PHYSICOCHEMICAL PROCESSES
AT THE INTERFACES

Sorption of Heavy Metal Ions by Glass Beads-Immobilized Calix[4]arenes Derivative[1]

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Abstract—Glass beads (*GB*) immobilized, 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix[4]arene (*CA*) are prepared and used as a new sorbent in sorption study of removal heavy metal ions. A calixarene derivative bonded to amino-functionalized glass beads sorbent was synthesized via a self assembly technique for sorbent of selected heavy metal ions in aqueous. In order to absorb selected heavy metal ions in aqueous, a calixarene derivative bonded to amino-functionalized glass beads sorbent was synthesized via a self assembly technique. The sorbent which is named *GB-APTS-CA* was characterized using infrared (*FTIR*) spectroscopy, scanning electron microscopy (*SEM*), elemental analysis and thermal analysis (*TGA/DTG*). The influences of some experimental parameters including pH of the sample solution, weight of sorbent, concentration and temperature have been investigated. The sorption data were evaluated using the Langmuir, Freundlich and Dubinin Radushkevich (*D-R*) isotherm. The obtained maximum sorption capacity for Cu(II), and Pb(II) is 0.06 mmol g^{-1} and 0.02 mmol g^{-1}, respectively. Thermodynamic parameters such as the standard free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were calculated to determine the nature of sorption process. Thus, *GB-APTS-CA* is favorable and useful for the removal of Cu(II) and Pb(II) metal ions.

INTRODUCTION

In spite of the existence of too many studies nowadays in this subject, one of the most significant environmental problems is the growing discharge of metals from different industries into the soil, water and air. As it is the case for most of these metals, even in trace amounts their toxicity potential is too much that cannot be neglected [1]. The investigation of heavy metals at trace level in environment is one of the targets of analytical chemists, due to their important roles in our life. Recently, mechanically stable synthetic or natural inorganic solid matrices have been utilized in many applications, such as sorption of cations from aqueous and non-aqueous solvents [2], ion-exchange reactions [3], chemically bonded phase in chromatography [4], or catalytic reactions [5–6].

Calixarenes are such cyclic oligomers composed of phenol units and are very well known as attractive and excellent ionophores because they provide a unique three-dimensional structure with almost unlimited derivatization possibilities. Accordingly, calixarenes and its derivatives exhibit outstanding complex ability toward ions and organic molecules [7]. They have been successfully applied to the separation of cations and molecules in liquid chromatography [3].

In the present work glass beads were selected as immobilization matrix because of their excellent mechanical properties and, because they can be modi-

fied by including a variety of functional groups [8]. When compared to other potential immobilization material, glass beads have a large surface area, are chemically and biologically inert, can be sterilized, and have superior physical properties.) [9]. Moreover, this support has been used to obtain immobilized derivatives of calixarene derivative for selected metal ion removal. Nonporous glass beads have a very low density of silanol groups. For this reason we first etched surface of the glass beads with aqueous NaOH to increase density of the silanol, and then, by using a silane coupling agent introduced amino groups to the glass beads [10]. The modification of the glass beads was performed by treatment of etched glass beads with silane coupling agent 3-aminopropyl-triethoxysilane (APTS) and CA, respectively. The modified glass beads were characterized by using the scanning electron microscopy (SEM), fourier transform infrared (FTIR) spectroscopy, elemental analysis and thermal gravimetric analysis (TGA).

In this study, usefulness of GB-APTS-CA as a sorbent for the removal of selected divalent two heavy metals (Pb(II) and Cu(II)) is systematically evaluated. The aim of this paper is to enhance the sorption property of GB by immobilizing calixarene derivative onto its surface. In addition to this influence of process parameters such as sorbent weight, pH, metal concentration and temperature on the sorption properties is investigated.

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MATERIALS AND METHODS

Apparatus

FTIR spectra were recorded by a Perkin Elmer 100 FTIR spectrometer. Thermogravimetric curves were obtained on a Setaram Termogravimetrik Analyzer/Setsys analyzer at temperature range of 298–1073 K. Elemental analysis was performed with a Leco CHNS 932 microelementel analyzer. SEM was performed in a ZEISS EVO LS 10 SEM at accelerating voltage of 20 kV. Before scanning process, all samples were dried and coated with gold to enhance the electron conductivity. Selecta-Ivmen 100D thermostatic shaker was used for the sorption experiments. Metal concentration of the supernatant was determined by a flame atomic absorption spectrometer (ContrAA 300, Analytikjena). The pH value was monitored with Jenway 3010 model digital pH meter with glass and saturated calomel electrode, calibrated on the operational stage using standard buffer solution at 298 ± 1 K. All aqueous solutions were prepared with ultra pure water obtained from a Millipore Milli-Q Plus water purification system.

