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ORIGINAL RESEARCH PAPER

Nanoporous Xerogel for Adsorption of Pb^{2+} and Cd^{2+}

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Abstract

Classical xerogels are robust, inexpensive and nontoxic materials with low-ordered nanoporous structures. In water streams where the pH is higher than the Point of Zero Charge, the surface of classical xerogels such as tetraethoxy orthosilan (TEOS) xerogel is negatively charged. It was assumed that a xerogel can work as a strong adsorbent for metal ions without further modification. Therefore, the capability of TEOS xerogel for adsorption of two heavy metal ions, Pb2+ and Cd2+, from aqueous solution was studied. The batch experiments revealed that the adsorbent has higher adsorption capacity for Pb2+ (58.82 mg/g) and Cd2+ (35.71 mg/g) as compared with the reported low-cost adsorbents. Kinetics and thermodynamic studies were employed to explain the adsorption mechanism. It was concluded that the adsorption of both ions on TEOS xerogel obey chemisorption mechanism. However, the reaction of Pb2+ with the adsorbent is thermodynamic controlled and the one of Cd2+ is kinetic controlled.

1. INTRODUCTION

Xerogels are silane based materials which are obtained from drying or ageing of sol-gels. Acid or base hydrolysis of tetra-alkoxysilanes such as tetraethoxy-orthosilane (TEOS) results in formation of silanols which are readily polymerized at neutral pH. These polymers are called sol-gels [1]. Upon drying, sol-gel finds a glassy like texture that can be grinded to powder. Choosing different precursors or any change at any step of the preparation modifies the chemical, physical and mechanical properties of the final xerogel [2]. Because of their robust mechanical properties, versatile chemistry, cost-effective and easy preparation, xerogels have found numerous applications in sensors fabrication, biomacromolecules immobilization, optic devices, separation and adsorption technologies [2-4]. The surface of a xerogel particle is covered by free silanols, which influence the surface potential. The reactions of these free silanols with the ions H^+ and OH^- determine the surface potential. Thus, the xerogel surface potential is pH dependent [5].

$Si\text{-}OH + H^+ \rightarrow Si\text{-}OH_2^+$

$Si\text{-}OH + OH^- \rightarrow Si\text{-}O^- + H_2O$

The pH where the particle is neutral is called the point of zero charge (PZC). At pHs higher than PZC, the surface is negatively charged. The opposite is observed at pHs lower than PZC. The typical values of PZC for the silica based materials are between 2.4 and 3.5 [6]. Therefore, in aqueous medium with a pH close to neutral, a classical xerogel such as TEOS xerogel carry a net negative charge due to the hydrolysis of the unpolymerized silnols [5]. This is why they do not show affinity for adsorption of anionic species [7]. The inorganic structure of a classical xerogel does not show a notable hydrophobic interaction necessary for adsorption of organic molecules [8]. However, the negative charge of this surface is assumed to help adsorption of metal ions. To examine this assumption and evaluate the adsorption power of these materials for heavy metal ions, the adsorption of two heavy metal ions, Pb^{2+} and Cd^{2+}, on TEOS xerogel was studied.

Contamination of water streams by heavy metal ions such as Pb^{2+} and Cd^{2+} is a serious environmental problem as rapid industrialization, especially in the countries with vulnerable infrastructures, has opened unexpected ways for the disposal of toxic heavy metals into the environment [9]. Although various methods including filtration, chemical precipitating, chemical oxidation/reduction, electrochemical processes, coagulation, solvent extraction, electrolysis and bioremediation have been employed for removal of toxic metallic ions from water resources [10], ion exchange and adsorption seem to be more attractive because of simplicity and economic reasons. This is why a broad spectrum of adsorbents from activated carbon, low-cost natural waste materials to sophisticated mesoporous silica based materials have been examined for different adsorption purposes [11-13]. In view of the existing literature on this subject, results of this study are presented and discussed.

2. Experimental procedure

2.1. Chemicals and instrumentation

All chemicals used in this research were purchased from Merck Company and standard solutions of $Pb(NO_3)_2$ and $Cd(NO_3)_2.4H_2O$ were prepared by dissolving the appropriate amount of the salts in deionized water. A Shimadzu (Tokyo, Japan) flame atomic absorption spectrometer model AA680 equipped with an air-acetylene flame was used for measuring the metal ion concentrations.

