Experimental modeling of the adsorption kinetics of Cd (II) and Pb (II) ions by Calix [4] arene surface

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ABSTRACT

The removal of Cd^{2+} and Pb^{2+} ions from wastewater using *p-tert*-butyl-calix[4] arene was investigated in terms of initial pH, initial concentration, adsorbent dosage, contact time and temperature. The maximum adsorption occurred at the pH value of 6. The adsorbent studied exhibits high efficiency for Cd (II) and Pb (II) adsorption and the equilibrium states could be achieved in 10 min. Adsorption kinetics data were modeled using the first order, the pseudo-first and pseudo-second order, Elvoich equations and intra-particle diffusion models. The results show that pseudo-second order kinetic model was found to correlate the experimental data as well.

Keywords: Adsorption, Kinetic models, Heavy metals, Calix[4] arene

INTRODUCTION

Polluted water has always been a serious problem to the environment. Besides, various water pollutants including pesticides, dyes and surfactants, pharmaceuticals are emerging classes of aquatic contaminants. Both human and veterinary pharmaceuticals have been increasingly detected in sewage, natural, surface and ground water [1–5]. The reason why they may be dangerous for the environment is that these substances, generally developed with the aim to perform a biological effect on human beings, may also affect other living organisms in a nonpredictable way. The presence of heavy metal ions from the transition series, viz, Cu, Fe, Ni, Pb, Cd, etc. in the environment is of major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end products [6]. Heavy metals contamination exists in aqueous waste stream from many industries such as metal plating, mining, tanneries, painting, car radiator manufacturing, as well as agricultural sources where fertilizers and fungicidal spray intensively used. The removal of heavy metal in an effective manner from water and wastewater is, thus, ecologically very important. There are many reported and established technologies for the recovery of metals

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from wastewater, which include chemical precipitation [7], flotation [8], biosorption [9–11], electrolytic recovery, membrane separation [12], removal by adsorption on minerals [13,14] and activated carbon adsorption [15,16].

A calixarene is a macrocycle or cyclic oligomer based on a hydroxyalkylation product of a phenol and an aldehyde [17,18]. The word calixarene is derived from calix or chalice because this type of molecule resembles a vase and from the word arene that refers to the aromatic building block. Calixarenes have hydrophobic cavities that can hold smaller molecules or ions and belong to the class of cavitands known in host-guest chemistry. Calixarene nomenclature is straightforward and involves counting the number of repeating units in the ring and includes it in the name.

Therefore, the present objective of this study is to evaluate the cadmium and lead divalent removal potential and adsorption ability of Cd (II) and Pb (II) ions using Calix[4] arene surface was investigated. 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 for changing the bulk concentration, and pseudo first-order rate equation and pseudo second-order, Elovich model and intraparticle diffusion model for the adsorbent phase concentration.

EXPERIMENTAL
Material
$Cd(NO_3)_2.4H_2O$ (molecular weight, 308.48 g/mol) and $Pb(NO_3)_2$ (molecular weight, 331.20 g/mol) were supplied by Merck, Germany (maximum purity available). All solutions were prepared with deviations of less than ±0.1% from the desired concentrations.

Parent calixarene was obtained from Aldrich and used without further purification. The ligands were synthesized following the procedure proposed by Ref. 19. The solvents, methanol and chloroform (from Merck, p.a.), were used without further purification.

Batch Adsorption experiments
All adsorption experiments were carried out at room temperature (25°C). Solutions were placed in glass flasks and gently agitated on a rotary shaker. After agitating the flasks for predetermined time intervals samples were withdrawn from the flasks. The adsorbent was separated from the solution by centrifugation (REMI make) at 1000 rpm for 5 minutes. The metals ion concentration was determined atomic absorption device Shimadzu-AA-680. The amount of Cadmium and Lead adsorbed (q_e) in mg/g at time t was computed by using the following equation [20]:

$$q_e = \frac{(C_i - C_t)V}{W} \qquad (1)$$

Where C_i and C_t are the Cd and Pb concentrations in mg/L initially and at a given time t, respectively, V is the volume of Cd and Pb solutions in L, and w is the weight of sorbent in g.