Materials

Toluene, methyl alcohol, 3-amonopropyltriethoxysilane (APTS) and Pb(II) and Cu(II) nitrates were also obtained from Merck. Methyl alcohol used in the synthesis of the new sorbent was of analytical grade and they were not purified any more. Calixarene compound was synthesized according to the literature [11].

Sorbent Preparation

Glass beads (GB) were first silanized by 3-aminopropyl triethoxy silane (APTS) to immobilize calixarene derivative on them. For the activation of GB surfaces, GB was refluxed with 4 mol dm^{-3} NaOH for 30 min. The glass beads were rinsed with water subsequently filtered and the beads were dried in an oven at 393 K for 24 h [12].

In the next step, to form functional groups on its surface, about 6 cm^3 of 3-aminopropyl triethoxysilane (APTS) and 10.0 g of activated glass beads were added into 100 cm^3 of toluene and magnetically stirred at 400 rpm under solvent reflux for 72 h. After filtration, the resulting aminopropyl glass beads (GB-APTS) were washed with 150 cm^3 toluene and 150 cm^3 acetone and then dried in an oven at 383 K for 24 h. The resulting product may be stored for later use [13].

In the final step, 5.0 g of the aminopropyl glass beads 50 g dry toluene and 50 cm^3 methylene were suspended into glass flask. CA (3.5 g) was then added to the stirred reaction mixture. The reaction mixture was stirred at 298 K for 36 h. The product was filtered and washed with dry toluene and dried. A representation of this reaction is shown in Fig. 1.
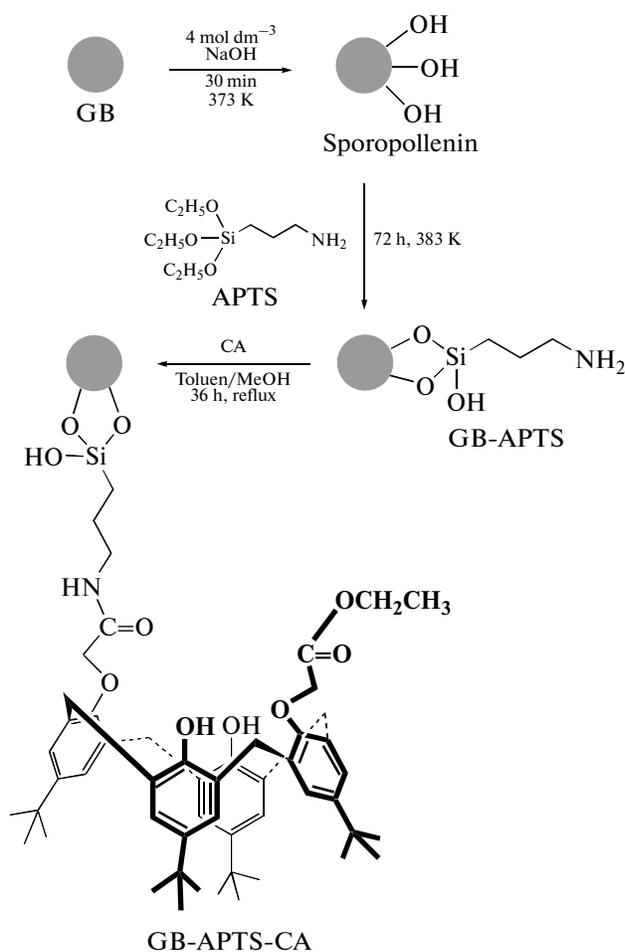
Fig. 1. Possible structure of the glass beads bonded 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonyl-methoxy-26,28-dihydroxycalix[4]arene.

Sorption Studies

Sorption studies were carried out by batch process. 0.025 g sorbent was placed in glass flask with 20 cm^3 solution of metal ion of desired concentration. The mixture was shaken in temperature controlled shaker incubator for 24 h at 298 K $\pm$ 1. The mixture was then filtered and final concentration of metal ion was determined in the filtrate by AAS. All experiments were performed in triplicate. The amount of metal ions sorbed were computed from the difference between the C_o and the C using the relationship,

