Removal of Pb(II) from Water using Al_2O_3-SiO_2 Nanoparticles

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ABSTRACT

In this study, Al_2O_3-SiO_2 nanoparticle by the weight ratio 50:50 of Al_2O_3/$SiO_2$was studied to obtain an effective adsorbent for the removal of Pb(II)ion from aqueous solution. In this research, a simple ,economic and environment-friendly method has been presented for the preparation of Al_2O_3-SiO_2 nanoparticle via sol-gel method. The structure of prepared nanoparticle was characterized by FTIR, BET, SEM, XRD and EDX. The SEM analysis shows that the average size of the particles is about 40 nm and BET analyzer data shows that the average pore size and surface area of the material are 4.9522 nm and 163.58 m^2/g respectively. Various factors influence the adsorption of Pb(II) ion such as contact time, the amount of adsorbent and pH value of the solutions which were investigated by batch experiments. The adsorption was fast; nearly 98% of Pb (II) could be removed within 10 min. The equilibrium data was applied to Langmuir, Freundlich, Tempkin, isotherm models. Adsorption isotherm fitted well by Freundlich model. The maximum adsorption capacity is 37.03 mg/g at pH = 8.0. Kinetics data revealed that the overall adsorption process followed pseudo-second-order. This study proves that Al_2O_3-SiO_2 nanoparticle was an effective adsorbent for removal of Pb(II) ion from aqueous solutions.

Key Words: Al_2O_3-SiO_2 nanoparticle, Adsorption, Pb(II), Isotherms, Kinetic.

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INTRODUCTION

One of the main concerns of environmental and health sciences is the protection of human nutrition from heavy metal contamination. Heavy metals are not biodegradable and, even at low concentration, tend to accumulate in thehuman body, causing numerous diseases and damages to organs such as the kidneys, liver and lungs [1]. Harmful health effects of lead are well-documented. It may cause a range of physiological disorders from neuropsychologic dysfunction (headaches, hearing problems, learning disabilities, behavioral problems, pate damages, etc.) to death [2] So far, several extraction methods such as co-precipitation [3],solvent extraction [4], electrolysis [5] and solid phase extraction[6، 7] have been developed to extract heavy metal ions. Solid phase extraction (SPE), with different organic and in organic adsorbents, has been extensively used to preconcentrate and extract heavy metals from different samples. Among the adsorbents used in SPE, biomaterial [8، 9], magnetic nanoparticle [10], gold nanoparticle [11], and nanocomposite material [12، 13] have gained more consideration. Here, we have demonstrated the use of SiO_2–Al_2O_3 mixed-oxides. SiO_2–Al_2O_3 mixed oxides or their composites are widely used as catalysts and ceramic materials [14-21]. Clay minerals [14], zeolites [15، 19],mullite [17], and SiO_2–Al_2O_3 catalysts [14-21] are examples of materials where the Al - O -Si bond structures orSiO_2–Al_2O_3 interfaces control their final proficiency for the desired application. The reason for choosing these particular mixed oxides was their unique properties such as low thermal expansion and conductivity, low dielectric constant, excellent creep resistance, robust chemical and thermal stability, good high-temperature strengthand oxidation resistance [20]. Although, we have found out that the SiO_2–Al_2O_3nanoparticle was ineffective as a support in catalytic activity, since it is a synthesized nanoparticle with good porosity and special surface,it could help us to study the adsorption process better [16،

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18-21]. Arshadi et al. used it for the adsorption of toxic colorsof water [22].The aim of this work is to study the adsorption efficiency of Pb(II) ion from aqueous solutions using nanoparticle SiO_2–Al_2O_3 under batch conditions. The adsorption kinetics of metals, contact time, adsorbent dosage and pH effect are investigated. Langmuir ،Freundlich, and Temkin adsorption isotherms have been determined and the mechanism of adsorption of Pb(II)ion on the adsorbent has been discussed.

