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Surface modification of glass beads with glutaraldehyde: Characterization and their adsorption property for metal ions

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ABSTRACT

In this study, a new material that adsorbs the metal ions was prepared by modification of the glass beads surfaces with glutaraldehyde. First, the glass beads were etched with 4 M NaOH solution. Then, they were reacted with 3-aminopropyl-triethoxysilane (APTES). Finally, silanized glass beads were treated with 25% of glutaraldehyde solution. The characterization studies by using Fourier Transform Infrared Spectroscopy (FT-IR), Thermal Gravimetric Analysis (TGA), elemental analysis and Scanning Electron Microscopy (SEM) indicated that modification of the glass beads surfaces was successfully performed. The adsorption studies exhibited that the modified glass beads could be efficiently used for the removal of the metal cations and anion (chromate ion) from aqueous solutions via chelation and ion-exchange mechanisms. For both Pb(II) and Cr(VI), selected as model ions, the adsorption equilibrium was achieved in 60 min and adsorption of both ions followed the second-order kinetic model. It was found that the sorption data was better represented by the Freundlich isotherm in comparison to the Langmuir and Redlich–Peterson isotherm models. The maximum adsorption capacities for Pb(II) and Cr(VI) were 9.947 and 11.571 mg/g, respectively. The regeneration studies also showed that modified glass beads could be re-used for the adsorption of Pb(II) and Cr(VI) from aqueous solutions over three cycles.

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1. Introduction

The treatment of waters containing heavy metals is a great concern because of their high toxicity to plants, animals and human beings [1]. Various methods, such as chemical precipitation [2], ion exchange [3,4], membrane processes [5–8], and adsorption [9–11], etc., have been used for the removal of the heavy metal ions from aqueous solutions. Among these methods, adsorption has increasingly received more attention in recent years because it is simple, relatively low cost and effective especially for medium or low metal ion concentrations [12–14].

Among different adsorbents, inorganic supports modified with both inorganic and organic functionalities have been used in various areas, notably in metal ion preconcentration [15,16], ion exchange [17], and different engineering applications [18]. Recently, glass beads have been used as supporting material for surface modification due to their arbitrarily controllable and narrow size dispersion, mechanical strength and low cost [19]. Modification of glass beads can be achieved by chemisorption of the active species onto the etched glass beads surface. General procedure used for the surface modification of inorganic support material (i.e., silica gel, etc.) has been described in the literature [20].

The aim of this work was to prepare a new adsorbent by modification of the glass beads with glutaraldehyde (GA) for the removal of the heavy metal ions from aqueous solution. The modification of the glass beads was performed by treatment of etched glass beads with silane coupling agent (3-aminopropyl-triethoxysilane (APTES)) and glutaraldehyde (GA), respectively. The product (modified glass beads) was characterized by using the Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FT-IR) spectroscopy, elemental analysis and Thermal Gravimetric Analysis (TGA). After observing the feasibility for the adsorption behavior of modified glass beads for various metal cations and anion (chromate ion) from aqueous solution, the detailed adsorption experiments were carried out for Pb(II) and Cr(VI) ions as cationic and anionic model ions.

2. Materials and methods

2.1. Materials

Glass beads (average diameters of $9-13\,\mu m$) and APTES were supplied from Aldrich (Germany). Glutaraldehyde (25% solution in

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water), hydrochloric acid, potassium chromate, chromium(III) chloride, copper(II) chloride, nickel(II) chloride, zinc(II) chloride, lead(II) chloride, cobalt(II) chloride and sodium chloride were of analytical grade and obtained from Merck (Darmstadt, Germany). All aqueous solutions were prepared with ultra pure water obtained from a Millipore Milli-Q Plus water purification system.

2.2. Surface activation of glass beads

Prior to silanization, the glass beads (50g) were etched in 4M NaOH solution (200 mL). The suspension was refluxed at 100 °C for 15 min. Then, it was poured into ultra pure water (800 mL) at room temperature. The etched glass beads were filtered through a Whatman No. 42 filter paper (particle retention $2.5 \,\mu m$) using a filtration set that consisted of a vacuumed nuche Erlenmeyer. The residue on the filter was washed with ultra pure water until neutralization without any loss of glass beads and dried in a vacuum oven at 120 °C for 24 h.