$$\left(q = \frac{(C_o - C)V}{W} \right). \tag{1}$$

Where q is the amount of metal ion sorbed onto unit amount of the adsorbent (mmol g^{-1}), C_o and C are the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol dm^{-3}), V is the volume of the aqueous phase (dm^3), and W is the dry weight of the adsorbent (g).
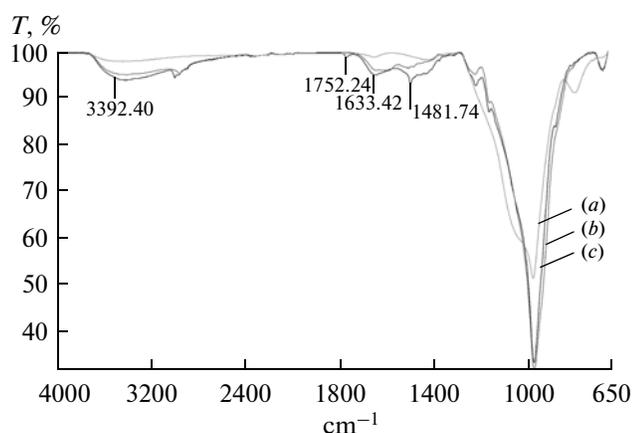
Fig. 2. *FTIR* spectra of the *GB* (*a*), *GB-APTS* (*b*) and *GB-APTS-CA* (*c*).
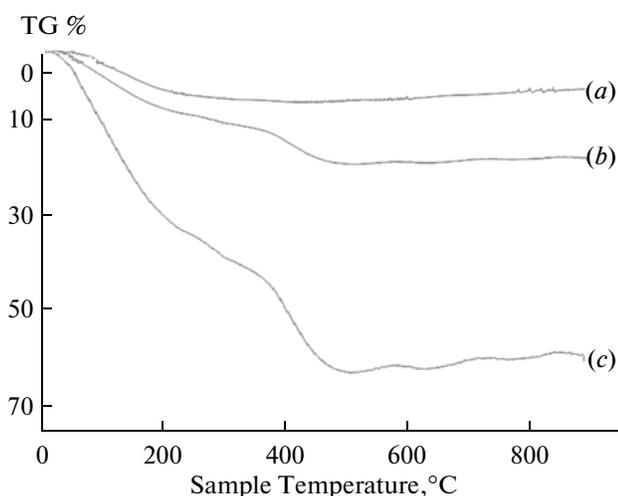
Fig. 3. *TGA* plots for *GB* (*a*), *GB-APTS* (*b*) and *GB-APTS-CA* (*c*).

Sorbent Weight Effect of the Sorption

A series of 50 cm^3 glass flasks each containing 20 cm^3 of metal ion solution (10 mmol dm^{-3}) were treated with varying amount of adsorbent (0.01–0.1 g). The flasks were shaken in shaker incubator at 298 K and after equilibrium (24 h) the solutions were filtered. The amount of metal ions in filtrate was then determined by AAS. The amount of metal sorbed in each case was calculated from Eq. (1).

pH Effect of the Sorption

Metal sorption is affected by acidity of a solution in two ways. Firstly, protons in acid solution can protonate binding sites of the chelating molecules. Secondly, hydroxide in basic solution may complex and precipitates many metals. Therefore the first parameter to be optimized in a solution is pH [14].

The effect of pH in the range 2.0–7.0 for the sorption of metal ions on GB-APTS-CA was studied by batch process as follows: 20 cm^3 of metal ions solution

(10 mmol dm^{-3} initial concentrations) was put in a bottle. The pH of solution was adjusted by adding 0.1 mol dm^{-3} HNO_3 or 0.1 mol dm^{-3} NaOH. The initial concentration of metal ions in this solution was then determined. 20 cm^3 of this solution was taken in glass flask and treated with 0.025 g sorbent and after equilibrium, the final concentration of metal ions was determined.

RESULT AND DISCUSSIONS

Characterization

Based on the elemental and thermogravimetric analysis, the amount and the density of the functional groups immobilized on the glass beads surface were measured. The elemental analysis was carried out on the synthesized sorbent in order to determine C, N and H contents [15]. The C, H and N values for the GB and GB-APTS composition were 0%, 0% and 0%, 15.37%, 8.41% and 3.51% respectively, and for the GB-APTS-CA sorbent they were 26.56%, 7.44% and 1.61%, respectively.

The obtained sorbent named GB-APTS-CA was also characterized by FTIR spectra. FTIR spectra for the GB, GB-APTS and GB-APTS-CA samples are shown in Fig. 2 (*a-b-c*). The FT-IR spectrum of the GB is shown in Fig. 2 (*a*). The strong and broad band in the region of approximately 900–1100 cm^{-1} may be assigned to Si–OH stretching peak. This peak can be an indication of water in the glass structure [16]. The FTIR spectrum of the GB-APTS is shown in Fig. 2 (*b*). The spectrum shows a band in the region of 1600–1650 cm^{-1} indicating the presence of N-H deformation. The GB-APTS spectrum also shows a new peak at 1490 cm^{-1}, which can be attributed to the CH_2 deformation of the APTS compounds.

The FT-IR spectrum of the GB-APTS-CA is shown in Fig. 2 (*c*). The strong and broad band in the region of 3600–3000 cm^{-1} may be assigned to interstitial water molecule and –OH group. The spectrum also shows a strong band in the region of 1633–1481 cm^{-1} indicating the presence of aromatic groups. The absorbance at 1752 cm^{-1} correspond to stretching vibrations of carbonyl (C=O) bond [17–18].