2.2. Preparation of the adsorbent

To prepare TEOS xerogel, the starting materials (TEOS, H_2O, HCl with mole ratio of 1: 4: 0.0015, respectively) were mixed in a glass container and sonicated in a water bath at room temperature for 30-45 min until a clear one-phase solution was obtained. To this solution an equivalent volume of phosphate buffer solution (0.1 M, pH 7) was added at room temperature. The resulting mixture was cast in a disposable aluminum cap and stirred by a bar until the sol-gel formed. Following gelation, the cast was allowed to age at room temperature and weighed intermittently for about 20 days until no further weight loss was observed. The final product, dried xerogel, was ground to fine powder and sized through a 250 μm sieve.

2.3. Adsorption experiments

Batch experiments were conducted by mixing a known amount of xerogel in a known volume of the metal ion solution (taken from the stock solutions containing 1000 mg/L of the corresponding salt) and the resulting mixture was agitated (200 rpm) for the intended period of time at 298 K and desirable pH. The solution was then allowed to sit at the same temperature for one hour. Then the supernatant was separated and filtered before subjecting it to analysis by the Atomic Absorption Spectrometer. The effect of each influential parameter on the adsorption such as contact time was examined through varying the selected parameter in the above mentioned procedure. The effect of the glass container and the paper filter on the adsorption data were taken into account in the bank samples. All the reported data are the average of at least triplicate measurements.

2.4. Equilibrium isothermal adsorption

Using the aforementioned batch equilibrium method and the optimum conditions for the adsorption of each cation, the isothermal adsorption of $Pb^{2+}$and Cd^{2+} on TEOS xerogel was studied at 298 K. The Cd^{2+} solutions (25 ml) with varying concentrations (25 to 200 mg/L in the presence of 50 mg of TEOS xerogel) and the Pb^{2+} solutions (50 ml) with varying concentrations (25 to 300 mg/L in the presence of 150 mg TEOS xerogel) were used in these experiments. The removal percentage and the amount of the adsorbed metal ions per gram of the xerogel at equilibrium (q_e) were calculated using the following equations:

$$\% \text{ Removal} = [(C_i - C_e) / C_i] \times 100 \qquad (1)$$

$$q_e = [(C_i - C_e) / w] \times V \qquad (2)$$

C_i and C_e are the initial and equilibrium concentrations of the metal ion in the solution (mg/L), respectively. V shows the volume of the solution (L) and w is the amount of the xerogel used in the mixture (g).

2.5. Pore size analysis

Pore size analysis was performed on a Micromeritics Gemini VII2390 Surface Area Analyzer. Fine powder xerogels (about 10 mg) were used for this analysis with no extra treatment or preconditioning to remove possible bound air or water. The pressure was measured as nitrogen was adsorbed or desorbed at a constant temperature controlled by liquid nitrogen. Surface areas were determined automatically by the StarDriver V1.02a. The software employs the isotherm data using the multipoint BET (Brunauer–Emmett–Teller) method [14].

$$q_e = q_m K_{BET} X/(1 - X)[1 + (K_{BET} - 1)X] \qquad (3)$$

X is the amount (mol or mg) of solute adsorbed per g of the adsorbent at equilibrium. K_{BET}, q_m and q_e are the equilibrium constant (L/g), saturation capacity (mol or mg/g) of adsorbent for solute and the adsorption capacity (mg per g of the adsorbent) at equilibrium, respectively.

