

Sorption of Cu(II) onto silica gel immobilized calix[4]arene derivative with tripodal structure

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Abstract This study contains the synthesis of silica gel-immobilized calix[4]arene derivative (TR-CL[4]P) as a new sorbent and its sorption studies towards Cu (II) ion in aqueous solution. The aldehyde pointed calix[4]arene derivative **5** was synthesized and then it was immobilized onto 3-aminopropylsilica gel (APS). In batch sorption experiments, the experimental results showed that TR-CL[4]P is effective sorbent towards Cu (II) ion. Therefore, the effect of solution pH, sorption time, temperature and initial metal ion concentration onto Cu (II) sorption was investigated. Maximum Cu(II) removal was obtained at 30 °C, 30 min and pH 6.0 for TR-CL[4]P and the batch sorption capacity was found as 17.8 mg/g. The characteristics of the sorption process for Cu (II) ion were evaluated by using the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption isotherms. Also, thermodynamic parameters, i.e., ΔG , ΔS , and ΔH were calculated for the system.

Keywords Calix[4]arene · Silica gel · Immobilization · Sorption · Isotherms

Introduction

Heavy metal pollution is spreading throughout the world with the expansion of industrial activities. Many industries, especially plating and battery, heavy metals are released in wastewaters. Many methods such as chemical precipitation, membrane filtration, coagulation, complexing, solvent

extraction, ion exchange and adsorption are used to removal of heavy metals from wastewaters. Among them, inorganic supports immobilized with ion-chelating agents have received considerable attention for separation processes of heavy metals from aqueous solutions. The technique is the result of advances in the development of commercial extractants for metal ion separation in the hydrometallurgical industries [1].

The increasing number of recent publications on adsorption of toxic compounds shows that there is widespread interest in the synthesis of adsorbent resins able to totally eliminate organic pollutants. Various chemical and physical processes are currently in use. Solid phase extraction (SPE) using sorbents is one of the most efficient and well-established procedures in the field of separation science, which finds application in various fields like environmental, food, clinical, pharmaceutical, and industrial chemistry. SPE is usually performed using a small column or cartridge containing an appropriate sorbent. The sorbents may be of mineral or organic origin. Among these, modified silicas (C8 and C18), ion exchangers [2], graphitized carbon black [3], various polymeric sorbents polystyrene-divinyl benzene, (PS-DVB) [4], immunosorbents [5], molecularly imprinted polymers [6], conductive polymers [7], porous polymers [8], polysaccharides such as chitin [9, 10], starch [11, 12] and chitosan [13, 14] etc. are reported. In this respect, the supramolecular chemistry has provided a much better solution to search for molecular structures that can serve as building blocks for the production of sophisticated molecules by anchoring functional groups oriented in such a way that they provide a suitable binding site. This was achieved with the development of macrocyclic molecules such as synthetic crown ethers, cryptands, spherands [15], natural cyclodextrins [16, 17], and calixarenes [18–20].

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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 [21, 22]. Generally two strategies have been adopted by the different groups in order to enhance the affinity of calixarenes toward metal ions; either there have been incorporated different ionophoric groups including carbonyl, amide, nitrile and other suitable functionalities onto the calix-platform, or the calixarene units were fixed in a polymeric matrix. Various studies have been carried out in this regard, for instance, Tabakci et al. [23] have reported the synthesis of aminopropyl silica gel-immobilized calix[4]arene polymer as sorbent and it was used for Cu(II) removal from aqueous solutions by sorption. Also, Yilmaz and co-workers [24] have prepared the adsorbents from cellulose-grafted with calix[4]arene polymers and their sorption properties studied. A chelating resin has been synthesized by linking calix[4]arene-semicarbazone derivatives on chloromethylated polystyrene divinyl benzene copolymer for the separation of La^{3+} , Ce^{3+} , Th^{4+} and U^{6+} [25]. The obtained results have importance especially in wastewater treatment to obtain environmentally safe industrial effluent and they should also assist supramolecular chemists in designing and synthesizing more sophisticated host molecules for the removal of toxic pollutants.

The importance of favorable amide ($\text{O}=\text{C}-\text{NH}$), nitrile ($\text{C}\equiv\text{N}$) and amine (NH_2) functionalities for cation binding has recently been explored by various groups in the design of calix[4]arene cation sorbents, which are still relatively rare [26]. In this study to contribute to this area we prepared compound **5** with two calix[4]arene units using 1,3,5-Tris(formylphenoxy)methyl benzene **4**. Then, it was immobilized onto 3-aminopropyl silica gel. The prepared silica gel-immobilized calix[4]arene derivative (TR-CL[4]P) containing amide, Schiff base and amine groups was used for Cu(II) ion as sorbent.

