at the beginning. This is likely due to the larger surface area of diatomite at the beginning for the adsorption of heavy metal ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [30-32].



**Figure 3.** Effect of contact time for the removal of Pb (II) onto diatomite

The optimum contact time for Pb (II) removal was determined at 75 min. The removal rate of Pb (II) gradually decreased with increase in contact time. Initially, the rate of Pb (II) uptake was higher because all sites on the adsorbent were vacant and Pb (II) concentration was high, but decrease of sorption sites reduced the uptake rate. Similar results were found in the study of Mousavi *et al.* (2010) and Surchi (2011) [33-34].

### 3.4. Adsorption isotherms

Sorption is a physical and/or chemical process in which a substance is accumulated at an interface between phases. A number of different equations can be used to predict theoretical adsorption capabilities for different adsorbents. For this study, Langmuir, Freundlich, and Dubinin-Radushkevich isotherm equations have been used to predict adsorption capabilities of metals on diatomite.

The Langmuir isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful applications in many adsorption processes of monolayer adsorption. The Langmuir isotherm is written as follows:

$$q_e = K_L q_m C_e / (1 + K_L C_e) \quad (4)$$

where  $q_m$  is the maximum monolayer adsorption capacity of the adsorbent (mg g<sup>-1</sup>), and  $K_L$  is the Langmuir adsorption constant (L mg<sup>-1</sup>), which is related to the free energy of adsorption.

Eq. (1) can be rearranged in the following linear form:

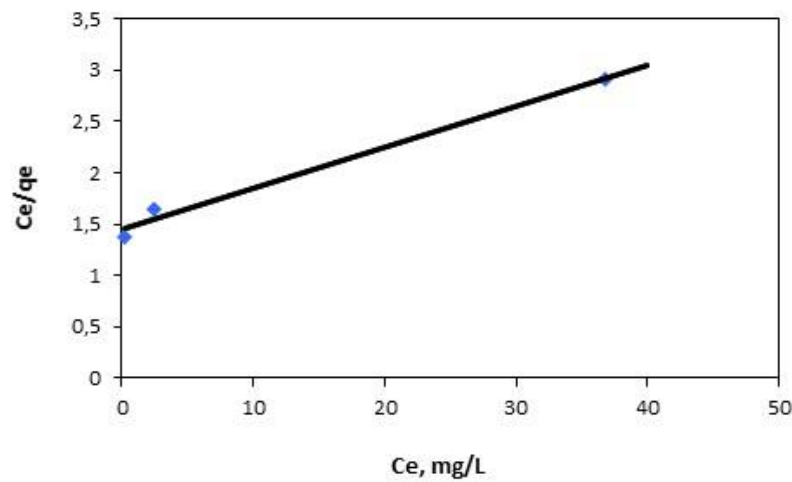
$$C_e / q_e = 1 / K_L q_m + C_e / q_m \quad (5)$$

The plot of  $C_e/q_e$  versus  $C_e$  gives a straight line with slope  $1/q_m$ , and intercept  $1/K_L q_m$ . Fig. 4 presents the plot of  $C_e/q_e$  vs  $C_e$  for the Pb (II) removal by adsorption onto diatomite.

Freundlich isotherm is the oldest and most widely used adsorption equation for solid-liquid systems. The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. This experimental model can be applied to non-ideal sorption on heterogenous surfaces as well as multilayer sorption. The empirically derived Freundlich isotherm is defined as follows:

$$q_e = K_f C_e^{1/n} \quad (6)$$

where  $K_f$  (L/g) and  $n$  (dimensionless) are the constants that can be related to the adsorption capacity and the adsorption nonlinearity intensity, respectively.

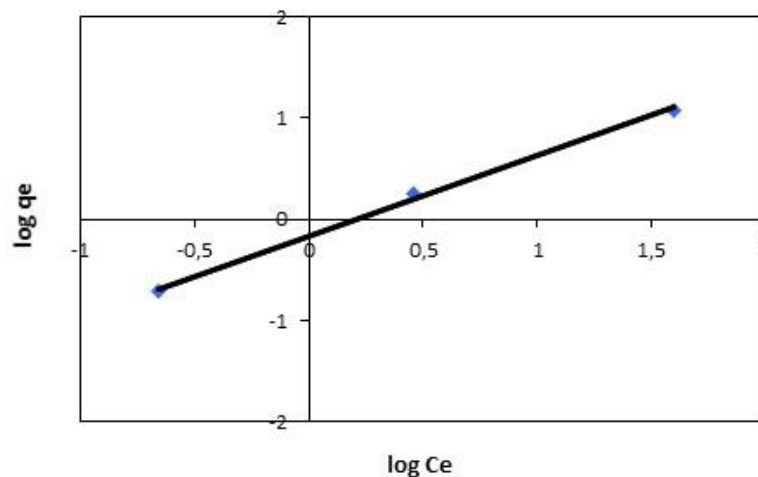


**Figure 4.** Langmuir plots for the adsorption of Pb (II) on diatomite, adsorbent dosage = 4 g L<sup>-1</sup>, pH 4, initial Pb (II) concentration=1-10-100 mg L<sup>-1</sup>, T=303.15