Figure 3 shows the TGA results of GB (*a*), GB-APTS (*b*), and GB-APTS-CA (*c*). The TG curve of GB (Fig. 3 *a*) shows a weight loss of 4.06% in the temperature range of 100–225°C, which is due to the loss of adsorbed water in the GB [19]. For GB-APTS, the TGA profiles show a loss of moisture at 60–100°C (Fig. 3 *b*). A significant weight loss (12.17%) can be observed in the TGA curve of GB-APTS from 300 to 500°C, which can be attributed to the weight loss of APTS molecules [20]. GB-APTS-CA is more thermally stable than GB-APTS and showed three decomposing transitions. TGA profiles of GB-APTS-CA (Fig. 3 *c*) firstly, shows 6.1% weight loss between 100 and 130°C which probably corresponds to desorption of the physically sorbed water molecules. Secondly, the
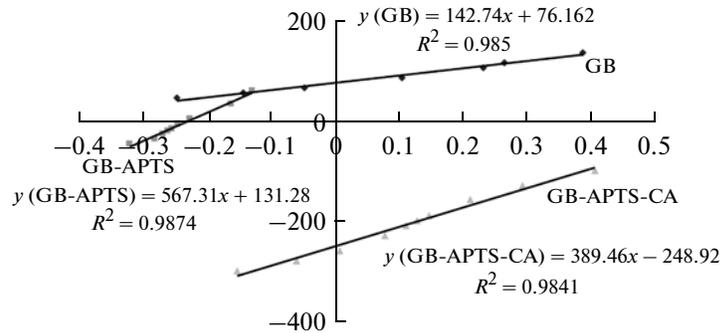
Fig. 4. Graphical presentation of the $\log[g(\alpha)] - \theta$ plot of *HM* equation.

weight loss (16.87%) of GB-APTS-CA occurred mainly in the temperature range of 150–350°C which could be attributed to the loss of organic groups from the glass beads surface [21] and finally, between 400–650°C the TGA profiles shows 13.0% weight loss due to the loss of organic groups and probably some =Si–OH condensation from the glass beads surface.

In the kinetic studies of the thermal systems the mass-temperature relation, which can determine the behavior of the degradation reactions, can be examined. In the present study, Horowitz Metzger (HM) equations [22] were used for calculating the activation energy (E_a). The kinetic analysis of a thermal degradation process begins by expressing the reaction rate by a general equation such as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \tag{2}$$

where t is the time, α is the extent of reaction, T is the temperature, $k(T)$ is the temperature-dependent rate constant and $f(\alpha)$ is a temperature-independent function that represents the reaction model. α is calculated according to:

$$\alpha = \frac{W_0 - W}{W_0 - W_f}. \tag{3}$$

Where W_0 is the initial mass of the sample (g), W is the mass of the sample (g) at a time and at temperature T (K) and W_f is the final mass of the sample (g). The rate of degradation process can be described as the product of two separate functions of temperature and fractional conversion. The rate constant $k(T)$ is given, generally, by the Arrhenius equation:

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right), \tag{4}$$

where A is the pre-exponential or frequency factor and E_a is the apparent activation energy. Thus, Eq. (4) may be rewritten as:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right). \tag{5}$$

The thermodynamic activation parameter of the decomposition process of the complexes such as energy

of activation (E_a) was evaluated graphically employing the *HM* method and using the following relation:

$$\log[g(\alpha)] = \frac{E\theta}{2.303RT_m^2}. \tag{6}$$

Here R is the gas constant and $\theta = T - T_m$, where T_m is the temperature of maximum reaction rate and T is the temperature in Kelvin at any instant. A plot of $\log[g(\alpha)]$ versus θ (Fig. 4) should give a straight line whose slope is $E/RT_m^2 g(\alpha) = -\ln(1 - \alpha)$ indicates random nucleation model for the degradation of the material.

The aim of this calculation is to compare the E_a values of GB, GB-APTS and GB-APTS-CA and to estimate their thermal stability. The value of E_a for the GB is lower than the E_a for GB-APTS. The results of E_a for GB and GB-APTS are 2.0×10^5 and 1.2×10^6 kJmol^{-1}, respectively. The E_a value became slightly increased for the GB-APTS-CA and calculated as 2.3×10^6 kJmol^{-1}. The high values of the energy of activation, E_a of the GB-APTS-CA reveals the high stability of due to their covalent bond character [23].

SEM images of the GB, GB-APTS and GB-APTS-CA were given in Fig. 5a–5c, respectively. GB surface roughens, almost spherical. A picture of this stage is shown in Fig. 5a. After the immobilization of the GB surface with APTS this rough skin vanishes and new flatter surface regions appear (Fig. 5b). It seems that the roughness was occurred after binding of CA on the surface of GB-APTS (Fig. 5c). It can be seen that the surface modification was carried out successfully [10, 24].