RESULTS AND DISCUSSIONS
Effect of contact time
The removal of lead and copper ions increased with time and attains saturation in about 10 min. basically, the removal of adsorption is rapid, but it gradually decreases with time until it reaches equilibrium. Fig. 1 represents the percent removal of Cd(II) and Pb(II) ions versus the contact time for the initial concentration and by using the optimum pH value which was obtained for the two heavy metals.
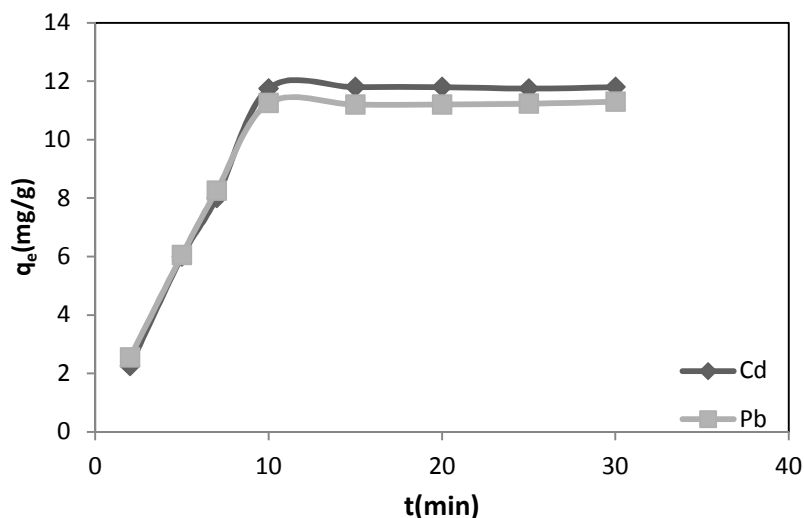
Fig. 1. Effect of contact time on the amount of ions adsorption by calix[4] arene, Conditions: initial concentration 5 mg/L; adsorbent dosage 10 mg/L; T = 298±1K.
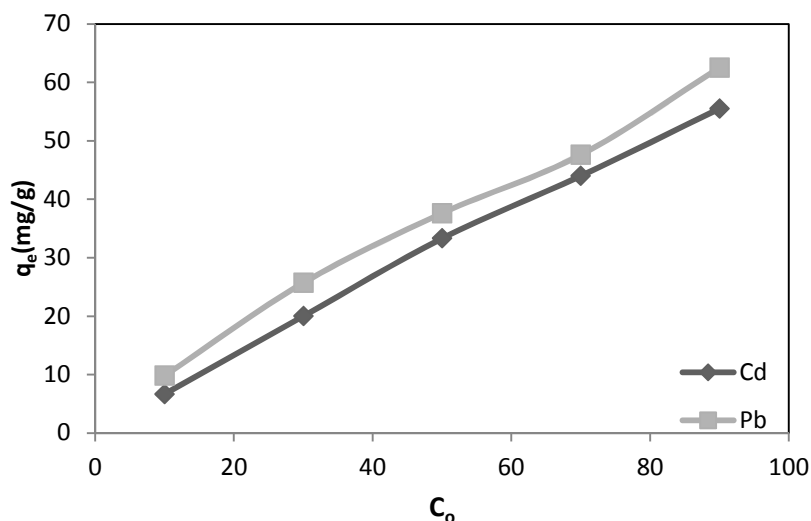

Fig. 2. Effect of initial concentration on the amount of ion adsorption by calix[4] arene, Conditions: Contact time 10 min; adsorbent dosage 10 mg/L; T = 298±1K.

Effect of initial metal ion concentration
In batch absorption systems, available adsorbate initial concentration in solution plays an important role as a driving force which overcomes mass transfer resistance of adsorbate between aqueous and solid phase [21]. In the present study, the adsorption experiments are performed to study the effect of metals ion initial concentration by varying it from 10, 30, 50, 70 and 90 mg/L, while maintaining the calix[4] arene amount 0.01 g/L and

obtained results are presented in Fig. 2. The increase in adsorption capacity with increase in metals ion concentration may be due to the higher adsorption rate and utilization of all active sites available for the adsorption at higher concentration.