This equation can be rearranged in the linear form by taking the logarithm of both sides as:

$$\log q_e = \log K_f + 1/n \log C_e \quad (7)$$

The values of  $K_f$  and  $1/n$  may be calculated by plotting  $\log q_e$  against  $\log C_e$ . The slope is equal to  $1/n$  and the intercept is equal to  $\log K_f$ . Fig. 5 presents the plot of  $\log q_e$  as a function of  $\log C_e$  for the Pb (II) removal.



**Figure 5.** Freundlich plots for the adsorption of Pb (II) on diatomite, adsorbent dosage = 4 g L<sup>-1</sup>, pH 4, initial Pb (II) concentration=1-10-100 mg L<sup>-1</sup>, T=303.15

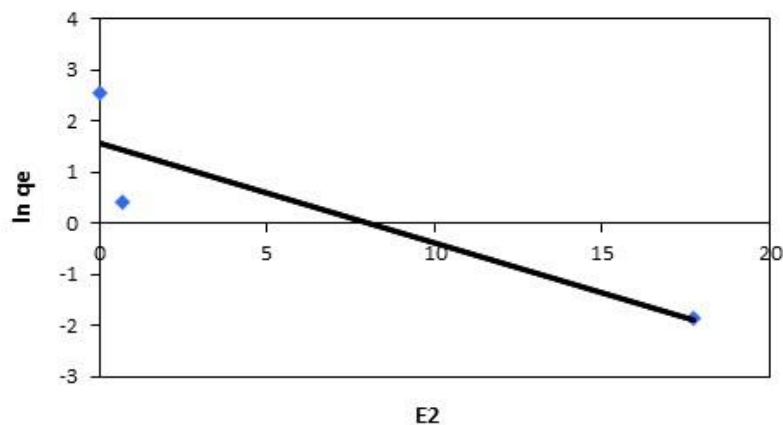
Dubinin-Radushkevich (D-R) proposed an equation for the analysis of isotherms in order to determine if the adsorption occurred by a physical or chemical process. The D–R equation is more general than the Langmuir model because it does not assume a homogeneous surface, a constant sorption potential, or an absence of steric hindrance between adsorbed and incoming particles:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (8)$$

where  $q_e$  is the amount of metal cations adsorbed per g of biomass,  $q_m$  represents the maximum sorption capacity of the adsorbent,  $\beta$  is a constant related to sorption energy (D–R constant), and  $\epsilon$  is the Polanyi sorption potential calculated by Eq. (9)

$$\epsilon = R T \ln (1+1/C_e) \quad (9)$$

where  $C_e$  is the metal equilibrium concentration ( $\text{mg L}^{-1}$ ),  $R$  is the gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ), and  $T$  is the temperature (K). The Polanyi sorption approach assumes a fixed volume of sorption space close to the adsorbent surface and the existence of sorption potential over these spaces. The sorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having the same sorption potential. This sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate [35]. The slope of the plot of  $\ln q_e$  versus  $\epsilon^2$  gives  $\beta$  ( $\text{mol}^2 \text{J}^{-2}$ ) and the intercept yields the sorption capacity,  $q_m$  ( $\text{mg g}^{-1}$ ) (Fig. 6).



**Figure 6.** Dubinin-Radushkevich (D-R) plots for the adsorption of Pb(II) on diatomite, adsorbent dosage =  $4 \text{ g L}^{-1}$ , pH 4, initial Pb (II) concentration =  $1-10-100 \text{ mg L}^{-1}$ ,  $T=303.15$

The Langmuir, Freundlich and Dubinin-Radushkevich isotherms parameters for the adsorption of Pb (II) ions onto diatomite are listed in Table 2.