Experimental

Materials and equipments

High-purity aminopropyl silica (APS) was purchased from Aldrich (No: 364258). Analytical TLC was performed on precoated silica gel plates (SiO_2 , Merck PF254). Acetone, CH_2Cl_2 and MeOH were distilled from CaSO_4 , CaCl_2 and over Mg, respectively. Tetrahydrofuran and toluene were dried by refluxing over sodium/benzophenone and CaH_2 , respectively, fractionally distilled and then stored over molecular sieves. All chemicals were purchased from Merck and Fluka and employed without further purification. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck) was used to prepare metal

ion solution. The solution (1,000 mg/L) was prepared by dissolving appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in deionized water. The working solutions were prepared by diluting the stock solutions to appropriate volumes. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

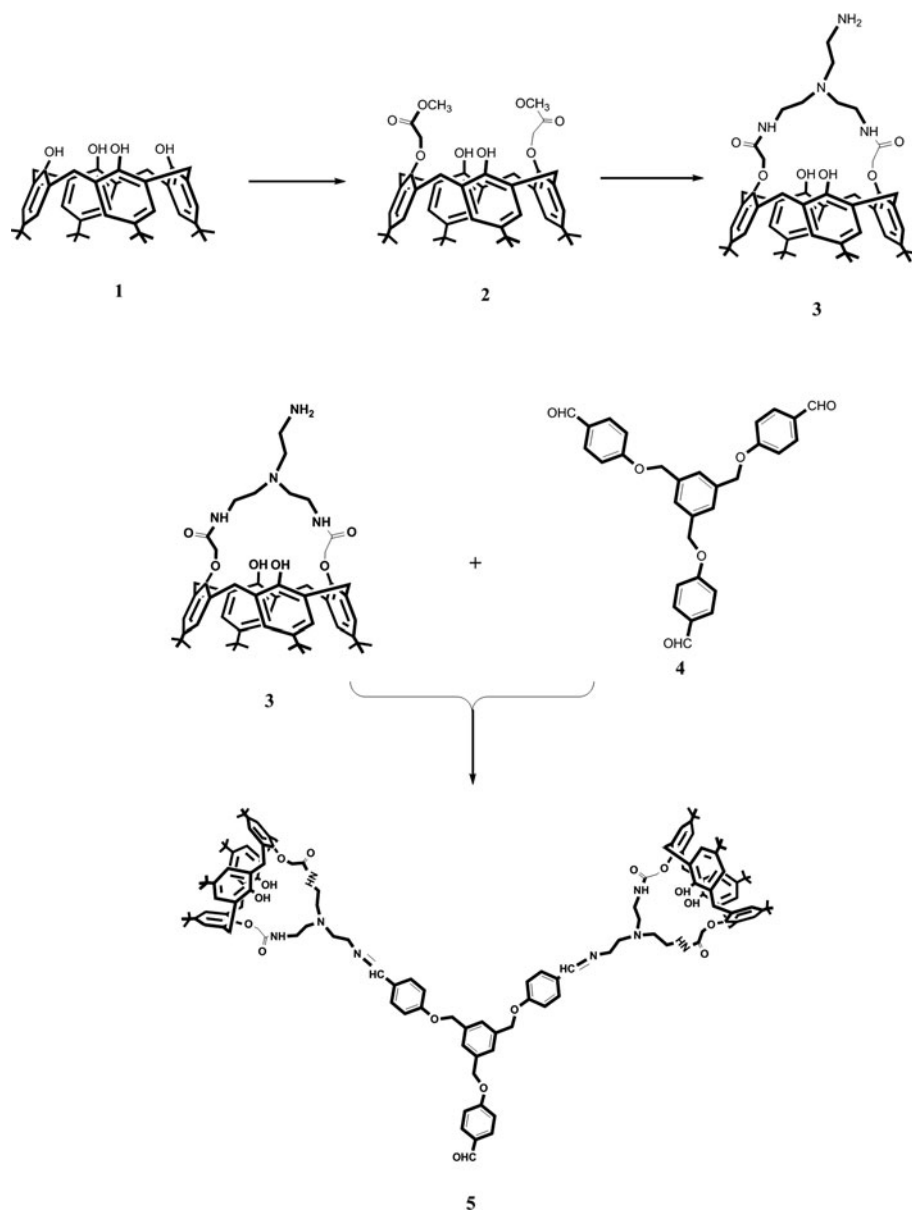
Melting points were determined on a Gallenkamp apparatus in a sealed capillary. ^1H NMR and ^{13}C -NMR spectra were recorded with a Varian 400 MHz spectrometer in CDCl_3 . FT-IR spectra was recorded with a Perkin-Elmer Spectrum 100. Thermal gravimetric analysis (TGA) was carried out with Setaram thermogravimetric analyzer. The sample weight was 15–17 mg. Analysis was performed from 40 to 1,000 °C at heating rate of 10 °C/min in argon atmosphere with a gas flow rate of 20 mL/min. Elemental analyses were performed on a Leco CHNS-932 analyzer. The metal ion concentrations were measured using ContraAA 300 (Analytic JENA).