2.3. Silanization of glass beads

The etched glass beads (10g) were transferred into a 300 mL capacity of flask containing dried toluene (20 mL) and nitrogen was bubbled through the mixture. Then, APTES (6 mL) was added to the slurry and the mixture was stirred at 80 °C overnight under nitrogen atmosphere. The glass beads were filtered and washed with toluene (40 mL), dichloromethane (40 mL), and acetone (40 mL), respectively. Finally, silanized glass beads (APTES-glass beads) were dried at room temperature for 24 h.

2.4. Surface modification of APTES-glass beads with glutaraldehyde

The APTES-glass beads (10 g) were suspended in aqueous 25% of GA solution (33 mL) and stirred at 25 °C for 4 h. After filtration of the suspension, the residue was washed with methanol (40 mL) and dried under vacuum at 80 °C for 24 h to obtain the glutaraldehyde-APTES-glass beads (GA-APTES-glass beads).

2.5. Characterization of GA-APTES-glass beads

TGA of the samples (15–17 mg) was performed with Seteram thermal gravimetric analyzer at temperature range of 25-800 °C with 10°C/min heating ramp in argon atmosphere (gas flow rate: 20 mL/min). The surface morphology of samples was examined by SEM (Jeol, JSM 5310, Japan). FT-IR analysis was carried out by a single channel Fourier transform spectrophotometer (PerkinElmer 1605). The samples were pressed in KBr pellets and FT-IR spectrums were obtained at wave number between 4000 and 400 cm⁻¹ with a resolution of 2 cm^{-1} . Elemental analyses of the samples were performed by using Leco TruSpec® C/N analyzer (USA).

2.6. Adsorption studies

The adsorption behavior of the GA-APTES-glass beads for various metal cations (Pb²⁺, Cu²⁺, Ni²⁺, Co²⁺, Cd²⁺, Cr³⁺, Zn²⁺) and anion (CrO_4^{2-}) was investigated by means of the batch experiments at 25 °C. GA-APTES-glass beads (0.02 g) were mixed with 20 mL of the corresponding aqueous metal ion solutions (25 mg/L) over a period of time on a shaker at 220 rpm. Then, the concentration of metal ion in each filtered solution was determined by using an atomic absorption spectrometer (ContrAA 300, Analytikjena). The amount of metal ion adsorbed was calculated according to Eq. (1).

$$q = \frac{(C_o - C_e)V}{m} \tag{1}$$

1660 4000 3600 3200 2800 2400 2000 1600 1200 800 400

Fig. 1. FT-IR spectrum of etched glass beads (A), APTES-glass beads (B) and GA-APTES-glass beads (C).

where q is metal ion adsorbed (mg/g); C_0 is initial concentration of metal ion (mg/L); C_e is concentration of metal ion in solution at equilibrium (mg/L); V is solution volume (L); m is the amount of GA-APTES-glass beads (g).

The adsorption of both Pb(II) and Cr(VI) ions by GA-APTES-glass beads was investigated at pH range of 1.21-4.75 and 1.02-6.21, respectively. The solution pH was adjusted by 0.1 M NaOH or 0.1 M HCl. Ionic strength of the solutions was adjusted to 0.01 M with KNO₃. The effects of contact time (5–240 min), initial metal concentration (5-250 mg/L) and amount of adsorbent dosage (0.5-8 g/L)were also investigated for both Pb(II) and Cr(VI).

3. Results and discussion

3.1. Characterization of GA-APTES-glass beads

3.1.1. FT-IR spectrums

FT-IR spectrums of the glass beads (Fig. 1) exhibited a Si-O-Si absorption band between 900 and 1170 cm⁻¹ which is assigned to silica network, and a strong band at 476 cm⁻¹ due to a Si-O-Si bending vibrational mode. The FT-IR spectrum clearly marked the presence of amide group at 3450 cm^{-1} (N–H stretching) and 1650 cm⁻¹ (N–H bending). The presence of the anchored propyl group was confirmed by C-H stretching vibrations appeared at 2930 cm⁻¹. The binding of GA on the APTES-glass beads was confirmed by a distinct peak at 1730 cm^{-1} , due to C=O stretching of aldehyde group (Fig. 1(c)). The -CO and -NH- groups can also be seen from Fig. 1 at around 1660 and 1469 cm⁻¹, respectively.