Experimental

Al_2O_3-SiO_2 nanoparticles xerogel powder with values of 50 and 50 wt% alumina to silica were prepared according to the following steps.

In the first stage, appropriate amount of 16 ml of H_2O and 18 ml of C_2H_5OH were mixed, and then 5.0 g of $AlCl_3$.$6H_2O$ was dissolved in the mixture, while stirring was done for about 30 min for complete hydrolysis.

In the second stage, 5.3 ml of TEOS was added to a mixture comprising 1.7 ml H_2O and 22.25ml C_2H_5OH. The mixed solution was continuously stirred for about 90 min at 50°C and then cooled to room temperature.

Finally, in the third phase, the silica sol and alumina sol were mixed together at room temperature, and then a desired amount of 11.76 ml propylene oxide (PO) was poured into the solution. The mixture was stirred for 10 minutes and allowed to stay at room temperature for 2 hours. The gel was aged at room temperature for one day and then dried at 60 ° C for 24 hours and heated to a furnace at 3 ° C / min for 2 hours at a final temperature of 600 ° C to reach Powder body.

MATERIALS AND EQUIPMENT

All the chemicals are of analytical grade and used directly without any further purification. TEOS and aluminum chloride ($AlCl_3$, $6H_2O$), lead (II) nitrate [Pb $(NO_3)_2$, $6H_2O$], propylene oxide (PO) and ethanol were purchased from Merck. Co, Germany. In the synthesis stages, deionized distilled water was used. X-ray spectroscopy was carried out using X-ray diffraction device (Philips) equipped with copper lamp(Cu-Ka).Fourier transform Infrared spectroscopy (Japan−FT−IR−JASCO−410) was employed to detect the chemical structure of the samples. SEM (JEOL, JSM 6390LV, Japan) with EDX (JEOL, JSM-6480LV) detection was used to determine surface morphology and the qualitative element composition of the material at an accelerating voltage of 20 kV. The surface area of the nanoparticles was determined by Brunauer–Emmett–Teller (BET) flame photometer technique using an atomic absorption spectrophotometer (Shimadzu AA-680).

Adsorption experiments of Al2O3–SiO2 nanoparticle

The Al_2O_3–SiO_2 nanoparticle were used as adsorbent for the removal of lead ion from aqueous system. A stock solution (1000ppm) of lead ion was prepared by dissolving the exact amount of Lead in deionized water. The solution with the desired concentration was prepared by successive dilutions of the stock solution. We have studied the effect of pH (3.0–9.0), sorption kinetics time (10–70 min) and adsorption isotherms (initial concentration 20–100 mg/L) of metal ion while analyzing adsorption behavior of the nanoparticle (100 mg in 25 ml of solution of metal ion at different concentration). The pH was maintained at 8.0 in all conditions. The contact time was maintained at 10 min for the adsorption experiments. After reaching the equilibrium, the residual concentration of the metal ion inthe aliquot was determined by atomic absorption spectroscopy (AAS). Adsorption data obtained in this experimental study was evaluated with Freundlich, Temkin and Langmuir isotherms models.

DISCUSSION AND CONCLUSION

Examination of X-ray diffraction pattern

XRD patterns of Al_2O_3–SiO_2 nanoparticle sample with 50:50weight ratio Al_2O_3/SiO_2 shown in Fig. 1. The broad XRD peak detected around 2theta = 23 for sample indicates an amorphous Al_2O_3–SiO_2 structure. It is then concluded that Al_2O_3–SiO_2 materials prepared are mainly of amorphous nature of a random arrays of silica and alumina tetrahedral structures interconnected over three dimensions.

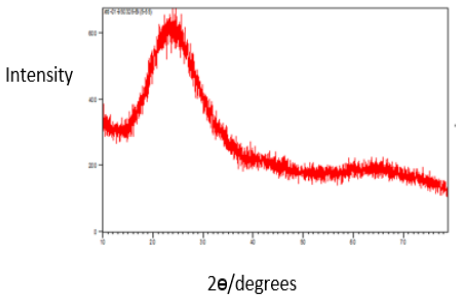

Fig. 1. X-ray diffraction patterns of the prepared Al2O3–SiO2 nanoparticle.