Synthesis

Compounds **1** and **2–4** were prepared according to known previous procedures [27–30]. The synthesis of compound **5** and its immobilization onto 3-aminopropyl silica gel as illustrated in Figs. 1 and 2 have been carried out as follows.

Synthesis of compound 5

To a solution of **4** (0.2 g, 0.42 mmol) in CHCl_3 (30 mL) was added a solution of compound **3** (0.75 g, 0.86 mmol) in MeOH (10 mL) and refluxed for 24 h. The reaction was monitored with TLC. After the reactants had been consumed, the solvent was completely evaporated under reduced pressure and the residue was triturated with MeOH (20 mL) and filtered off to give **5** as a yellow solid. Yield 82%. FT-IR: 1678 cm^{-1} (CHO), 1644 cm^{-1} (C=N); ^1H -NMR (CDCl_3): 0.87(s, 36H, $\text{C}(\text{CH}_3)_3$), 1.32 (s, 36H, $\text{C}(\text{CH}_3)_3$), 2.83 (t, 4H, $J = 7.4\text{ Hz}$, NCH_2), 2.88 (m, 8H, NCH_2), 3.35 (d, 8H, $J = 13.3\text{ Hz}$, ArCH_2Ar), 3.54 (m, 8H, CONHCH_2), 3.74 (t, 4H, $J = 7.4\text{ Hz}$, CNCH_2), 4.12 (d, 8H, $J = 13.3\text{ Hz}$, ArCH_2Ar), 4.49 (s, 8H, OCH_2), 5.11 (m, 4H, PhOCH_2), 5.18 (m, 2H, PhOCH_2), 6.45 (m, 3H, Ph-H), 6.70 (s, 8H, Ar-H), 6.94 (m, 4H, Ph-H), 7.07 (d, 2H, $J = 8.8\text{ Hz}$, Ph-H), 7.11 (s, 8H, Ar-H), 7.46 (s, 4H, Ar-OH), 7.48 (m, 4H, Ph-H), 7.84 (m, 2H, Ph-H), 7.97 (s, 2H, CHN), 8.18 (t, 4H, $J = 5.2\text{ Hz}$, NHCO), 9.89 (m, 1H, CHO). ^{13}C -NMR (CDCl_3) δ : 31.06, 31.53, 31.90, 34.13, 34.17, 38.82, 55.73, 60.44, 69.80, 69.89, 70.02, 70.09, 74.83, 114.96, 115.34, 125.59, 126.11, 126.21, 126.39, 128.07, 129.85, 129.95, 130.50, 130.55, 131.75, 132.22, 137.22, 137.38, 137.54, 137.83, 138.01, 138.20, 143.13, 148.25, 148.82, 150.02, 160.58, 160.67, 160.76, 161.41, 161.47, 161.52, 163.66, 163.72, 168.56, 190.89.

Fig. 1 Synthesis of compound **5**

Anal. calcd. for $C_{138}H_{168}N_8O_{16}$: C, 75.52; H, 7.72; N, 5.11
 Found: C, 76.01; H, 7.96; N, 5.56.