Sorbent Weight

Sorbent dosage is an important parameter because it determines the capacity of the sorbent for a given initial concentration of the solute. Thus, the amount of a sorbent strongly influences the extent of sorption due to increased surface area of the sorbent which in turn increases the number of binding sites [25] On the other hand, the quantity of sorbed solute per unit weight of sorbent decreases with increasing sorbent amount which may be due to complex interaction of several factors. An important factor at high sorbent dosages is that
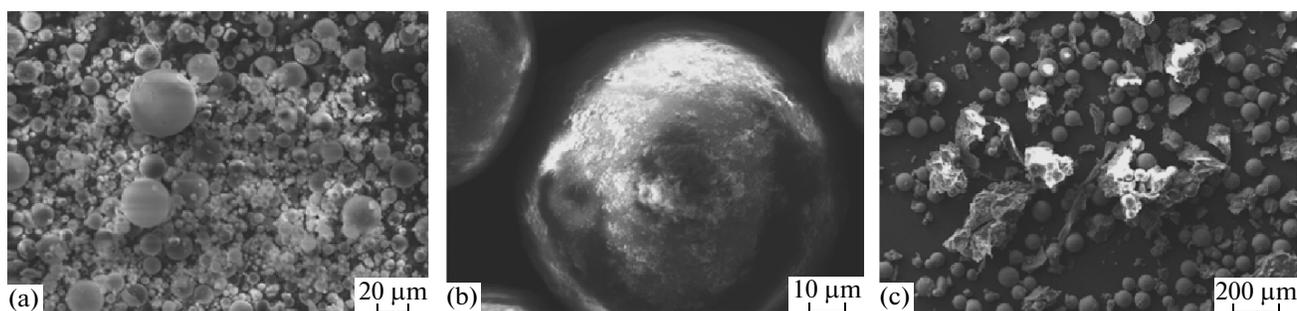
Fig. 5. *SEM* photographs (a) *GB*, (b) *GB-APTS*, (c) *GB-APTS-CA*.
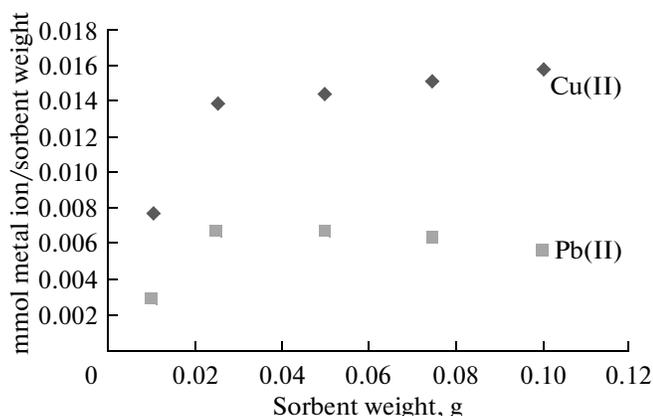
Fig. 6. Sorbent weight effect of the sorption of Cu(II) and Pb(II) ions on to *GB-APTS-CA* at 298 ± 1 K.
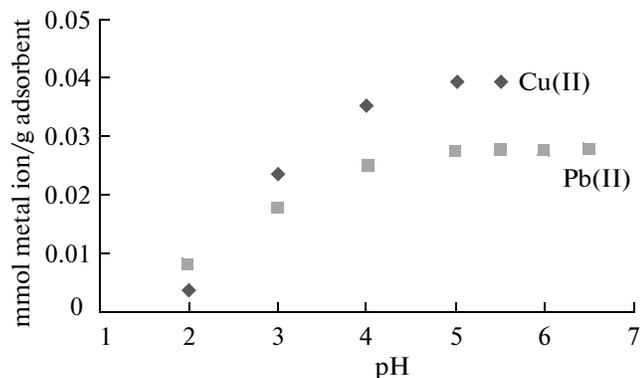
Fig. 7. pH effect of the sorption of Cu(II) and Pb(II) metal ions onto *Gb-APTS-CA* at 298 ± 1 K.

the available solute is insufficient to completely cover the available exchangeable sites on the sorbent, usually resulting in low solute uptake [26].

The sorbed metal ions using various amounts of the sorbents are given in Fig. 6. Experiments were carried out at 10 mmol dm^{-3} of metal, 20 cm^3 solutions at 298 K ± 1. It was observed from this figure that the increase in sorbent amount has a positive effect on the percentage metal ions removal for GB-APTS-CA.

pH Effect

pH of the initial solution has been reported to be an important parameter affecting the uptake of heavy metal ions from aqueous solutions by sorbents. The effect of pH on Cu(II) and Pb(II) ion sorption on GB-APTS-CA is shown in Fig. 7. In strong acidic solutions, sorbent shows low sorption capacities, probably due to the surface protonation of the modified surfaces. This is partly because hydrogen ions themselves are strongly competing with sorbate. The resulting positively charged surface seems to have low binding ability toward Cu(II) and Pb(II) ions and the surface ligands are closely associated with the hydronium ions (H$_3$O$^+$) and restricted the approach of metal cations as a result of the repulsive force [27, 28]. The sorption efficiencies improved by increasing the pH of solution to pH 5.0 and are relatively constant for metal ion sorption at higher pH values. Hence, the optimum pH value for Cu(II) and Pb(II) sorption is 5.0.