Studying FT-IR spectrum

The FTIR spectra analysis was recorded between 4000 $cm^{-1}$and 400 cm^{-1}. Fig. 2 presents the FTIR spectra of Al_2O_3–SiO_2 nanoparticle calcined at 600C°. The bands at 3400–3600 $cm^{-1}$and a peak at 1664 cm^{-1}identified the bending modes of residual water in the samples.

All the Al–O and Si–O related vibrations appear only in the region of 1200–400 cm^{-1}.

The band at around 1080 cm^{-1} is due to the asymmetric stretching vibration of (Si/Al)O_4 units of Si/Al mixed oxides.

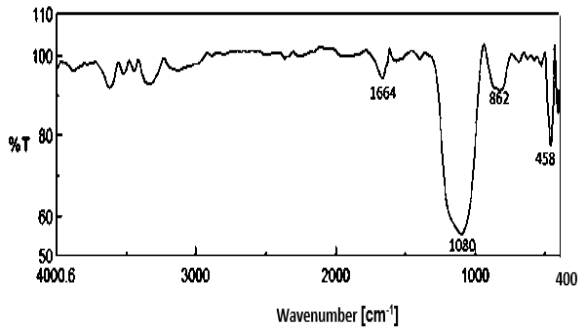

Fig. 2. FT-IR spectra of the prepared Al2O3–SiO2 nanoparticle.

X-ray analysis SEM–EDX

Fig. 3 shows the SEM images of Al_2O_3–SiO_2 nanoparticle at 600 C° with analysis EDX. The morphology showed that the nano composite is spherical with a smooth surface. The average particle size was found in the range of 30–40 nm based on the SEM analysis (Fig. 3a). The SEM elemental detection X-ray analysis (SEM–EDX) clearly suggests the presence of aluminium, silicon and oxygen elements (Fig. 3b).

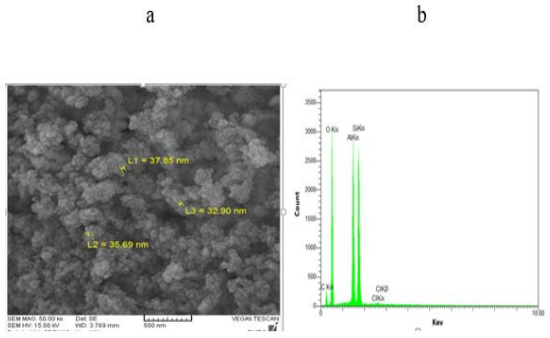

Fig. 3. SEM micrograph of Al2O3–SiO2 nanoparticle (a) and EDX analysis (b)

Porosity study

Nitrogen absorption and desorption test were used to evaluate porosity type, specific surface area and pore volume. Fig. 4 shows the nitrogen sorption isotherm which was synthesized with weight ratio of aluminum to silica 50:50 and calcined at 600 ° C.

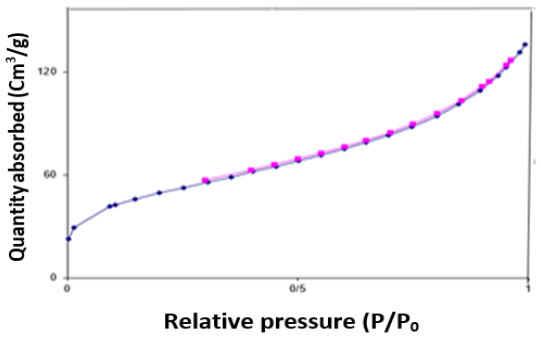

Fig. 4. Nitrogen sorption isotherm of Al2O3–SiO2 calcined at 600C°.