2.6. Kinetic and thermodynamic studies

The kinetics of the metal ion removal from the aqueous solutions was investigated under the optimum conditions of 298 K by determining the amount of the adsorbed metal ion at different time intervals (5 to 90 min). The experiments were carried out in total volumes of 25 ml and 50 ml aqueous solutions containing 20 and 50 mg of the adsorbent with the initial concentrations of 100 mg/L of Cd^{2+} and Pb^{2+} respectively. The outcome of these experiments was analyzed in the pseudo-first order Eq. (4), pseudo-second order Eq. (5), and intraparticle diffusion Eq. (6). kinetic models using the following equations [15]:

$$\log(q_e - q_t) = \log qe - (k_1/2.303)t \qquad (4)$$

$$(t/q_t) = 1/k_2(q_e)^2 + (1/q_t)\ t \qquad (5)$$

$$q_t = k_{dif}\,(t^{1/2}) \qquad (6)$$

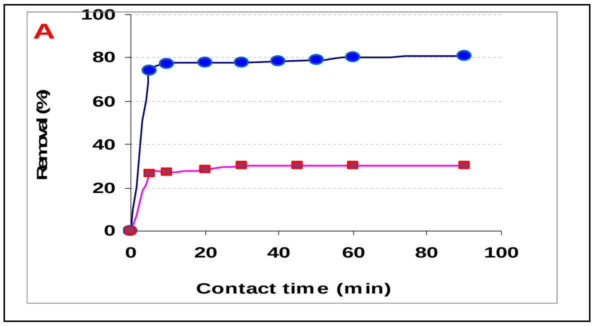
Where q_e and q_t are the adsorption capacities (mg per g of the adsorbent) at equilibrium and time t, respectively. And, k_1 (1/min), k_2 [(g/mg)/min], and k_{dif} [(mg/g) $min^{1/2}$] are the rate constants.

3. Results and discussion

Results of the equilibrium adsorption isotherm (EAI) studies reveal the mechanism that works between adsorbent and adsorbate. These results provide researchers with valuable information about the surface of the adsorbent, its capacity and affinity for the adsorbate [16]. EAI is usually obtained when the adsorption is studied under optimum conditions. Therefore, the optimal values for the influential parameters of the Cd^{2+} and Pb^{2+} adsorption on TEOS were first sought.

3.1. Contact time

The effect of contact time on the adsorption of metal ions on TEOS xerogel was investigated in the presence of a constant amount of the adsorbent (1 mg/mL). Results are presented in Figure 1A. Although the available adsorption sites for both ions were the same, Cd^{2+} occupied only about 25% of the sites in the first 10 min of the experiment, while Pb^{2+} occupied more than 70%. It was found that Pb^{2+} was able to occupy even more sites than Cd^{2+} as the contact time increased. The maximum adsorption of $Pb^{2+}$and Cd^{2+} was found to be 75% and 35%, respectively, under the applied conditions. Taking into account these results, a contact time of 90 min was selected for the EAI studies.



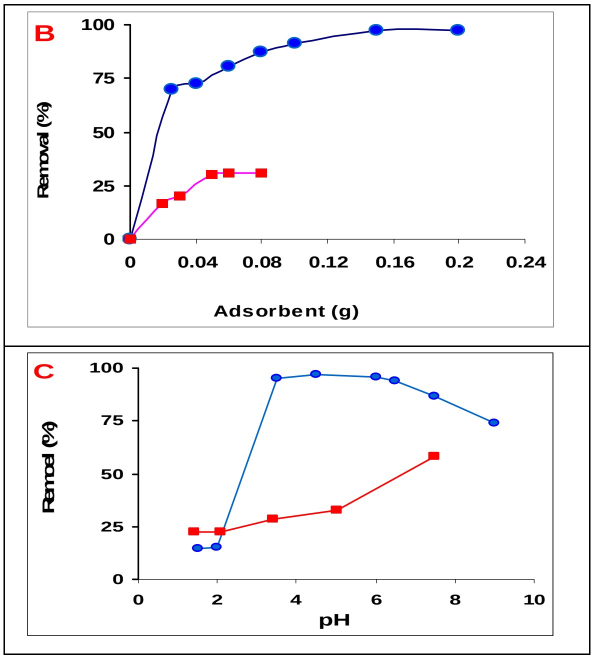


Fig. 1. Effect of **A)** contact time, **B**) adsorbent amount, and **C**) pH on the adsorption of Pb^{2+} (●) and Cd^{2+} (■) on the TEOS xerogel. These experiments were carried out at 298 K using fixed volumes of Pb^{2+} solution (50 ml) and Cd^{2+} solution (25 ml) with the initial metal ion concentrations of 100 mg/L.