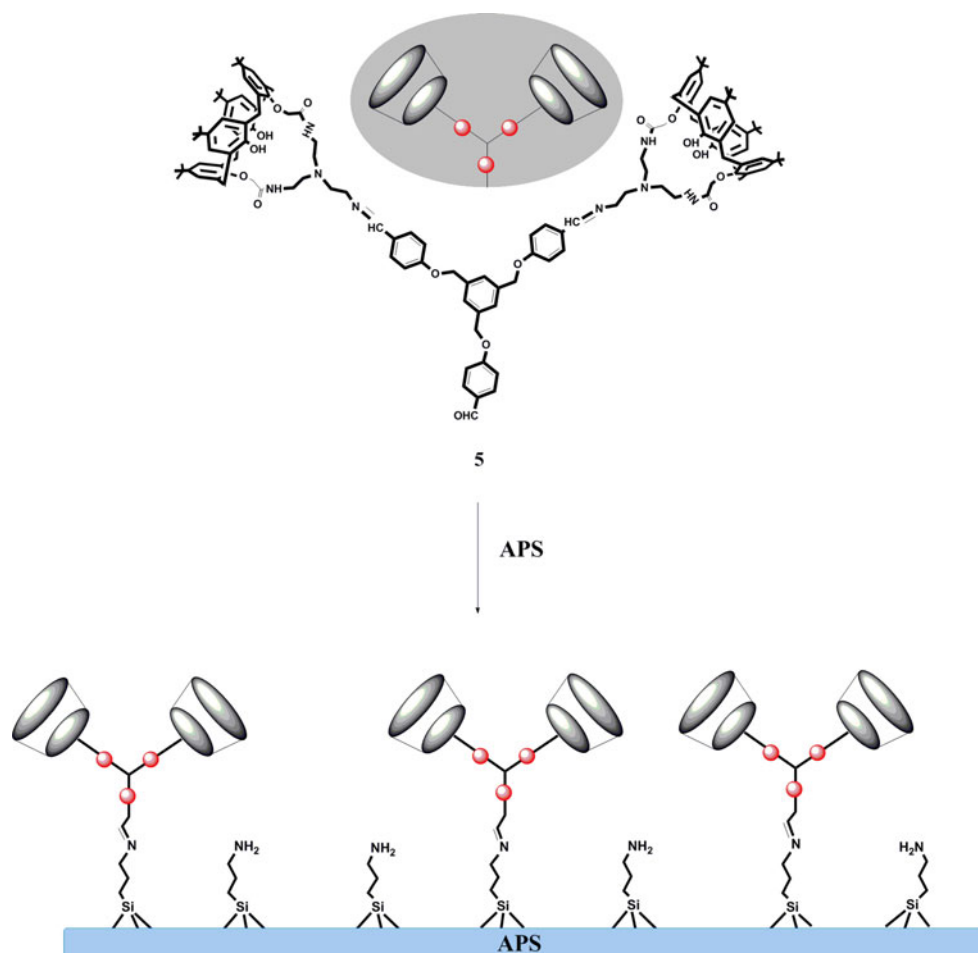
Immobilization of compound **5** onto APS

Compound **5** (0.35 g, 0.16 mmol), APS (1.0 g, 1,522 mmol-NH₂/g) and dry toluene (25 mL) were added to a 50 mL round-bottomed flask equipped with a magnetic stirrer and the mixture was refluxed for 5 h under nitrogen atmosphere. The cooled mixture was filtered and washed with warm toluene, dichloromethane, methanol and distilled water in sequence three times. The product was dried at 120 °C to give 1.12 g of TR-CL[4]P under vacuum, for 3 h and kept in a desiccator before use.

Analytical procedure for sorption

The sorption studies were carried out by using the batch method, where a series of samples of TR-CL[4]P sorbent (0.025 g) were suspended in 10.0 cm³ of aqueous solution with Cu (II) cation. The suspensions were mechanically stirred for predetermined time period at room temperature and the solid was separated by filtration. The experimental parameters studied are as follows: effect on pH (2.0–7.0), temperature (303–333 K) and ion concentration ($1.0\text{--}8.0 \times 10^{-4}$ mol L⁻¹). The pH values were measured with pH meter (Orion, 420A+). The effect of pH was studied by adjusting the pH of metal solutions using diluted HCl and NaOH solutions at 30 °C.

Fig. 2 Immobilization of compound **5** onto APS



Experiments were repeated three times in each case. Initial and equilibrium metal ion concentrations in the aqueous solutions were determined by ContrAA 300 Spectrometer. The amount of metal ions sorbed by sorbent was calculated as

$$q = (C_o - C) \frac{V}{m} \quad (1)$$

where q is the amount of metal ions adsorbed onto unit amount of the adsorbent (mmol g^{-1}), C_o and C the concentrations of metal ions in the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol L^{-1}), V the volume of the aqueous phase (L) and m is the dry weight of the adsorbent (g).