In the case of Al_2O_3–SiO_2nanoparticle, the curve includes type IV curve with type H_1 hysteresis loop in the IUPAC classification, which is a characteristic of a mesoporous structure with cylindrical pores [23، 24]. The desorption cycles of the isotherms show a hysteresis loop, which is generally attributed to the capillary condensation that occurs in the mesopores [25].The hysteresis loop is usually associated with filling and emptying of mesopores through capillary condensation.

Table 1. Adsorption data derived from adsorption–desorption isotherm for Al_2O_3–SiO_2 nanoparticle using BET methods

Sample	SBET (m2/g)	Average pore diameter (nm)	Pore volume(cm3/g)
Al_2O_3–SiO_2	168.58	4.9522	0.2086

The pore size distribution study was obtained from the BET method [26، 27]. Fig. 4. Table 1 summarizes specific surface area, pore size distribution and total pore volume results for nanoparticle silica- alumina calcined at 600 °C .The results show that the prepared solid nanoparticle is an efficient adsorbent.

Effect of the pH

The pH is an important parameter for adsorption of metal ions from aqueous solution as it affects the solubility of the metal ions, concentration of the counter ions on the adsorbent and the degree of ionization of the adsorbate during the reaction. The pH also strongly influences the adsorption availability of heavy metals [28، 29]. To study the effect of this parameter on metal sorption by mixed oxide nanoparticle, A 30mg sample of adsorbent was suspended in 25 mL solution of 20 mgL^{-1}Pb(II) ion, which contains 5.0 mL of buffer solution (pH 3.0, 5.0, 7.0, 8.0 and 9.0) and shaken (150 rpm) at room temperature in an automatic shaker for 30.0 min. After reaching the adsorption equilibrium, the suspensions were separated and the residual metal concentrations were analyzed.

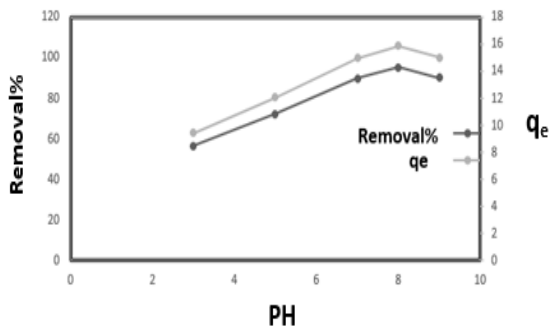

Fig. 5. The effect of pH on the removal efficiency and sorption capacity.

Fig. 5 shows that the maximum percent removal of Pb (II) ion by the adsorbent was observed at pH 8. This parameter was important because the pH of solution influences the distribution of active sites on the surface of nano composite Al_2O_3–SiO_2. At lower pH, the concentration of H^+ ion is high causing a competition for vacant adsorbent sites between the H^+ ion and metal ions. Therefore, at low pH, the removal efficiency is low. This result is consistent with the results obtained by Boudrahem et al. [28]. At the higher pH, the OH^-on the surface of Al_2O_3–SiO2nanoparticle provides the ability of binding cations. The decrease in pH leads to the neutralization of surface charge, and OH^- is displaced from the surface. Therefore pH 8.0 was considered as optimum condition for adsorption of Pb (II) ion. The results show that by increasing pH from 3 to 8for Pb (II) the removal efficiency increased from 56.70% to 95.25% and the adsorption capacity increased from 9.45 to 15.87 mg g^{-1} showing that the most percentage of adsorptionis related to pH 8.0.

Effect of the amount of adsorbent

We studied the dependence of the adsorption of Pb (II) ion on the amount of Al_2O_3–SiO_2nanoparticle at room temperature and pH 8.0 by varying the adsorbent amount from 30 to 500mg in presence 25 ml solution of the mixture of 20 mg L^{-1}Pb (II) ion. The suspension was then shaken (150 rpm) at 25 °C for 30 min. After reaching the adsorption equilibrium, the suspensions were separated and the residual metal concentrations were analyzed. The results are shown in Fig. 6. The adsorption reached a maximum with 100 mg of the adsorbent for Pb (II) ion, and the maximum percentage removal was about 96% for Pb ion.