Effect of pH
The experiments carried out at different pH values showed that there was a change in the quantity of adsorbed cadmium and lead ions on the solid phase of calix[4] arene

powder over the entire pH range of 2 to 8, as shown in Fig. 3. This Fig., indicated the strong force of interaction between the cadmium and lead ions and the adsorbent powder that, H^+ ion could influence the adsorption capacity. Electrostatic repulsion decreases with the increasing in pH due to reduction of positive charge density on the adsorption edges thus resulting in an increase metal adsorption. [22] Here the interaction is more at pH=6 due to the competence of acidic H^+ ion with Cd^{2+} and Pb^{2+} ions for the adsorption sites.

Effect of adsorbent dose

The effect of adsorbent dose on the removal of Cd and Pb ions for constant concentrations (5 mg/L) were investigated by agitating with different adsorbent dosage over the range of 5 -30 mg. The study reveals that amount adsorption increases with increase in the calix[4] arene (Fig. 4). This attributes the increased calix[4] arene surface area and availability of more adsorption sites.
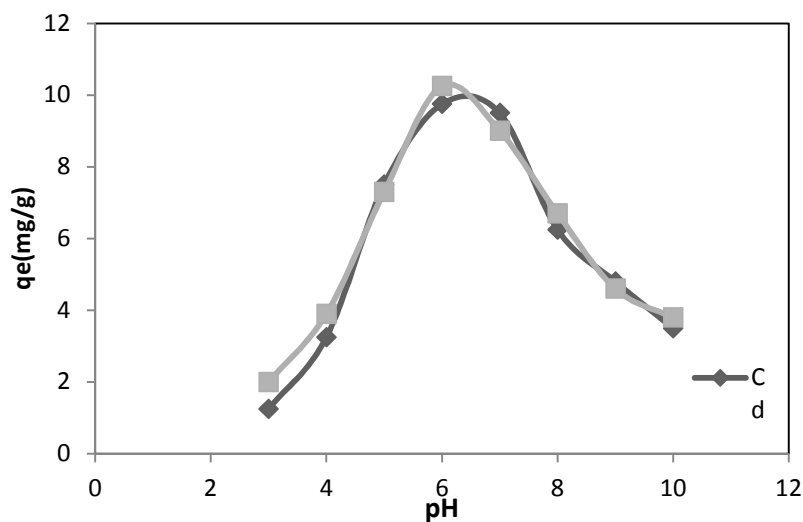

Fig. 3. Effect of solution pH on the adsorption for Pb^{2+} and Cd^{2+} on calix[4] arene. Conditions: initial concentration 5 mg/L; adsorbent dosage 10 mg/ L; contact time 10min; and T = 298±1K.
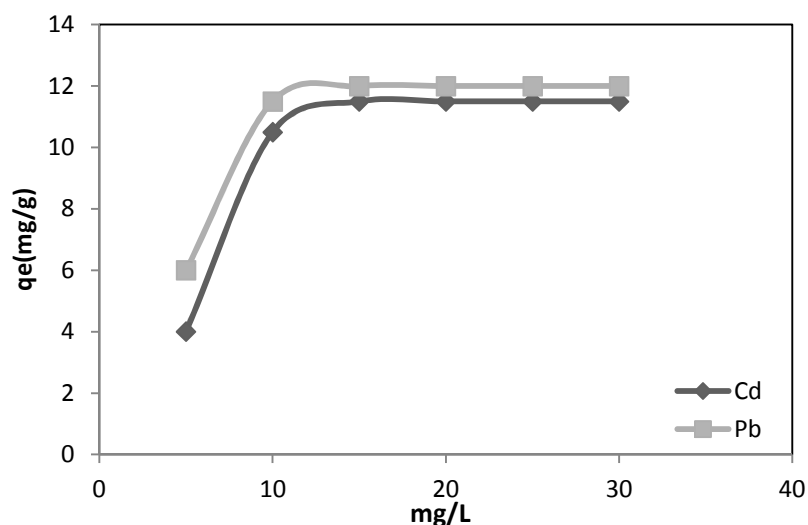

Fig. 4. Effect of adsorbent dosage on the adsorption for Pb^{2+} and Cd^{2+} ions on calix[4] arene. Conditions: initial concentration 5 mg/L ; pH 6; contact time 10 min and T = 298±1K.