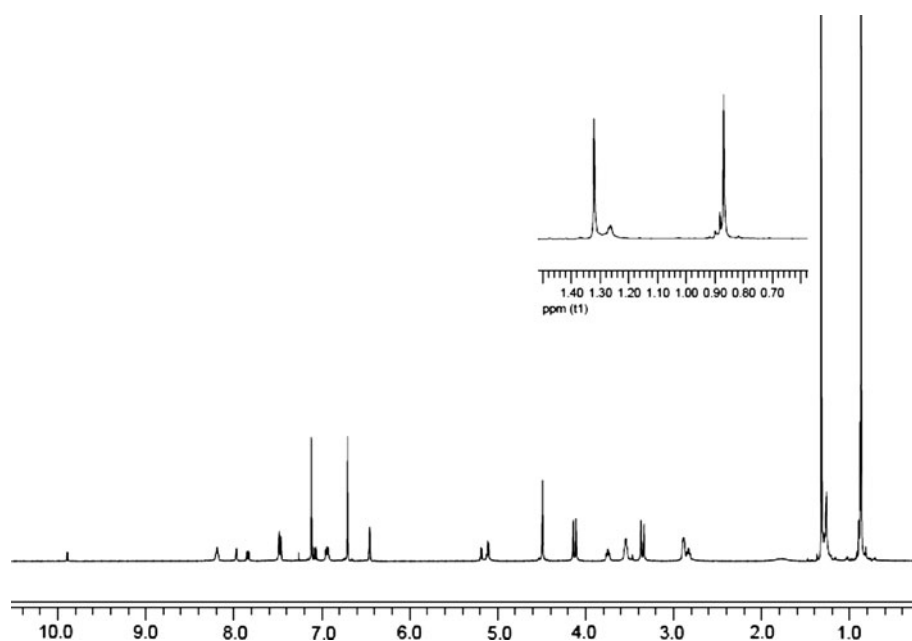
Results and discussion

Preparation of TR-CL[4]P as sorbent

The preparation of compound **5** contains the condensation of compound **3** and **4** in $\text{CHCl}_3/\text{MeOH}$ media and the synthetic route is presented in Fig. 1. The $^1\text{H-NMR}$ and

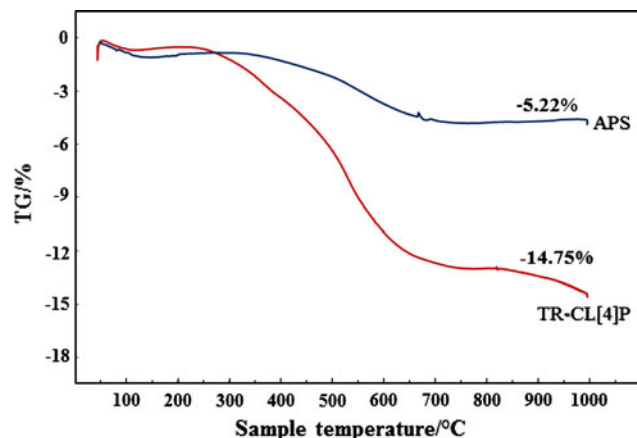
$^{13}\text{C-NMR}$ techniques were used for the characterization of compound **5** and The $^1\text{H-NMR}$ spectra of compound **5** was depicted in Fig. 3. TR-CL[4]P as a novel sorbent was prepared using the aldehyde pointed calix[4]arene derivative compound **5** as organic ligand and 3-aminopropylsilica gel (APS) as shown in Fig. 2. The prepared TR-CL[4]P sorbent was characterized using TGA, FT-IR and elemental analysis techniques. Carbon, hydrogen, and nitrogen elemental analyses showed a clear consistency with the increasing amount of silylating agent on the surface, as shown in Table 1. Depending on the contents of carbon, the bonded calixarene amount onto TR-CL[4]P was found to be approximately $0.142 \text{ mmol g}^{-1}$. This value confirmed that compound **5** is covalently bonded on APS's surface.

Figure 4 shows TG curves of TR-CL[4]P and APS materials. The total losses at temperature range of $40\text{--}1000 \text{ }^\circ\text{C}$ are 5.22 and 14.8% for APS and TR-CL[4]P, respectively, due to the breakage of the calixarene units anchored on the silica-gel surface together with the condensation of remaining silanol groups to produce siloxane. The results indicate that the compound **5** was successfully immobilized to silica gel. Also, from the FT-IR results

Fig. 3 $^1\text{H-NMR}$ spectrum of compound **5****Table 1** Elemental analysis results of APS and TR-CL[4]P materials

Surface	C (%)	H (%)	N (%)	Bonded amount (mmol g ⁻¹) ^a
APS	5.48	1.23	2.09	1.522
TR-CL[4]P	28.95	3.28	2.46	0.142

^a Bounded amount (mmol/g) = %C × 10/12n, where %C is the mass percentage of increasing carbon between TR-CL[4]P and APS and n is the number of carbon in the ligand

**Fig. 4** TG curves of APS and TR-CL[4]P

(Fig. 5), it was observed that compound **5** immobilized onto APS due to 3340 cm⁻¹, 1509–1605 cm⁻¹ and 1059 cm⁻¹ bands corresponded to Si–OH and Calix–OH, benzene rings (C–H), Si–O–Si, respectively. Moreover, the band of CH=O vibration of **5** observed at 1678 cm⁻¹ was

disappeared and two different imine C=N bands for TR-CL[4]P were observed at 1668 and 1644 cm⁻¹.