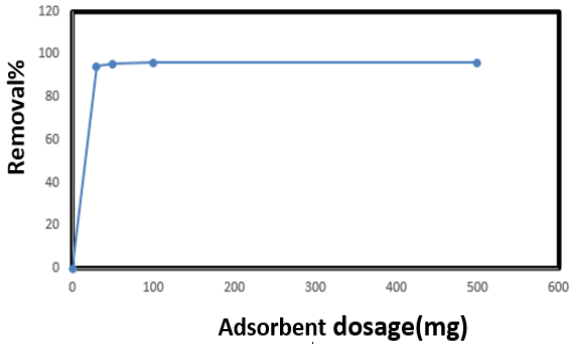

Fig. 6. Percentage removal of Pb (II) ion at different amounts of adsorbent.

Effect of contact time

The effect of time on the removal of metal ions by Al_2O_3–SiO_2nanoparticle was also studied. Fig. 7 shows the removal of metal ions with contact time. The selected nano-sorbent (100mg) was mixed with 25.0 mL of 20 mg L^{-1} of the Pb(II) ion, at pH 8.0, in a 50.0 mL measuring flask, and shaken for different selected time intervals (10.0 ,30.0, 50.0, and 70.0 min). The procedure of combination of nano-sorbent with adsorbed metal ion was completed as described above.The removal efficiency of lead ion reached the maximum value after 10 min and then decrease was observed for contact times of up to 70 min. This may be because initially all adsorbent sites were vacant and the solute concentration gradient was high. Therefore, the optimum contact time for adsorption of the lead ion was considered to be 10 min.

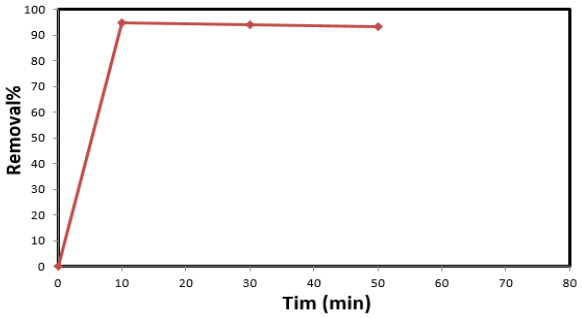

Fig. 7. Percentage removal of Pb(II) ion at different times.

Adsorption isotherm study

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. Adsorption isotherm is important to describe how solutes interact with the sorbent. Developing an appropriate isotherm model for adsorption is essential to the design and optimization of adsorption processes. Several isotherm models have been developed for evaluating the equilibrium adsorption of

compounds from solutions, such as Langmuir, Freundlich, Redlich–Peterson, Dubinin–Radushkevich, Sips, and Temkin [30]. The sorption behavior of the Al_2O_3–SiO_2 for Pb(II) were evaluated by analyzing Langmuir, Freundlich, and Temkin isotherm. The concentration for these studies was increased in the range of 20-100 mg L^{-1} for Pb(II) .The Pb(II) adsorbed at equilibrium (qe) was calculated by the following equation:

$$qe = V(C_\circ - Ce) / M$$

where V is the volume of solution (L) and M is the dry mass of adsorbents (g); $C_\circ$ and Ce are the initial and equilibrium concentration of Pb(II) in solution (mg/L), respectively.