Sorption Isotherm

The sorption equilibrium of metal ions between aqueous solution and the sorbent can be described by a sorption isotherm. The sorption experiments were performed by using different initial concentrations of metal ions at 298 K.

In an attempt to describe the sorption behavior, the Langmuir, Freundlich and Dubinin Radushkevich model isotherms were adopted. The Langmuir sorption isotherm is most widely used for the sorption of a pollutant from liquid solutions. The model is based on several basic assumptions for example, sorption takes place on specific homogeneous sites within the sorbent, a metal ion occupies a site, the sorbent has a finite capacity for the sorbate and all sites are identical and energetically equivalent [29]. The linear form of the Langmuir equation is represented as follows [30],

$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o b}. \qquad (7)$$

Where q_e is the amount of solute sorbed on the surface of the sorbent (mmol g^{-1}), C_e is the equilibrium ion concentration in the solution (mmol dm^{-3}), q_o is the maximum surface density at monolayer coverage and b is the

Langmuir adsorption constant (dm³ mmol⁻¹). The plot of C_e/q_e versus C_e for the sorption gives a straight line of slope $1/b\,q_o$ and intercepts $1/q_o$ (Fig. 8).

The Freundlich isotherm assumes multilayer sorption onto heterogeneous surface and can be calculated using Eq. (8). This model also predicts that the metal ion concentration on the material will increase as long as the metal ion concentration in the solution increases and this isotherm model is not restricted to the monolayer in the sorbent [29].

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

Where q_e is the equilibrium solute concentration on adsorbent (mmol g⁻¹), C_e is the equilibrium concentration of the solute (mmol L⁻¹), K_F is the Freundlich constant (mmol g⁻¹) which indicates the sorption capacity and represents the strength of the absorptive bond and n is the heterogeneity factor which represents the bond distribution. The plot of ln q_e versus ln C_e should give a straight line with a slope of $1/n$ and the intercept of logK_F (Fig. 9).

The isotherm model suggested by Dubinin and Radushkevich (D-R) has been used to describe the liquid phase sorption and on the basis of D-R equation adsorption energy can be estimated. The model is often expressed as [31],

$$\ln q_e = \ln qm - k\varepsilon^2. \qquad (9)$$

Where ε (polanyi potential) is $\lfloor RT\ln(1 + 1/C)\rfloor$, q_e is the amount of solute adsorbed per unit weight of adsorbent (mol g⁻¹), k is a constant related to the adsorption energy (mol²(kJ²)⁻¹), and q_m is the adsorption capacity (mol g⁻¹). Hence by plotting $\ln q_e$ vs. 2 it is possible to generate the value of q_m from the intercept, and the value of k from the slope (Fig. 10).

The mean free energy (E), calculated by the Dubinin−Radushkevich isotherm, is presented in Table 1. The energy values were calculated using the equation:

$$E = (-2k)^{1/2}. \qquad (10)$$

The adsorption mean free energy gives information about sorption mechanism. If E value lies between 8 and 16 kJ mol⁻¹, the sorption process takes place chemically while $E < 8$ kJ mol⁻¹, the sorption process is carried out physically. The mean sorption energy was calculated as 15.43 and 14.43 kJ mol⁻¹ for Cu(II) and Pb(II), respectively. This value indicated that removal of Cu(II) and Pb(II) on GB-APTS-CA mainly proceeds chemically [32].