3.2. Adsorbent dose

The effect of the adsorbent dose on the lead and cadmium uptake was studied at 298 K, applying a contact time of 90 min. The number of the adsorbing sites increases as more adsorbent is used. This increases the removal of Pb^{2+} and Cd^{2+} from the aqueous solutions. In a fixed volume of solution containing a set amount of ions, adsorption reaches a plateau due to the competition of the solvent molecules with the adsorbing sites for the adsorbate particles as shown in Figure. 1B. The optimal amounts of TEOS xerogel were found to be 3 and 2 mg/mL for Pb^{2+} and Cd^{2+}, respectively, under the applied conditions.

3.3. Effect of Ph

One of the most significant variables governing metal ion sorption is pH. It determines the surface charge of the adsorbent by influencing the extent of ionization of the associated functional groups [5, 17], and also affects the degree of ionization and chemical specifications of metal ions. At low pH(s), protons compete with metal cations for the active sites and inhibit higher adsorption, as observed in the results illustrated in Figure 1C [18]. At higher pH(s), metal ions tend to form hydroxides with low solubility. The Pb^{2+} and Cd^{2+} ions form hydroxides at pH(s) higher than 6.5 and 8 respectively [19,20]. This is why the corresponding experiments were carried out in two different ranges of pH: 2-6.5 and 2-8. According to the results shown in Figure 1C, pH 5 was selected as a safe pH for optimum uptake of both lead and cadmium ions by TEOS xerogel.

3.4. Effect of ionic medium

Figures 2A and 2B show the effect of various concentrations of NaCl and KCl on the Pb^{2+} and Cd^{2+} uptake by the xerogel, respectively. This data discloses that addition of either NaCl or KCl, especially at lower concentrations, has a minor effect on the Pb^{2+} adsorption. In contrast, it drops the Cd^{2+} uptake to about 45%.

It seems that Na^+ and K^+ have been able to compete with Cd^{2+} for the adsorbing sites of TEOS xerogel [21]. Cadmium uptake decreased more in the presence of $Na^{+,}$ presumably due to the higher density of positive charge on this ion which enhances the electrostatic attraction between the sorbent and sorbate [22]. These observations corroborate the greater affinity of the xerogel active sites for Pb^{2+} than Cd^{2+}.

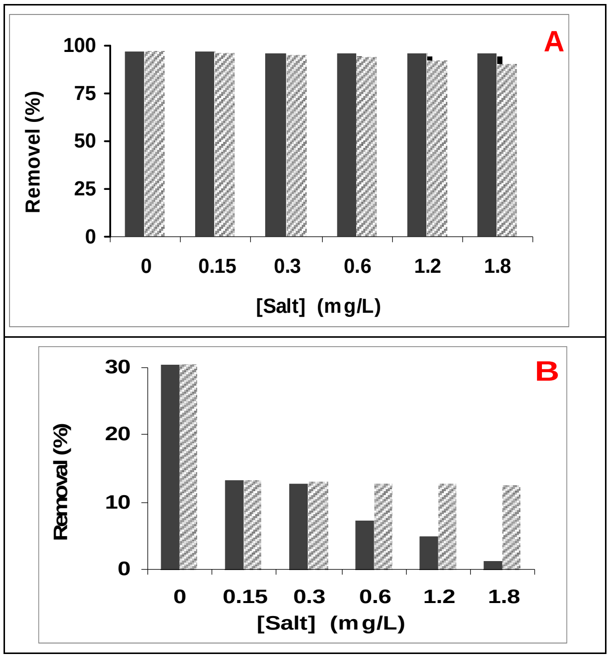


Fig. 2. A) Adsorption of Pb^{2+} on TEOS xerogel (3 mg/L), **B)** Cd^{2+} on TEOS xerogel (2 mg/L) in the presence of various concentrations of NaCl (dark bars) and KCl (dashed bars). The initial concentrations of Pb^{2+} and Cd^{2+} were 100 mg/L. These experiments were carried out at pH 5 and 298 K with a contact time of 90 min.