**Table 2.** Langmuir, Freundlich, and Dubinin-Radushkevich isotherm constants for adsorption of Pb (II) onto diatomite

pH	Langmuir			Freundlich			Dubinin-Radushkevich		
	$q_m$	$K_L$	$R^2$	$K_f$	$1/n$	$R^2$	$q_m$	$-\beta$	$R^2$
2	26	0.53	0.972	0.62	0.85	0.997	4.8	0.19	0.793
4	25	0.69	0.999	0.50	0.87	0.999	4.4	0.23	0.786
6	19	0.39	0.988	0.36	0.85	0.995	3.8	0.30	0.802
8	19	0.24	0.929	0.24	0.86	0.998	3.0	0.38	0.777

When the  $R^2$  values are compared in Table 2, the Freundlich isotherm model fits better than the other isotherm models. The magnitudes of  $K_f$  and  $n$  show easy separation of Pb (II) ions from the aqueous solution and indicate favourable adsorption. The intercept  $K_f$  value is an indication of the adsorption

capacity of the adsorbent; the slope  $1/n$  indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. In case of  $n=1$  indicates linear adsorption and equal adsorption energies for all sites. Values of  $n<1$  shows that the marginal adsorption energy decreases with increasing surface concentration. As seen from Table 2,  $n$  value (1.176) indicated the high bond strength between adsorbate and adsorbent, and it also illustrated the adsorbent surface was heterogeneous. The Freundlich adsorption capacity of diatomite studied in this work is similar to the results observed for diatomite by other researchers [36-38].

### 3.5. Kinetic modeling

In the present work, different kinetic models such as pseudo-second order equation, Elovich equation and intra-particle diffusion equation are used to describe the Pb (II) adsorption onto the diatomite.

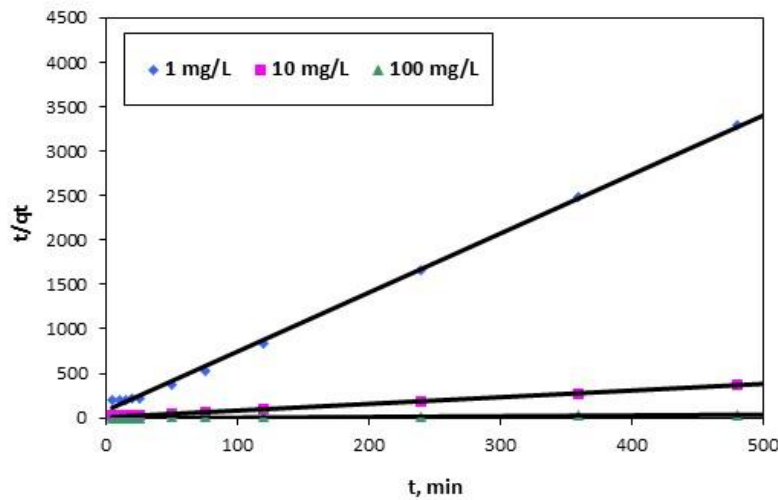
The pseudo-second order reaction kinetic rate equation is expressed as [39]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (10)$$

where  $q_e$  and  $q_t$  are the amount of heavy metal ( $\text{mg g}^{-1}$ ) adsorbed at equilibrium time and time  $t$  (d) and  $k_2$  is the second order reaction constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ), respectively. For the boundary conditions  $q_t = 0$  to  $q_t = q_t$  at  $t = 0$  to  $t = t$ ; the integrated form of Eq. (7) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

A straight line of  $t/q_t$  versus  $t$  indicates the application of the second order kinetic model. The values of  $k_2$  are determined from the slope of the plots (Fig. 7).



**Figure 7.** Pseudo-second order reaction kinetics for the adsorption of Pb (II) ion

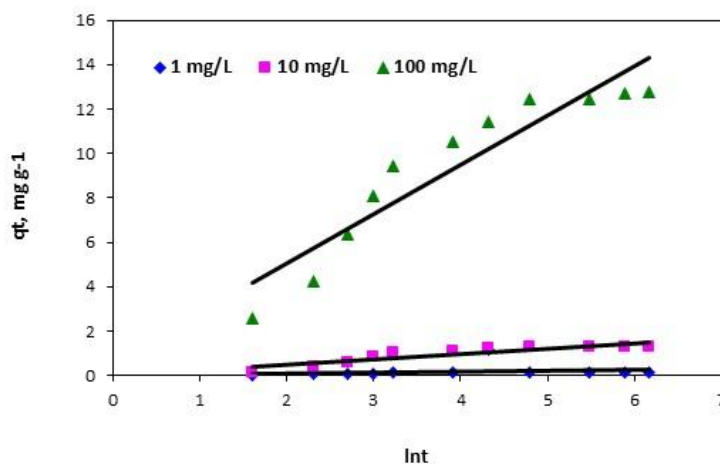
The Elovich equation is expressed as follows [40]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (12)$$

where  $\alpha$  is the initial adsorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ) and  $\beta$  is the desorption constant ( $\text{g mg}^{-1}$ ). To simplify the Elovich equation, Chien and Clayton (1980) assumed  $\alpha \beta \gg 1$  and by applying the boundary conditions  $q_t=0$  at  $t=0$  and  $q_t= q_t$  at  $t=t$  Eq (12) becomes [41-42]:

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \quad (13)$$

A straight line plot of  $q_t$  versus  $\ln t$  indicates the application of the Elovich model. The values of constants can be obtained from the slope and intercept of the plots (Fig. 8).