The Pb(II) removal efficiency (g) was calculated through the following equation:

$$\%\, Removal = (C_\circ - Ce) / C_\circ \times 100$$

The Langmuir equation [31] was used to describe the effect of metal concentration at constant temperature on the adsorption capacity.

$$Ce/q_e = Ce/q_m + 1/(b\, q_m)$$

Where Ce is the equilibrium concentration of the adsorbate (mgL^{-1}), qe is the amount of metal ion adsorbed (mgg^{-1}), and q_m and bare Langmuir constants related to the maximum adsorption capacity (mgg^{-1}) and the adsorption energy, respectively. The Langmuir equilibrium constant, K_L, can be obtained from:

$$K_L = q_m.b$$

The essential characteristics of the Langmuir isotherm can alsobe expressed in terms of a dimensionless constant of separation factor or equilibrium parameter, R_L, which is a dimensionless quantity and is calculated to predict effectiveness of adsorption by using the following equation:

$$R_L = 1/(1 + bC_0)$$

where b is the Langmuir constant and C_0 is the initial concentration Pb (II) ion. The R_L value indicates the shape of isotherm[32]. R_L values between 0 and 1 indicate favorable adsorption, while R_L>1, R_L = 1, and R_L = 0 indicate unfavorable, linear, and irreversible adsorption isotherms.The linear form of the Langmuir isotherm is shown in Fig8.

The Freundlich equation is defined as: [33]

$$\log q_e = logK_F + \frac{1}{n}\log Ce$$

where K_F and n represent the equilibrium constants in dicative of the adsorption capacity and adsorption intensity, respectively (if n>1, the adsorption is considered favorable) .

The linear Freundlich isotherm plot for the sorption of the Lead ion onto nanoparticle is shown in Fig. 8.

Table 2 shows the linear Freundlich sorption isotherm constants and coefficients of determination (R^2). Based on the R^2 values, the linear form ofthe Freundlich isotherm appears to produce a reasonable model for sorption lead, the adsorption isotherm data for the lead ion was better with Freundlich isotherm as compared to Langmuir isotherms, which were determined by the correlation coefficients (R^2) in Table 2.

The maximum adsorption capacity (q_m) calculated by Langmuir isotherm has been shown in Table 2. The maximum adsorption capacities for Pb(II) are 37.03.

The adsorbent-adsorbate interaction was related to heat of adsorption of metal ions described by Temkin isotherm model:

adsorption of metal ions described by Temkin isotherm model:

$$q_e = AlnK_T + AlnCe$$

$$A = {RT}/{b}$$

where constant b (J/mol) is the variation of adsorption energy and K_T is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. Temkin isotherm constants calculated from slope and intercepts of the plot q_e versus ln Ce were listed in Table 2. In the Temkin isotherm model heat of adsorption drops linearly because of adsorbent-adsorbate interaction which can be interpreted from good correlation coefficient.

Table 2. Parameters driven from different isotherm models for Pb(II) sorption by Al_2O_3-SiO_2nanocmposite.

Isotherm models	Parameters	Pb(II)
Langmuir	q_m (mg/g)	37.03
	b (L/g)	0.003
	R^2	0.8219
	R_L	0.943
Freundlich	K_F(mg/g)	7.18
	n	1.677
	R^2	0.9729
Tempkin	A (J/mol)	6.776

	K_T	3.324
	R^2	0.884

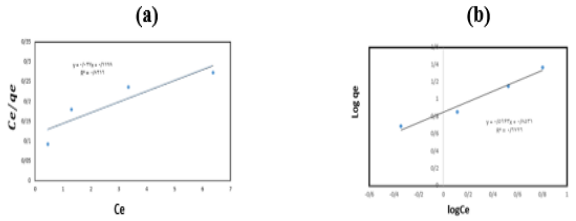

Fig. 8. Langmuir adsorption isotherm Al_2O_3–SiO_2 nanoparticle using Pb(II) (a). Freundlich adsorption isotherm of Al_2O_3–SiO_2 nanoparticle using Pb(II) (b) at room temperature

Study of the adsorption kinetics

The adsorption kinetics of metal ions with mixed oxide nanoparticle was investigated by two kinetics models: Lagergren pseudo-first-order and pseudo-second-order models, for Eqs. (4) and (5), respectively [34].