3.1.2. TGA analysis

The thermal stability of the glass beads, APTES-glass beads and GA-APTES-glass beads was evaluated by TGA and its 1st derivative (dTGA) (Fig. 2(a) and (b)). Upon heating in TGA, the glass beads showed a weight loss of about 3.07% at temperatures ranging from 50 to 250 °C, mainly due to the loss of physically adsorbed water on the material. The weight loss of APTES-glass beads was 4.65% at a broad temperature range of 50–250 °C. Similarly, between these temperatures, the weight loss of GA-APTES-glass beads was 11.14%. The weight loss (approx. 2.57%) of APTES-glass beads started at temperature range of 325-625 °C. The main degradation of APTES-glass beads occurred at 423 °C. GA-APTES-glass beads were more thermally stable than APTES-glass beads and showed two decomposing transitions at 264 and 431 °C. In addition, the major weight loss of GA modified glass beads was about 12.73% within the temperature range of 300-600 °C.





Fig. 2. TGA (a) and their first derivatives (b), of activated (etched) glass beads, APTESglass beads and GA-APTES-glass beads.

Table 1

 $Percentages\,(\%)\,of\, carbon\,(C)\, and\, nitrogen\,(N)\, content\, of\, the\, glass\, beads, APTES-glass\, beads\, and\, GA-APTES-glass\, beads.$

Surface	Carbon (%)	Nitrogen (%)	mmol/g
Glass beads	Not detected	Not detected	-
APTES-glass beads	14.14	1.53	1.30
GA-APTES-glass beads	22.09	1.54	1.33

3.1.3. Elemental analysis

Carbon and nitrogen elemental analyses showed a clear consistency with the increasing amount of silylating agent (APTES) on the surface of glass beads as shown in Table 1. It was also confirmed by the results that GA was covalently bonded on the surface of APTESglass beads. The APTES was introduced on the surface of glass beads with amount of 1.30 mmol/g. In addition, the GA was introduced on the surface of APTES-glass beads with amount of 1.33 mmol/g.

3.1.4. Scanning Electron Microscopy (SEM)

SEM images of the etched (activated), APTES-glass beads and GA-APTES-glass beads were given in Fig. 3(a)-(c), respectively. It can be seen that the surface modification was carried out successfully. It seems that the roughness was reduced after binding of GA on the surface of APTES-glass beads.

3.2. Adsorption capability

Table 2 demonstrates the feasibility for the adsorption behavior of the GA-APTES-glass beads for various metal cations and anion (chromate ion) from the aqueous solutions. The original glass beads (not modified) showed no adsorption capability for metal ions. However, GA-APTES-glass beads exhibited significant adsorption





Fig. 3. SEM images of activated (etched) glass beads (a), APTES-glass beads (b) and GA-APTES-glass beads (c).

Table 2

Adsorption of various metal ions from aqueous solution by GA-APTES-glass beads (concentration of each metal ion: 25 mg/L, pH of the cationic metal solutions was adjusted to 4.0 ± 0.1 , pH of the Cr(VI) solution was adjusted to 2.1 ± 0.1 , amount of GA-APTES-glass beads: 1 g/L, contact time: 2 h, shaking speed: 220 rpm, temperature: $25 \degree$ C, ionic strength: 0.01 M).

Metal ion	Adsorption, $%(n=3)$	
Cu(II)	73 ± 6	
Pb(II)	76 ± 3	
Ni(II)	71 ± 4	
Cr(III)	70 ± 5	
Co(II)	74 ± 8	
Cd(II)	72 ± 6	
Zn(II)	72 ± 3	
Cr(VI)	75 ± 3	



Fig. 4. Effect of pH on the adsorption of Pb(II) and Cr(VI) by GA-APTES-glass beads (concentration of both Pb(II) and Cr(VI): 25 mg/L, amount of GA-APTES-glass beads: 1 g/L, contact time: 2 h, shaking speed: 220 rpm, temperature: 25 °C, ionic strength: 0.01 M).

capability for metal ions. Thus, our attempt to develop a new adsorbent for metal ions was achieved and further adsorption studies were performed by using Pb(II) and Cr(VI) as cationic and anionic model ions.

The GA-APTES-glass beads produced from the dispersion of APTES-glass beads in 25% of GA solution for 4h were used in the experiments because dispersion time longer than 4h had no enhancing effect on the adsorption capacity of GA-APTES-glass beads for both Pb(II) and Cr(VI).