Sorption studies

We carried out solid–liquid sorption studies of Cu(II) ion as transition metal cation by using TR-CL[4]P as sorbent. The results showed that TR-CL[4]P was an effective sorbent towards Cu (II) ion. From our previous works and various studies [19, 23, 24, 31], it was deduced that amide derivatized calixarenes are effective sorbents for these cations because NHC=O group is preferable to complex the more polarizable transition metal ions especially Pb, Hg, Cd and Cu due to cation– π interactions. The phenomenon may also reflect the “principle of hard and soft acids and bases” introduced by Pearson [32]. Moreover, while the type of sorbent and size of particles influence the sorption kinetics, equilibrium concentrations in both the liquid and solid phase are almost independent of these parameters [33].

In batch sorption experiments, the experimental results showed that TR-CL[4]P containing amide, amine and Schiff base groups was effective sorbent towards Cu (II) ion. Therefore, the effect of solution pH, sorption time, temperature and initial metal ion concentration onto Cu (II) sorption was investigated.

Optimum conditions for Cu (II) sorption

Effect of pH

The pH value of medium is one of the most important factors controlling the sorption of metal ions by modified

Fig. 5 FT-IR spectra of compound 5, APS and TR-CL[4]P

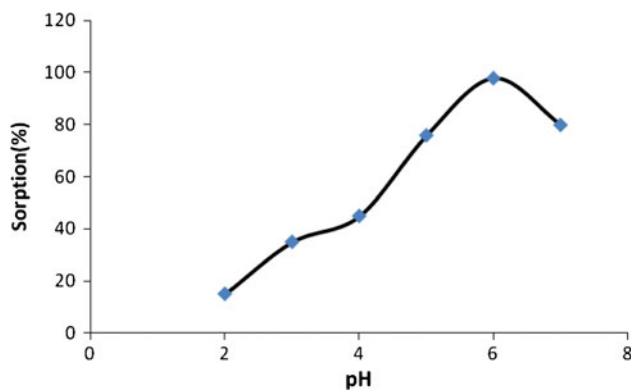
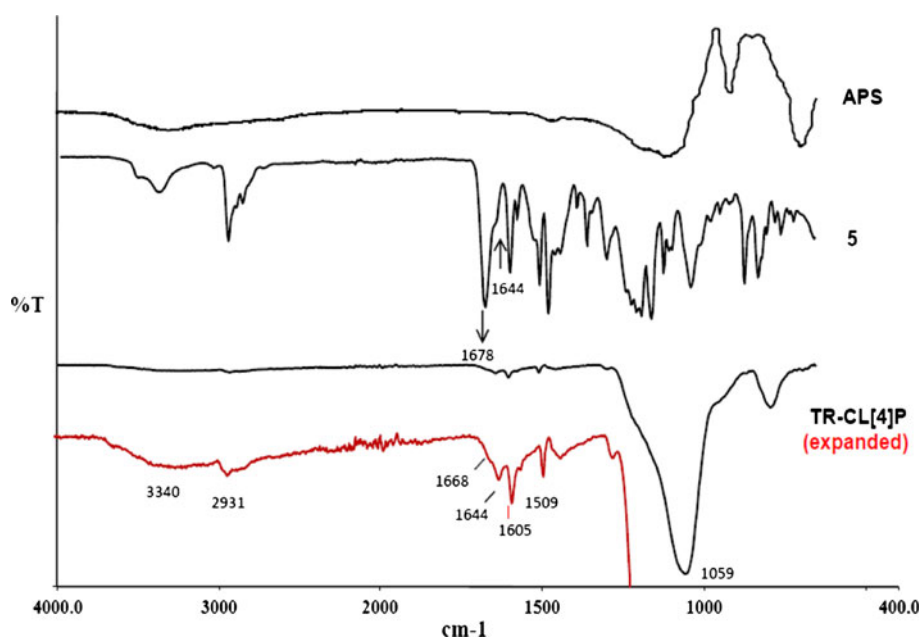


Fig. 6 Effect of pH on the removal of Cu (II)

silica gel. Since the TR-CL[4]P has the imine and amine groups, and these groups are protonable, pH dependencies of the Cu(II) ion uptake have to be determined [34]. The effect of solution pH on the Cu(II) removal was studied by varying the pH from 2.0 to 7.0 (Fig. 6), where the pH was adjusted by adding dilute solution of hydrochloric acid or sodium hydroxide. At low pH values (2.0–4.0), the sorptions were generally low for Cu(II) ion because the immobilized silica gel exhibited low affinity toward Cu(II) ion at pHs lower than 5.0. The decreasing of sorption capacity of the TR-CL[4]P surface at $\text{pH} < 5.0$ is due to its facility of being protonated. The maximum uptake of Cu(II) takes place at pH 6.0. The decreasing of sorption at about pH 6.5 may be due to hydrolysis of Cu(II) after this pH. The metallic ions could be suffering from hydrolysis, starting at pH higher than 5.5, forming $\text{Cu}(\text{OH})^+$ species, which promotes a diminution of the sorption capacity, because of the diminution of the formal charge of the metallic ions [23, 35].