3.5. Effect of other metal ions on Pb^{2+} and Cd^{2+} adsorption

Industrial wastewaters normally contain various metal ions. Studying the adsorptive ability of TEOS xerogel in a mixture of ions produces data that can be interpreted in terms of selectivity and specificity.

To see how Pb^{2+} adsorption is changed in the presence of other metal ions, the uptake of lead from the mixtures containing Pb^{2+} (100 mg.L) and varying concentrations of either Cd^{2+} or Zn^{2+} (Figure 3A) was investigated. Similar experiments were carried out to examine the Cd^{2+} adsorption in the presence of various concentrations of either Pb^{2+} or Zn^{2+} (Figure 3B). These results indicate that zinc ions interfere in the adsorption of both

Pb^{2+} and Cd^{2+}. This means the sorbent binding sites are not specific for the examined metal ions. However this conclusion is not surprising. Zn^{2+} is a smaller cation with the same number of charges to Pb^{2+} and Cd^{2+}. As a result, it competes with those ions for the adsorbing sites.

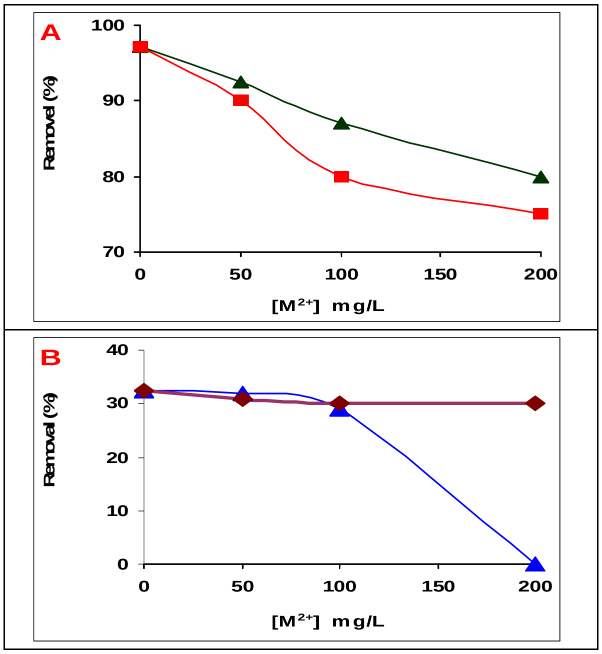


Fig. 3. A) Pb^{2+} adsorption in the presence of various concentrations (50, 100, 200 mg/L) of Cd^{2+} (■) and Zn^{+2} (Δ) on TEOS xerogel (3 mg/ml). **B)** Cd^{2+} adsorption in the presence of various concentrations (50, 100, 200 mg/L) of Pb^{2+} (◆) and Zn^{+2} (▲) on TEOS xerogel (2 mg/ml). The initial concentrations of Pb^{2+} and Cd^{2+} were 100 mg/L. These experiments were carried out at pH 5 and 298 K with a contact time of 90 min.

Figure 3B also discloses the greater impact of Zn^{2+} on the Cd^{2+} adsorption. This result is in agreement with the data illustrated in Figure 2, indicating stronger affinity of the xerogel for Pb^{2+}. Surprisingly, results in Figure 3A and 3B indicate that Cd^{2+} is able to interfere in the Pb^{2+} adsorption, while Pb^{2+} has negligible effect on the Cd^{2+} adsorption under identical conditions. This can be explained when the EAI and kinetics results are discussed in the following sections.

3.6. Equilibrium adsorption isotherms

EAI experiments were carried out to identify the possible mechanism of adsorption operating with the ions and TEOS xerogel. The collected data was analyzed by the linear form of the Langmuir, Freundlich, and Tempkin isotherm equations [16, 23]. The results in Table 1 show that the EAI data were best fitted in the Langmuir equation.

$$(C_e/q_e) = (C_e/Q^0) + 1/\, Q^0 b \qquad (7)$$

Where b is the equilibrium constant (L/mg) and Q^0 is the maximum adsorption capacity (mg/g) of the adsorbent.

Table 1. The Langmuir, Freundlich and Temkin isotherm equilibrium constants for Pb^{2+} and Cd^{2+} sorption on TEOS xerogel.