The Langmuir, Freundlich and D-R isotherm parameters for the sorption of selected metal ions onto GB-APTS-CA are listed in Table 1. The Langmuir model was found to be the most appropriate to describe the adsorption process of Cu(II) and Pb(II) ions on GB-APTS-CA. The fitness of the sorption equilibrium data on Langmuir isotherm implying that all the adsorption active sites are equivalent and the surface is uniformed. The Langmuir constant (b) calculated from the linear equation is 2.98×10^5 dm³ mmol⁻¹ and $4.91 \times$
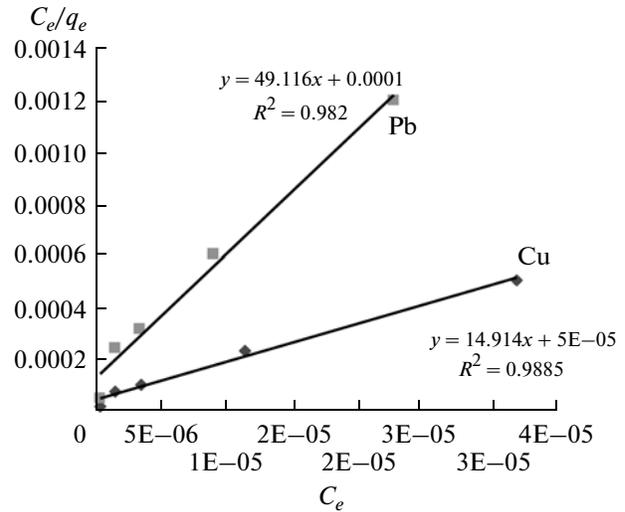
Fig. 8. Langmuir isotherm curves for Cu(II) and Pb(II) metal ion sorption on to *GB-APTS-CA*.
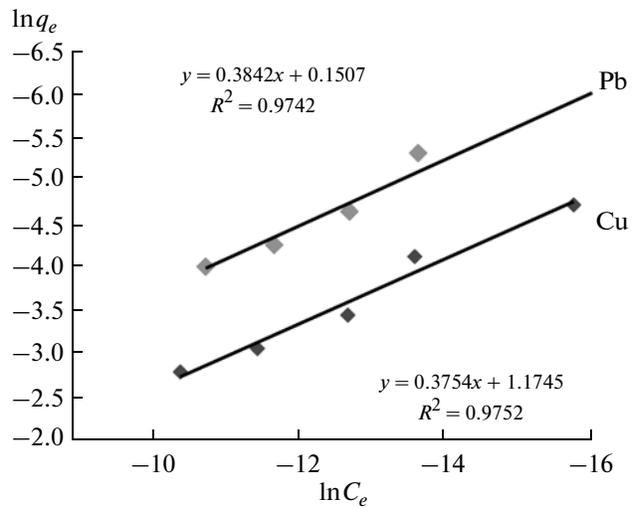
Fig. 9. Freundlich isotherm curves for Cu(II) and Pb(II) metal ion sorption on to *GB-APTS-CA*.
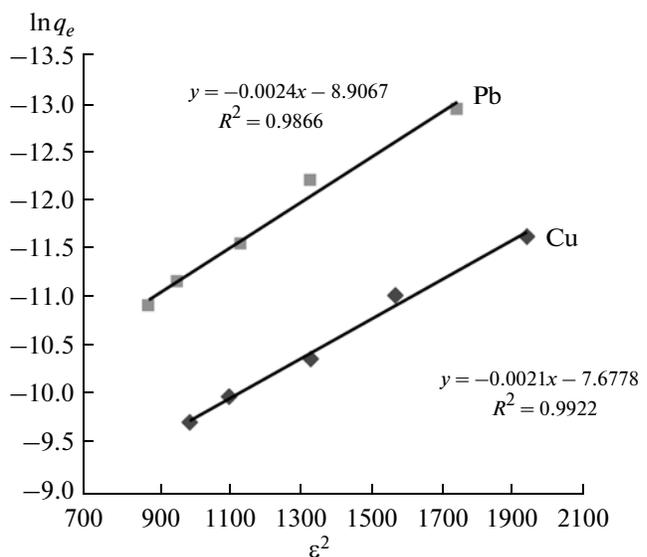
Fig. 10. *D-R* isotherm curves for Cu(II) and Pb(II) metal ion sorption on to *GB-APTS-CA*.

Table 1. Isotherms parameters for Cu(II) and Pb(II) by *Sp-APTS-CA*

Metal	Freundlich Isotherm		Langmuir Isotherm		D-R Isotherm		
	$1/n$	K_F	q_0	$b(\times 10^5)$	k	q_m	E
Cu(II)	0.37	3.24	0.06	2.98	0.02	0.46	15.43
Pb(II)	0.41	1.43	0.02	4.91	0.02	0.14	14.43

Table 2. Thermodynamic parameters for sorption of metal ions of *Sp-APTS-CA* (Metal ion concentration 5 mmol dm^{-3})

Metal ion	$\Delta H°$, kJ mol^{-1}	$\Delta S°$, JK^{-1} mol^{-1}	$-\Delta G°$, kJ mol^{-1}				
			293	303	313	323	328
Cu(II)	76.56	333.62	21.24	24.58	27.91	31.25	32.92
Pb(II)	60.74	274.24	19.83	22.58	25.33	28.08	29.46

10^5 dm^3 mmol^{-1} for sorption of Cu(II) and Pb(II), respectively. The high values of the Langmuir constants indicate the high affinity of the sorbent toward selected ions and the sorption mechanisms of the metal ions onto the sorbent are likely to be chemisorptions via coordination with the calixarene compound. The maximum sorption capacity (q_o) from the calculation is 0.06 mmolg^{-1} for Cu(II) and 0.02 mmolg^{-1} for Pb(II) with monolayer coverage of metal ions onto the sorbent.