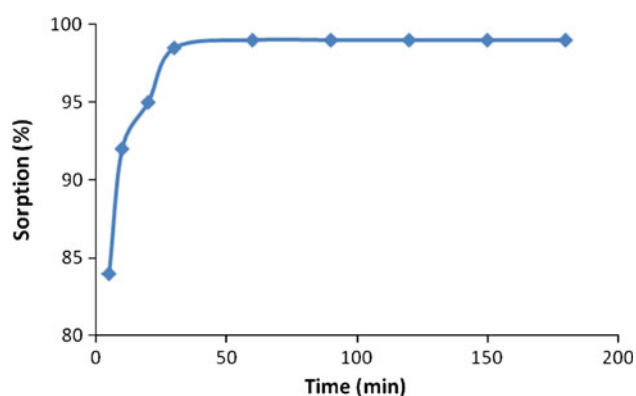


Fig. 7 The sorption equilibrium time on the removal of Cu (II) ($C_0 = 1.0 \times 10^{-4} \text{ mol L}^{-1}$; sorbent: 0.025 g; temperature: 30 °C)

Sorption time

Cu(II) cation sorption capacity was determined as a function of time to determine an optimum contact time for the sorption of Cu(II) ion on TR-CL[4]P and depicted in Fig. 7. The results indicated that the sorption equilibrium time is attained within 30 min for Cu (II) metal ion.

Effect of initial Cu(II) concentration

The effect of initial concentrations on Cu(II) ion sorption was investigated by varying the initial concentrations of Cu(II) using 0.025 g sorbent at pH 6.0 and 30 min of equilibration time and obtained results was presented in Fig. 8. As it can be seen from Fig. 8, the sorption yields (%) were decreased by increasing of initial Cu(II) concentration. Ozer et al. [36] indicated that all Cu(II) ions present in solution at lower concentrations could interact

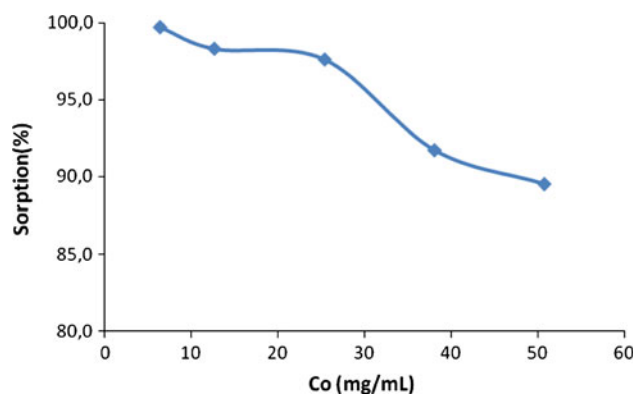


Fig. 8 Effect of initial Cu (II) concentration on the removal of Cu (II) (at pH 6.0, 30 °C)

with the binding sites and thus the sorption percentage was higher than those at higher initial Cu(II) ion concentrations. At higher concentrations, lower sorption yield is due to the saturation of sorption sites. These results show that the removal of Cu(II) are concentration dependent. Experimental data obtained from the effect of initial concentration on sorption capacity were fitted to Langmuir, Freundlich and D–R adsorption isotherms.

Adsorption isotherm

In order to optimize the design of an adsorption system, it is important to establish the most appropriate correlation for the equilibrium curves. In this study, three adsorption isotherms namely the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms were applied to the equilibrium data of adsorption of Cu(II) on TR-CL[4]P sorbent.

The Langmuir equation is valid for monolayer sorption on a surface with a finite number of identical sites and is expressed as [37]:

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \quad (2)$$

where q_e is the amount of solute adsorbed on the surface of the adsorbent (mmol g^{-1}), C_e the equilibrium ion concentration in the solution (mg L^{-1}), q_o (mg/g) is the maximum amount of the adsorbate per unit weight of the adsorbent to form a complete monolayer on the surface whereas b (L/mg) is Langmuir constant related to the affinity of the binding sites. When C_e/q_e is plotted against C_e , a straight line with slope $1/q_o$ and intercepts $1/bq_o$ is obtained. The Langmuir parameters for Cu(II) ion, q_o and b are calculated from the slope and intercept of the graphs (Fig. 9) and are given in Table 2.