		Pb^{2+}	**Cd^{2+}**
Langmuir	Q^0 (mg/g)	58.82	35.71
	b (L/mg)	1.21	0.01
	R^2	1	0.99
Freundlich	K_F (L/g)	18.56	1.09
	n	0.30	0.46
	R^2	0.90	0.98
Tempkin	B (kJ/mol)	23.41	14.80
	A (L/g)	0.999	0.999
	R^2	0.96	0.99

The Langmuir model suggests a monolayer adsorption of the sorbate particles on the equal, non-cooperative adsorbing sites [17,21]. Monolayer adsorption has been reported for the cases where a chemisorption mechanism works between the adsorbent and the adsorbate [24]. Analysis of the EAI data with the Dubinin-

Radushkevich equation resulted in the mean free energy of sorption higher than 8 kJ/mol for both Pb^{2+} and Cd^{2+} (data is not shown here) which supports the assumption of the chemisorption mechanism [7, 25]. The Langmuir coefficient, b in Eq. (7), is the ratio of the adsorption to desorption rate. It is considered as an index for the affinity of the sorbent for the sorbate [26]. The data in (Table 1) suggest that TEOS xerogel has higher affinity for Pb^{2+} than Cd^{2+}. This can explain the larger adsorption capacity, Q^0, for Pb^{2+} as compared with that of Cd^{2+}. The TEOS xerogel adsorption capacity for Pb^{2+} and Cd^{2+} is higher than those obtained from the adsorption studies on the low cost materials, but they are lower than the Q^0 values reported for the engineered mesoporous materials [27]. María Martínez et al reported Q^0 values of 49.935 and 27.880 mg/g for the Pb^{2+} and Cd^{2+} respectively, using grape stalk waste as adsorbent [19]. Pagnanelli et al reported Q^0 values of 15.75 and 6.98 mg/g for Pb^{2+} and Cd^{2+} respectively, using olive pomace [28].

In contrast to the Langmuir, the Freundlich Model does not insist on monolayer adsorption. This model was developed to describe experimental data. The constants k_F and 1/n extracted from the linear form of the Freundlich Eq. (8) are empirical values indicating the sorption affinity and intensity, respectively [29].

$$\ln q_e = (1/n)\ln C_e + \ln K_F \qquad (8)$$

The K_F values in Table 1 have the same trend as seen for the b values, obtained from the Langmuir equation, confirming higher affinity of TEOS xerogel for Pb^{2+}. As mentioned, the 1/n is interpreted in terms of adsorption intensity. The 1/n parameter is also considered as an index of the adsorbent surface heterogeneity [30]. The closer the heterogeneity parameter is to unity, the more homogeneous is the adsorbent surface [7]. The more homogenous the surface, the stronger the binding interaction. The 1/n data in Table 1 is also in favor of more intense adsorption of Pb^{2+} than Cd^{2+} on TEOS xerogel.

The core idea in the Temkin isothermal adsorption model lays on the assumption that the heat of adsorption linearly rather than logarithmically decreases as more particles are adsorbed on the surface. This indirectly assumes the existence of independent and equal binding sites similar to what was suggested by Langmuir. However, the Temkin model pays attention to the changes in the heat of adsorption as seen in equation (9) [31].

$$q_e = (RT/b_T)\mathrm{In}(A_T C_e) \qquad (9)$$

R is the universal gas constant (8.314 J/mol.K) and T is the absolute temperature in K. A_T (L/g) is the Temkin isotherm equilibrium binding constant and b_T is the Temkin isotherm constant. The linear form of the equation is shown in Eq. (10):

$$q_e = \beta \mathrm{Ln} A + \beta \mathrm{Ln} C_e \qquad (10)$$

The $\beta = RT/b_T$ relates to the heat of adsorption. The β values in (Table 1) clearly disclose the stronger interaction of Pb^{2+} with the adsorbent as compared with that of Cd^{2+}. However, the β values of both ions are higher than 8 kJ/mol. This confirms that a chemisorption mechanism works between these divalent cations and TEOS xerogel. The strong interactions of Pb^{2+} and Cd^{2+} with TEOS xerogel can be explained by considering the net negative charge of the adsorbent surface which encourages the interactions between the hard acids (Pb^{2+} and Cd^{2+}) and the hard bases (the oxygen atoms in the binding sites) [32]. Since lead is more electronegative than cadmium, 2.23 versus 1.69, it produces stronger interactions with TEOS xerogel.