Effect of temperature
To study the effect of temperature on the adsorption of cadmium and lead ions by calix[4] arene, the experiments were performed at temperatures of 298, 308, and 318 K. Fig. 5, shows the influence of temperature on the adsorption of cadmium and lead ions onto calix[4]arene.

Kinetic study
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. 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 Cd(II) and Pb(II) ions adsorption.

Simple First Order Model
The sorption kinetics may be described by a simple first order equation [23,24]. The change in bulk concentration of the system using the following a linear form simple first order rate Eq. (2):

$$logC_t = \frac{k_1}{2.303} t + logC_0 \qquad (2)$$

Where C_t and C_o are the concentration of metals ion 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 t (Fig. 6) for constant initial concentrations of metals ion was deviated considerably from the theoretical data.

A comparison of the results with the correlation coefficient is shown in Table 1, which indicates the failure in expressing this adsorption process by the simple first order kinetics.
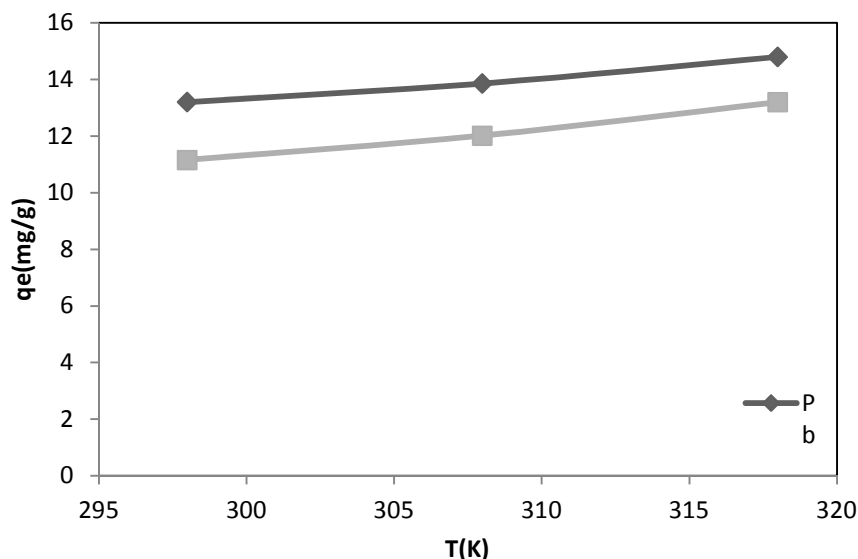

Fig. 5. Effect of temperature on the adsorption for Pb^{2+} and Cd^{2+} ions on calix[4] arene. Conditions: initial concentration 5 mg/L; pH 6; adsorbent dosage 10 mg/L; and contact time 10 min.
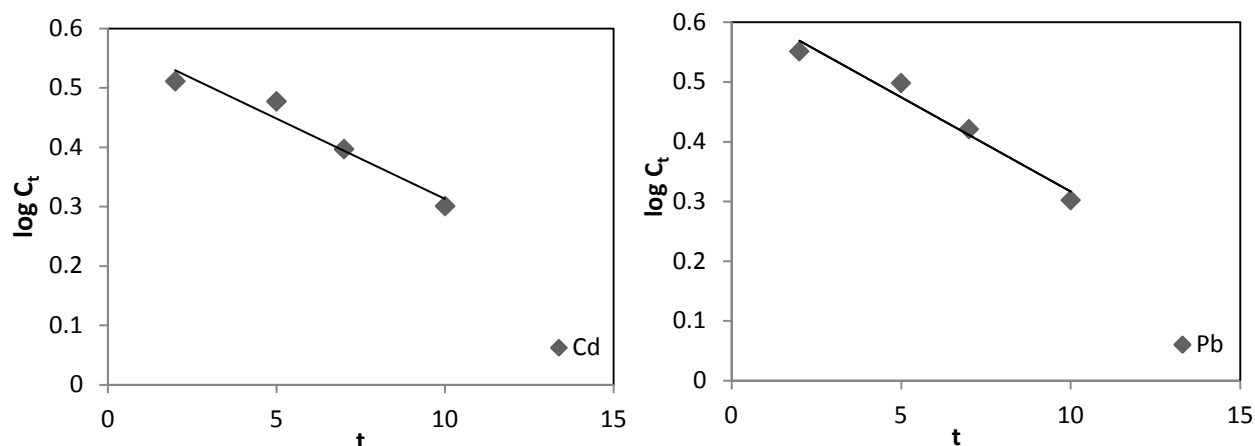
Fig. 6. Plot of the simple first order adsorption kinetics of Cd^{2+} and Pb^{2+} ions on calix[4] arene.