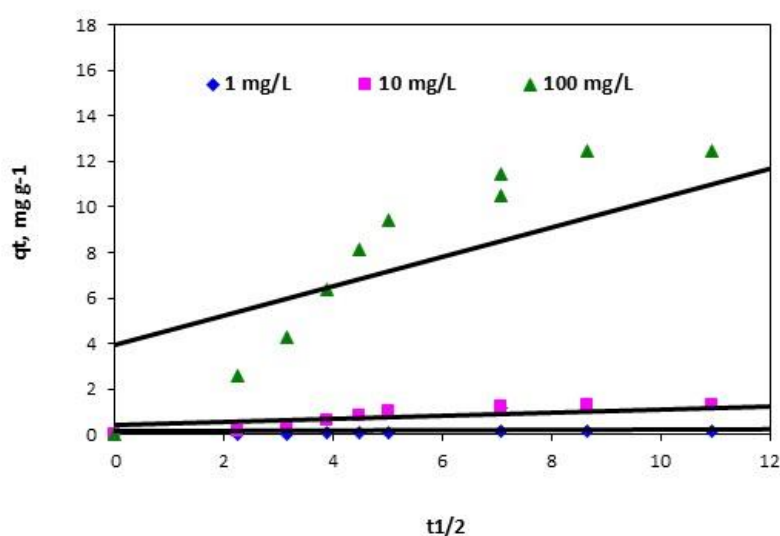
**Figure 8.** Elovich kinetics for the adsorption of Pb (II) ion

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. Generally, a process is diffusion controlled if its rate is dependent upon the rate at which components diffuse towards one another. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model as [43-45]:

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

where  $K_{id}$  is the intra-particle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) and  $C$  is the intercept. The values of  $C$  may indicate the thickness of the boundary layer, i.e., the larger intercept, the greater the boundary layer effect is [46-47].

A plot of  $q_t$  versus  $t^{1/2}$  indicates the application of the intra-particle diffusion model. The values of  $K_{id}$  were determined from the slope of the plots (Fig. 9).



**Figure 9.** Intra-particle diffusion kinetics for the adsorption of Pb (II) ion



The kinetic parameters of lead (II) onto diatomite are calculated from these plots and given in Table 3. Table 3 shows that the correlation coefficients ( $R^2$ ) for the Elovich and the intra-particle diffusion kinetic models are lower than the pseudo-second order kinetic model. Moreover, the calculated  $q_e$  values agree with experimental  $q_e$  values for the pseudo-second order kinetic model. It is probable that the adsorption system fits the pseudo-second order kinetic model. This indicates that for all the tested systems, the rate-limiting step is chemical sorption (chemisorption) between the adsorbents and the lead (II) ions.

**Table 3.** Adsorption kinetic parameters of Pb (II) onto diatomite

Kinetic equation and parameter	1 mg L <sup>-1</sup>	10 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>
Second-order kinetic equation			
$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.53	0.047	0.005
$q_2$ (mg g <sup>-1</sup> )	0.15	1.4	13
$R^2$	0.998	0.997	0.999
Elovich equation			
$\alpha$ (mg g <sup>-1</sup> min <sup>-1</sup> )	0.098	0.25	2.9
$\beta$ (g mg <sup>-1</sup> )	24	4.1	0.45
$R^2$	0.409	0.837	0.876
Intra-particle diffusion equation			
$K_{id}$ (mg g <sup>-1</sup> min <sup>-1/2</sup> )	0.007	0.068	0.65
$R^2$	0.154	0.635	0.671

#### 4. Conclusions

The following conclusions can be drawn:

- Adsorption of Pb (II) on diatomite is clearly affected by pH. The maximum percent removal of Pb (II) was observed at pH 4 and significantly decreased at higher pH values.
- Pb (II) removal is positively influenced by an increase in the adsorbent dosage. The maximum diatomite adsorption efficiencies for Pb (II) ion was obtained at the range of 70-77% for all concentrations studied.
- A time of 75 min was found for construction of the isotherms because the increment in contact time from 75 min to 480 min did not show any significant effect on efficiency.
- The adsorption isotherms of Pb (II) on diatomite can be described by the Freundlich model.
- The adsorption system fits the pseudo second order kinetic model.
- Diatomite was found to have a high adsorption capacity for removing lead (II) ion from aqueous solutions.

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