3.2.1. Effect of solution pH

The effect of solution pH on the adsorption of Pb(II) and Cr(VI) ions by the GA-APTES-glass beads was shown in Fig. 4. It was found that the adsorption capacity increased with increasing solution pH up to 4 for Pb(II) ion. This revealed the characteristic of chelation mechanism and might be attributed to the less significant competitive adsorption of hydrogen ions at higher pH [21,22].

From the pH dependence, the interactions between the solution and -CH=N- group of the GA-APTES-glass beads can be expressed by following the reactions (Eqs. (2) and (3)).

$$-CH=N-+H^{+} \rightleftharpoons -CH=NH^{+}-$$
(2)



Eq. (2) indicates the protonation and deprotonation reactions of the imine group of GA-APTES-glass beads in the solution and Eq. (3) represents the complex formation between Pb^{2+} ion and nitrogen of the imine group.

At lower solution pH, the protonation of -CH=N- was favored to form $-CH=NH^+-$ by the reaction in Eq. (2). If -CH=N- groups were converted into $-CH=NH^+-$, electrostatic repulsion between the Pb²⁺ and $-CH=NH^+-$ group of the adsorbent was occurred. Furthermore, at lower pH, decreasing the available -CH=N- group resulted in a decrease in the adsorption of Pb²⁺ as described in Eq. (3). With increasing solution pH, especially at pH \ge 4, the reaction in Eq. (2) proceeded to the left because the pK_a of $-CH=NH^+-$ is 4 [23]. This caused an increase in the number of -CH=N- sites, thus, increasing the adsorption of Pb²⁺ through Eq. (3) [24]. For solution pH above 5, adsorption experiments were not conducted because of Pb(OH)₂ precipitation.

Fig. 4 also illustrates the effect of solution pH on the adsorption of Cr(VI) by GA-APTES-glass beads. In contrast to Pb(II) ion, it was found that higher adsorption capacity for Cr(VI) was obtained at lower pH. It is known that Cr(VI) exists in various anionic forms (i.e., $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-} and HCr_2O^{7-}) in aqueous solution, depending on the pH and concentration. According to Ref. [25], Cr(VI) ions will exist as $HCrO_4^-$ in the aqueous solution under the experimental conditions of the present study.

A decrease in pH of the solution increases the electrostatic attraction between $-CH=NH^+-$ group and negatively charged Cr(VI) ion according to the anion-exchange mechanism as shown in Eq. (4). Hence, higher adsorption capacity for Cr(VI) was obtained.

$$-CH = NH^{+}/Cl^{-} + HCrO_{4}^{-} \rightarrow -CH = NH^{+}/HCrO_{4}^{-} + Cl^{-}.$$
 (4)

3.2.2. Effect of contact time and adsorption kinetics

The adsorption of Pb(II) and Cr(VI) as a function of contact time is shown in Fig. 5. It was observed that the sufficient time for the adsorption equilibrium of both Pb(II) and Cr(VI) was 60 min. The adsorption data was analyzed by using the pseudo-first-order and pseudo-second-order kinetic models.

The linearized form of pseudo-first-order rate equation is given as Eq. (5) [26].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 \cdot t}{2.303}$$
(5)

where q_e and q_t are the amounts of metal ion adsorbed (mg/g) at equilibrium and at time t (min), respectively. k_1 (1/min) is the adsorption rate constant of first-order adsorption.

The experimental data was also applied to the pseudo-secondorder kinetic model given as Eq. (6) [27,28].

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$$
(6)

where k_2 is the rate constant of pseudo-second-order chemisorption (g/(mgmin)). q_e and q_t are defined as the same as above.

For the studied concentration, the rate constants $(k_1 \text{ and } k_2)$ and theoretical equilibrium sorption capacities, q_e (calculated) were calculated from the slopes and intercepts of the linear plots of the pseudo-first-order and pseudo-second-order kinetic models and given in Table 3. It can be seen from the results that R^2 values obtained from the pseudo-second-order model are higher

598 Table 3

Metal ion	$q_e (\exp) (mg/g)$	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model			
		k ₁ (1/min)	q_e (cal) (mg/g)	<i>R</i> ²	$k_2 [g/(mgmin)]$	q_e (cal) (mg/g)	R^2
Pb(II) Cr(VI)	19.594 20.150	0.008 0.021	9.242 4.791	0.537 0.643	0.003 0.003	20.876 21.645	0.994 0.990