Table 1. Comparison of the simple first order, pseudo first- and second-order adsorption.

	Simple 1st order		Pseudo 1st order			Pseudo 2nd order		
	k_1	r^2	k_1	q_e	r^2	k_2	q_e	r^2
Cd	0.0624	0.9498	0.0711	12.41	0.9857	0.00015	92.5	0.9990
Pb	0.0727	0.9660	0.0809	11.99	0.9778	0.00016	80	0.9990

Pseudo Firs-order Model

The adsorption kinetics may be described by a pseudo first order equation [23, 25-28]. The linear form equation is the following:

$$\log(q_e - q_t) = \log(q_e) - k_1 t \qquad (3)$$

Where and are amounts of chromium adsorbed at equilibrium and at time (mg/g), respectively, and is the equilibrium rate constant of pseudo first-order adsorption, (1/min). Fig. 7 shows a plot of linearization form of pseudo first-order model. The slopes and intercepts of plots of versus were used to determine the pseudo first-order constant and equilibrium adsorption density. However, the experimental data deviated considerably from the theoretical data. A comparison of the results with the correlation coefficients is shown in Table 1. The correlation coefficients for the pseudo first order kinetic model obtained at all the studies concentrations were low. This suggests that this adsorption system is not a pseudo first-order reaction.

Pseudo Second-order Model

The adsorption kinetics may also be described by a pseudo second-order equation [25, 28]. The linear form equation is the following:

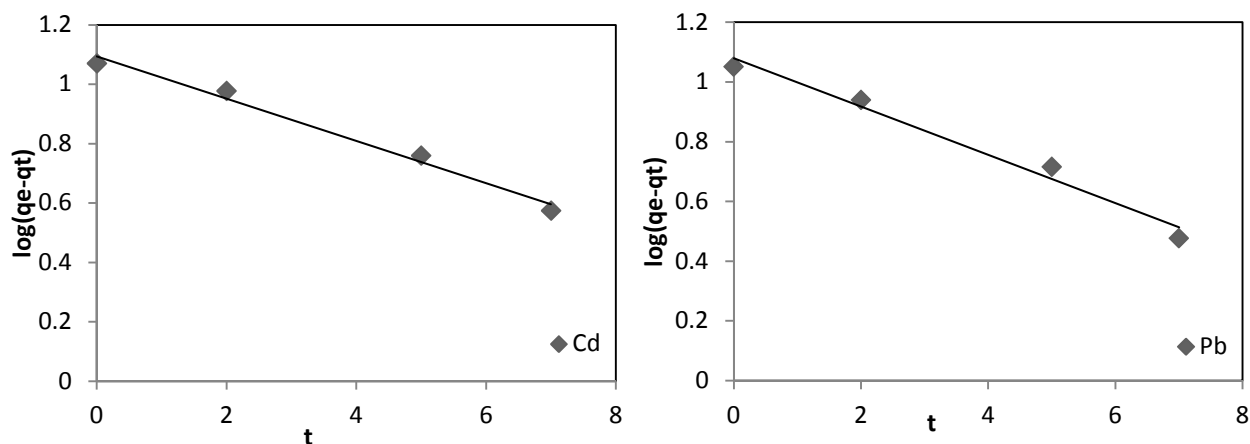$$t/q = 1/k_2 q_e^2 + t/q_e \qquad (4)$$

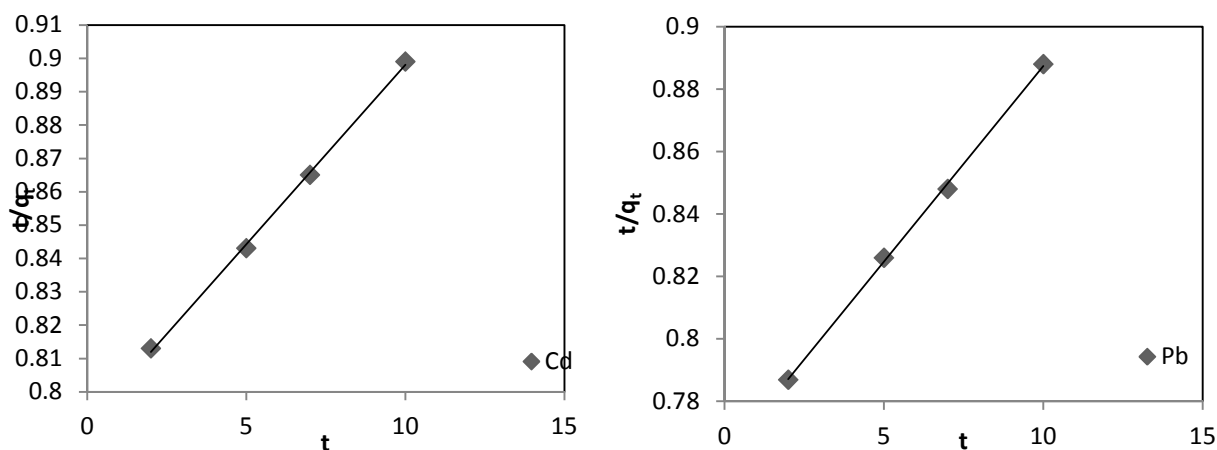**Fig. 7.** Pseudo first-order kinetics for adsorption of (a) Cd^{2+} and (b) Pb^{2+} ions by calix[4] arene.

Fig. 8. Pseudo second-order kinetics for adsorption of Cd^{2+} and Pb^{2+} ions by calix[4] arene.

Elovich Model

Where k_2 is the equilibrium rate constant of pseudo second-order adsorption (g/mg.min). The slopes and intercepts of plots t / q 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 versus t (Fig. 8) show good agreement of experimental data with the pseudo second-order kinetic model for different initial chromium concentrations. Table 1 lists the computed results obtained from the pseudo second-order kinetic model. These indicate that the adsorption system studied belongs to the second order kinetic model.

The Elovich model equation is generally expressed as [29, 30]:

$$dq_t/dt == \alpha \, exp \, (-\beta q^{\gamma}) \qquad (5)$$

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 assumed $\alpha \beta t$ and by applying the boundary conditions at and at equation (5) becomes $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ equation (5) become:

$$q_t = 1/\beta \, ln(\alpha \, \beta) + 1/\beta \, ln(t) \qquad (6)$$

If metals ion 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 $1/\beta \ln(\alpha \beta)$. Fig. 9 shows a plot of linearization form of Elovich model at constant concentrations studied. 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.

The Intra-particle Diffusion Model

The intra-particle diffusion model is expressed as [21, 22]:

$$q = k_i\, t^{1/2} + C \qquad (7)$$

Where C is the intercept and k_i is the intra-particle diffusion rate constant (mg/g $h^{0.5}$), which can be evaluated from the slope of the linear plot of q versus $t^{1/2}$. Fig. 10 shows a plot of the linearized form of the intra-particle diffusion model.
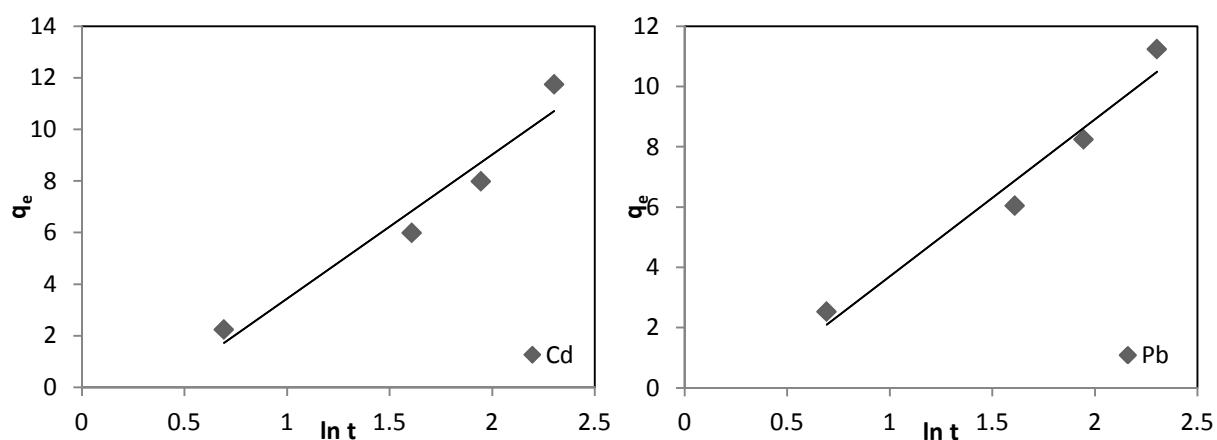

Fig. 9. Elovich model for adsorption of Cd^{2+} and Pb^{2+} ions on calix[4] arene.
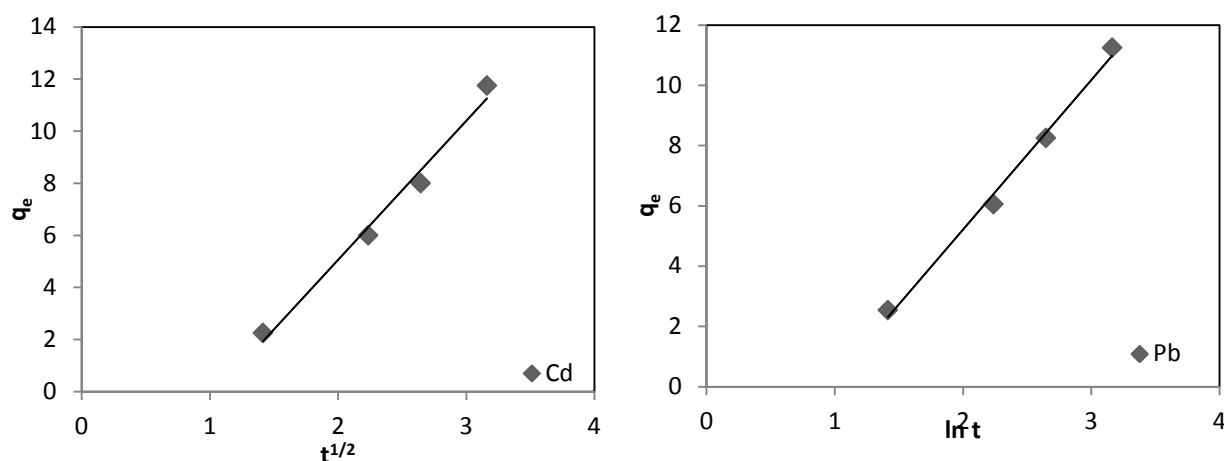

Fig. 10. Intra-particle diffusion model for adsorption of Cd^{2+} and Pb^{2+} ions on calix[4] arene.

Table 2. Comparison of the Elovich and Intra-particle diffusion model.

	Elovich			Intra-particle diffusion		
	β	α	r^2	k_i	C	r^2
Cd	0.1791	3.8023	0.9453	5.3269	4.6947	0.9853
Pb	0.1918	3.8998	0.9605	4.9560	5.6005	0.9934

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 [31].

CONCLUSION

Adsorption kinetic and equilibrium parameters for Cd^{2+} and Pb^{2+} ions on calix[4] arene were obtained in a batch system. Adsorption capacity was dependent on the initial metals ion concentration, contact time, pH of the metals ion solution, adsorbent dosage and temperature. The kinetics of adsorbent was experimentally studied and the obtained rate data were analyzed using the simple first order, pseudo first-order, the pseudo second-order, intra-particle diffusion and Elovich kinetic models. Based on the values of the correlation coefficient (r^2) obtained for all tested models, pseudo second-order was found to best correlate the rate kinetic data of calix[4]arene.

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