Thermodynamic Study

Temperature is an important parameter for the sorption process. Results of the thermodynamic study illustrate the effect of temperature (20, 30, 40, 50 and 55°C) on the sorption of metal ions by GB-APTS-CA. Also, the results reveal that uptake of metal ions increases with increasing temperature from 20 to 55°C.

The thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$, were obtained from the following equations [15, 33]:

$$K_D = \frac{(C_o - C)}{C} x \frac{V}{W}, \tag{11}$$

$$\log K_D = \frac{\Delta S°}{2.303 R} - \frac{\Delta H°}{2.303 R T}, \tag{12}$$

$$\Delta G° = \Delta H° - T \Delta S°. \tag{13}$$

Where C_o and C are the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol dm^{-3}), V is the volume of the aqueous phase (dm^{-3}), and W is the dry weight of the sorbent (g). Where $\Delta G°$ is the change in Gibbs free energy (kJ mol^{-1}), $\Delta H°$ is the change in enthalpy (kJ mol^{-1}), $\Delta S°$ is the change in entropy (J (mol K)$^{-1}$), T is the absolute temperature (K), R is the gas constant (8.314×10^{-3}, kJ mol^{-1} K^{-1}). From the slope and intercept of the linear plot of $\log K_D$ versus $1/T$ (shown in Fig. 11), the changes of enthalpy and entropy could be obtained.

The thermodynamic parameters are listed in Table 2. The negative values of $\Delta G°$ indicate that the sorption of the metal ions onto GB-APTS-CA is spontaneous and thermodynamically favorable [34]. The increase in the value of $-\Delta G°$ with increasing temperature indicates that the sorption process is more favorable at higher temperature. A positive $\Delta H°$ suggests that the sorption of metal ions onto GB-APTS-CA is endothermic, which is supported by the increasing sorption of these metal ions with the increase in temperature. In addition, the positive value of $\Delta S°$ suggests an increase in degree of freedom at the solid-liquid interface during sorption process, which reflects increased randomness at the solid/solution interface and metal ions affinity to GB-APTS-CA [35]. The magnitude of $\Delta H°$, related to the sorption energy, can indicate the type of binding mechanism involved, i.e., physical and/or chemical sorption. In physical sorption, the process is fast and usually reversible due to the small energy requirement. Energies of 4–8 kJ mol^{-1} are required by London, Van der Waals interactions compared from 8 to 40 kJmol^{-1} for hydrogen bonding. In contrast, the enthalpy associated with chemical sorption is about 40 kJ mol^{-1}, a
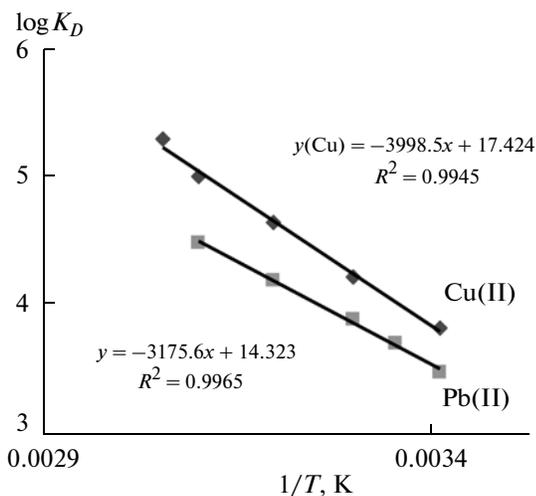
Fig. 11. Effect of temperature for the sorption of metal ions onto *GB-APTS-CA* (volume of solution 20 cm^3, 25 mg of *GB-APTS-CA*, metal ion concentration 10 mmol dm^{-3}).

value that has been recognized in the literature as the transition boundary between both types of sorption processes [32]. High $\Delta H°$ values were observed for Cu(II) (76.56 kJ mol^{-1}) and Pb(II) (60.74 kJ mol^{-1}) in the temperature range of 293−328 K. The calculated $\Delta H°$ values for selected metal ion sorption were higher than 40 kJ mol^{-1}, indicative of the strong interactions of the compound with the GB-APTS-CA surface at this temperature range and the sorption processes are likely to be chemisorption.

CONCLUSIONS

In this study, a novel hybrid material glass beads chemically modified by 5,11,17,23- tetra-tert-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxy-calix[4]arene has been synthesized and characterized. The results of the sorption of various metal ions such as Cu(II) and Pb(II) from aqueous solution on the synthesized GB-APTS-CA showed that this high efficient sorbent has good sorption capacity for Cu(II) and Pb(II). Moreover, the study indicated the best interpretation for the experimental data was given by the Langmuir isotherm equation. Sorption capacities of metal ions were in the following order: Cu(II) > Pb(II). The sorption thermodynamic parameters were calculated and determined. Thus, the high efficiency of GB-APTS-CA makes it a promising sorbent for the treatment of selected heavy metals from aqueous solutions.

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