Fig. 5. Effect of contact time on the adsorption of Pb(II) and Cr(VI) by GA-APTESglass beads (concentration of both Pb(II) and Cr(VI): 25 mg/L, amount of GA-APTESglass beads: 1 g/L, pH of Pb(II) and Cr(VI) solutions: 4.0 and 1.0, respectively, shaking speed: 220 rpm, temperature: $25 \degree$ C, ionic strength: 0.01 M).

than those obtained from the first-order kinetics. Additionally, in comparison to the first-order kinetic model, theoretical and experimental q_e values of second-order model are in a good accordance with each other. Therefore, it is possible to suggest that the adsorption of Pb(II) and Cr(VI) by GA-APTES-glass beads followed the second-order type reaction kinetics.

3.2.3. Effect of initial concentration of metal ions and adsorption isotherm models

The effect of initial concentrations of Pb(II) and Cr(VI) on their sorptions was investigated by varying the initial metal concentrations at optimum pH values and 1 h of equilibrium time. For both Pb(II) and Cr(VI), an increase in the initial concentration increased the amount of the metal ion adsorbed. For example, the amount of Cr(VI) adsorbed was determined as 4.9, 20.5 and 64.1 mg/g, for initial concentrations of 5, 25 and 100 mg/L, respectively. Similar trend was observed for the adsorption of Pb(II). For the same initial concentrations, the amount of Pb(II) adsorbed was determined as 4.7, 18.8 and 56.2 mg/g, respectively. This increase in loading capacity of the adsorbent in relation with the concentration of the metal ions can be explained with the high driving force for mass transfer [11].

The experimental data was analyzed by using the Langmuir, Freundlich and Redlich–Peterson isotherm models.

The Langmuir isotherm models the monolayer coverage of the adsorption surfaces and assumes that adsorption takes place on a structurally homogeneous surface of the adsorbent. The linear form of the Langmuir isotherm model can be presented as in Eq. (7) [29].

$$\frac{C_e}{q_e} = \frac{1}{Q_o \cdot b} + \frac{C_e}{Q_o} \tag{7}$$

where C_e is the concentration of metal ion (mg/L) at equilibrium, Q_o is the monolayer capacity of the adsorbent (mg/g) and *b* is the

Langmuir adsorption constant (L/mg).

Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. Linearized form of the Freundlich equation is given by the following equation [30].

$$\log q_e = \log k + \frac{1}{n} \log C_e \tag{8}$$

where C_e is the equilibrium concentration (mg/L), k is the sorption capacity (mg/g) and n is an empirical parameter.

The Redlich–Peterson isotherm [31] has a linear dependence on concentration in the numerator and an exponential function in the denominator. It approaches the Freundlich model at high concentrations and is in accordance with the low concentration limit of the Langmuir equation. Furthermore, the Redlich–Peterson equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to its high versatility. Linearized form of the Redlich–Peterson isotherm is as follows:

$$\ln\left[\frac{K_R \cdot C_e}{q_e} - 1\right] = \ln a_R + \beta \ln C_e \tag{9}$$

where K_R is Redlich–Peterson isotherm constant (L/mg), a_R is also a constant (L/mg)^{β} and β is the exponent which lies between zero and one. This isotherm model involves varying the isotherm parameter, K_R , to obtain the maximum value of correlation coefficient (R^2) for the linear regression of $\ln C_e$ vs. $\ln[(K_R \cdot C_e/q_e) - 1]$.

The values of the isotherm constants were obtained from the slope and intercept of the plots of each isotherm (Fig. 6). The isotherm constants and R^2 values for each model are given in Table 4. When R^2 values are compared, it can be concluded that adsorption of Pb(II) and Cr(VI) by GA-APTES-glass beads can be better described by Freundlich isotherm model.

The Chi-square (χ^2) test was also employed in this study to find out the best-fit isotherm model for the adsorption data. The mathematical statement of the Chi-square test can be given by Eq. (10)

Table 4

Langmuir, Freundlich and Redlich–Peterson isotherm parameters for the adsorption of Pb(II) and Cr(VI) from aqueous solution by GA-APTES-glass beads.