3.7. Kinetics adsorption of ions

Results of the kinetics of the Pb^{2+} and Cd^{2+} adsorption on TEOS xerogel were analyzed by the pseudo-first order, pseudo-second order, and intraparticle diffusion kinetic equations introduced in the experimental section. These results (Table 2) indicate that the kinetics data were best fitted in the pseudo-second order equation. It has been shown that the pseudo-second order equation can be applied in cases where chemisorption processes are the rate limiting step in the sorption mechanism. This is in agreement with the assumption concluded from the EAI results in this study. A monolayer ionic adsorption mechanism requires one-to-one interactions of the binding sites with the adsorbate particles. It is noteworthy that the pseudo-second order model was used for describing the adsorption of some divalent metal cations on peat where the EAI data was suitably fitted in the Langmuir isotherm model, indicating the existence of a chemiosorption mechanism [24].

Table. 2. Analysis of the kinetic studies on the adsorption of Pb^{2+}, Cd^{2+} on TEOS.

		Pb^{2+}	**Cd^{2+}**
Pseudo first order	q_t (mg/g)	18.17	3.36
	k_1 (min^{-1})	0.067	0.078
	R^2	0.86	0.87
Pseudo second order	q_t (mg/g)	71.43	15.38
	k_2 (g/mg.min)	0.02	0.08
	R^2	0.999	0.999
Intraparticle diffusion	K_i (mg/g.$min^{1/2}$)	5.15	1.23
	q_t (mg/g)	31.54	6.66
	R^2	0.49	0.54

The data in Table 2 suggests a four times higher kinetic constant for Cd^{2+} as compared with that of Pb^{2+}. This result can explain what was observed in Figure 3 where Cd^{2+} was able to inhibit the Pb^{2+} adsorption, but Pb^{2+} was not able to inhibit the Cd^{2+} adsorption, however, it had stronger interactions with TEOS xerogel. In view of the results illustrated in Figure 3, Table 1 and Table 2, it is assumed that the adsorption of these divalent cations on TEOS xerogel follows a chemisorption mechanism, but the reaction between Cd^{2+} and the adsorbent is kinetic controlled, while the reaction of Pb^{2+} with TEOS xerogel is thermodynamic controlled. In a mixture of Pb^{2+} and Cd^{2+}, cadmium needs lower activation energy to interact with the adsorbent, so it occupies the binding sites faster and inhibits Pb^{2+} adsorption.

There is no doubt that the random polymerization of the silanols in the sol state forms a sieve structure consisting of pores with various sizes and accessibility. It is known that the structural heterogeneity is further increased during drying a sol-gel to xerogel as some more unbounded silanols fall in cross-binding and shrink the xerogel skeleton [2]. To see how the sieve structure of TEOS xerogel affects the kinetics of these divalent cations, the results were also analyzed by the intraparticle diffusion equation. The results in Table 2 show that the kinetic data did not fit well in equation (6). This means that the sieve structure of TEOS xerogel did not produce diffusion barriers for either of the ions examined in this study.

The analysis of the gas adsorption results by the BET Eq. (3), suggested an average surface area of 316.80 m^2/g and pore size value of 20.82 A for TEOS xerogel (graphs and equations are not shown here). Considering the empirical atomic radii of lead and cadmium, 180 and 155 A respectively, it is assumed that both of Pb^{2+} and Cd^{2+} have access to the binding sites in the sieve structure of TEOS xerogel without confronting a diffusion barrier during adsorption.

4. Conclusion

The surface charge of the classical xerogels such as TEOS xerogel works as a strong driving force for adsorption of divalent cations. The adsorption proceeds without being disturbed by the presence of mono-valent cations. The nanoporous structure provides TEOS xerogel with high capacity for the adsorption. Although the divalent cations adsorption obeys a chemisorption mechanism, the physicochemical properties of the cations influence the kinetic and thermodynamic of the process.

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