Pseudo-first-order model is a simple kinetic analysis of adsorption in the form of

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad (4)$$

Pseudo-second-order model:

$$t/q_e = 1/(K_2 q_e^2) + 1/q_e\, t \quad (5)$$

where q_t (mg/g) is the adsorption at time t (min), q_e (mg/g) is the adsorption capacity at adsorption equilibrium and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the kinetic rate constants for the pseudo-first-order and the pseudo-second-order models, respectively. The adsorption kinetic data was fit to Eqs. (4) and (5), and the calculated results are shown in Table 3. Psuedo-first order and pseudo-second order plots are shown in Fig. 9. The correlation coefficients (R^2) for the pseudo-second-order adsorption model were all higher than of the pseudo-first-order Table 3 shows the different parameters of kinetics study, where we observe that the experimental value of adsorption capacity (q_e, mg/g) is also in agreement with the theoretical pseudo-second order kinetics (q_e, mg/g) model.

model. Therefore, the adsorption data well obeyed the pseudo-second-order kinetic model.

Table 3. Kinetics parameters for adsorption of Pb (II) ion on Al_2O_3–SiO_2 nanoparticles

Sample	Pseudo-first order reaction			Pseudo-second order reaction		
	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2	R^2
Pb(II)	65.350	0.153	0.6324	91.7	0.023	1.0

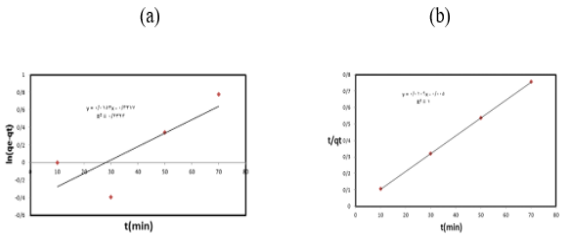

Fig. 9. Kinetic study of Pb(II) (a) psuedo-first order model and (b) psuedo-second order model.

Comparison of adsorption property

The adsorption properties of the Al_2O_3–SiO_2 nanoparticle to Pb(II) are compared with other reported adsorbents. The results are listed in Table 4. This demonstrates that the Al_2O_3–SiO_2 nanoparticle a good adsorbent for the removal of Pb(II) from aqueous solutions.

Table 4. Comparison of the maximum monolayer adsorption (q_m) of Pb (II) onto various adsorbents

Adsorbents Pb(II)	removal q_m (mg/g)	Reference
Al2O3–Fe2O3	23.75	[35]
Activated carbon-zeolite composite	2.65	[36]
Fe_3O_4-GS	27.95	[37]
thiol-SNHSi	17.15	[38]
Si-APTS-EDTA	7.15	[39]
Albumin-functionalized	15.15	[40]
Carbon nanotubes	17.4	[41]
Al_2O_3–SiO_2	37.03	This research

CONCLUSIONS

Al_2O_3–SiO_2 nanoparticle was successfully prepared. XRD analysis of the calcined Al_2O_3–SiO_2 nanoparticle at 600˚C indicates an amorphous silica–alumina structure. The morphology of the composites showed that the nanoparticle is spherical and the surface of the spherical nanoparticle is smooth and the average particle size was found in the range of 30-40 nm based on the SEM analysis. The EDX analysis of porus Al_2O_3–SiO_2nanoparticle suggests the presence of Si, Al and O elements, indicating the formation of Al_2O_3–SiO_2nanoparticle. The BET surface area and pore diameter were found to be 168.58 m^2/g and 4.9522 nm. The obtained porous Al_2O_3–SiO_2nanoparticle was able to remove Pb(II) from aqueous solutions. From the fact that equilibrium data fit well to Freundlich adsorption isotherm (R^2 = 0.9729) indicating a typical multilayer sorption and adsorbent-adsorbate interaction from Temkin isotherm model. The adsorption kinetics could be explained by pseudo-second-order model. The results showed that the prepared Al_2O_3–SiO_2nanoparticle was the best choice for Pb(II) ion

adsorption. Thus prepared Al_2O_3–SiO_2nanoparticle was used as a suitable adsorbent for adsorption studies of heavy metal including lead ion.

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