Isotherm model	Metal ion	
	Pb(II)	Cr(VI)
Langmuir model		
$Q_o (mg/g)$	126.582	121.951
<i>b</i> (L/mg)	0.037	0.052
R^2	0.936	0.885
χ^2	25.88	42.06
Freundlich model		
k (mg/g)	9.947	11.571
n	2.032	2.170
R^2	0.984	0.979
χ^2	3.88	4.94
Redlich–Peterson model		
K_R (L/mg)	48.011	91.987
$a_R (L/mg)^{\beta}$	3.045	5.449
β	0.625	0.657
R^2	0.963	0.947
χ^2	10.66	21.81



Fig. 6. The Langmuir isotherm plot for Cr(VI) (a) and Pb(II) (b). The Freundlich isotherm plot for Cr(VI) (c) and Pb(II) (d). The Redlich-Peterson isotherm plot for Cr(VI) (e) and Pb(II) (f) (amount of GA-APTES-glass beads: 1 g/L, pH of Pb(II) and Cr(VI) solutions: 4.0 and 1.0, respectively, contact time: 1 h, shaking speed: 220 rpm, temperature: 25 °C, ionic strength: 0.01 M).

as follows [32]:

$$\chi^2 = \sum \left[\frac{\left(q_e - q_m\right)^2}{q_M} \right] \tag{10}$$

where q_m is the equilibrium capacity obtained by calculating from the model (mg/g), and q_e is experimental data of the equilibrium capacity (mg/g). Small number of χ^2 indicates that data from the model is close to the experimental data whereas, large number of χ^2 indicates that data from the model is different from the experimental data. According to the χ^2 values (Table 4), the best-fit isotherm model was the Freundlich isotherm model. In fact, for our experimental data, Redlich-Peterson model supported the Freundlich isotherm model. This result can be also inferred from the value of β in Table 4, which is lower than unity (<1) [33].

3.2.4. Effect of adsorbent dosage

The percentages of both Pb(II) and Cr(VI) adsorption with varying amounts of GA-APTES-glass beads are presented in Fig. 7. In general, an increase in adsorbent dosage increased the percent removal of adsorbate. This is consistent with the expectation that higher adsorbent dosages will result in lower q values. The concentration of -CH=N- group is related to modified glass beads concentration through surface site density [34]. Therefore, percent of adsorption increased with increasing dosage of GA-APTES-glass beads, whereas q decreased.

3.2.5. Regeneration and re-usability of GA-APTES-glass beads

0.1 M NaOH (50 mL) and 0.1 M HCl (50 mL) were used for desorption of Cr(VI) and Pb(II), respectively, from the loaded GA-APTES-glass beads. After desorption of each metal ion, the GA-APTES-glass beads were washed with distilled water until neutralization and then dried. The adsorption process was repeated by using the regenerated adsorbent. It was found that after 3 cycles there is no change in either Cr(VI) or Pb(II) sorption capacity of the GA-APTES-glass beads. In desorption experiments, it has been observed that almost total recovery of both Cr(VI) and Pb(II) occurs,



Fig. 7. The variation of Pb(II) and Cr(VI) removal with amount of GA-APTES-glass beads (concentration of both Pb(II) and Cr(VI): 25 mg/L, pH of Pb(II) and Cr(VI) solutions: 4.0 and 1.0, respectively, contact time: 1 h, shaking speed: 220 rpm, temperature: $25 \degree C$, ionic strength: 0.01 M).

suggesting that the modified glass beads are regenerable and can be used several times.

4. Conclusion

The following conclusions can be made from the presented study. The results from the FT-IR, TGA, SEM and elemental analyses of the glass beads before and after modification clearly indicated that surface modification was successfully performed.

The GA-APTES-glass beads exhibited significant adsorption capability for both metal cations and anion (chromate ion). The adsorption of Pb(II) and Cr(VI) by GA-APTES-glass beads was explained according to the chelation and ion-exchange mechanisms, respectively. The sufficient time for the adsorption equilibrium of both Pb(II) and Cr(VI) was 60 min. In addition, adsorption of both ions followed the second-order kinetic model. In comparison to the Langmuir and Redlich–Peterson isotherm models, the Freundlich isotherm model better represented the sorption data. The maximum adsorption capacities for Pb(II) and Cr(VI) were 9.947 and 11.571 mg/g, respectively. For 25 mg/L of both Pb(II) and Cr(VI), optimum adsorbent dosage was 8 g/L. The regeneration studies also showed that modified glass beads can be used several times for the adsorption of Pb(II) and Cr(VI) from aqueous solutions.

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