To determine if the Cu(II) sorption process by TR-CL[4]P is favorable or unfavorable for the Langmuir type sorption process, the isotherm shape can be classified by a

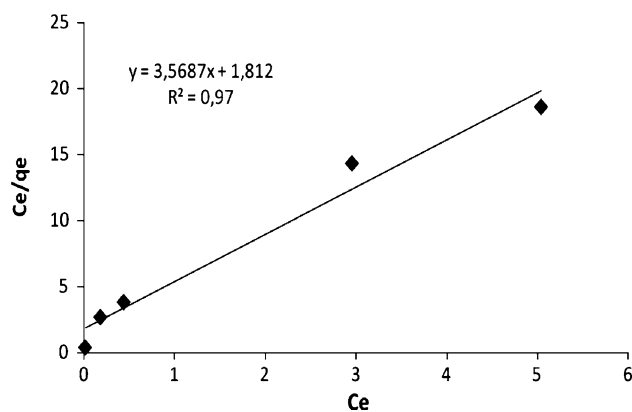


Fig. 9 Langmuir plot for the removal of Cu (II) (at pH 6.0)

term “ R_L ”, a dimensionless constant separation factor, which is defined below [38]

$$R_L = \frac{1}{1 + bC_o} \quad (3)$$

where R_L is a dimensionless separation factor and b is Langmuir constant (L/mg). The parameter R_L indicates the shape of the isotherm accordingly: $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible.

The calculating of R_L value as 0.33 indicated that sorption of Cu(II) on TR-CL[4]P was favorable at 6.35 mg/L initial Cu(II) concentration at 30 °C and pH 6.0.

The Freundlich adsorption model [39], which assumes that the adsorption occurs on heterogeneous surfaces, is given by the following equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where K_f is the Freundlich constant (mmol g^{-1}) which indicates the adsorption capacity and represents the strength of the adsorptive bond and n is the heterogeneity factor which represents the bond distribution. Values of K_f and n were calculated from the intercept and slope of the

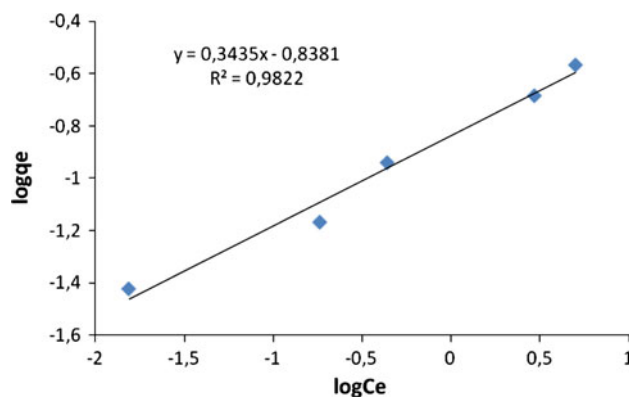


Fig. 10 Freundlich plot for the removal of Cu (II) (at pH 6.0)

Table 2 Langmuir, Freundlich and D–R isotherm parameters

Langmuir isotherm parameters			Freundlich isotherm parameters			D–R isotherm parameters			
q_o (mg/g)	b (L/mmol)	R^2	K_f (mmol/g)	n	R^2	q_m (mmol/g)	k (mol ² k J ⁻²)	E (kJ mol ⁻¹)	R^2
17.80	1.97	0.97	1.45	2.91	0.9822	0.269	0.0049	10.2041	0.9265

plots of $\log q_e$ versus $\log C_e$ (Fig. 10). The Freundlich isotherm data are given in Table 2. It has been shown using mathematical calculations that n was between 1 and 10 representing beneficial sorption [40]. On the comparison of the R^2 values given in Table 2, we can conclude that Freundlich equation represents a slightly better fit to the experimental data than the Langmuir equation in sorption of Cu (II) on TR-CL[4]P. This led to the conclusion that the surface of the TR-CL[4]P is made up of small heterogeneous adsorption patches.

Although direct comparison of TR-CL[4]P with other sorbent materials is difficult, owing to the different applied experimental conditions, it was found, in general, the adsorption capacity of TR-CL[4]P for Cu(II), using equilibrium experiments, determined to be around 17.80 mg Cu(II)/g TR-CL[4]P, is higher than calixarene based APSIC[4]P sorbent prepared by our group [23], fly ash + wollastonite [41], fly ash, dead fungal biomass (*Schizophyllum commune*) [42], sawdust [43], bagasse fly ash [44], peanut hulls [45], cork bark [46], natural zeolite [47], olive pomace [48] and powder activated carbon [49]. The values of sorption properties of Cu(II) in different sorbents used in the literature were summarized in our previous study [23]. It may be observed that the uptake of Cu(II) on TR-CL[4]P is greater than some other sorbents.

To distinguish between physical and chemical sorption, the data were applied to D–R isotherm model [50]. The linear form of (D–R) isotherm equation is

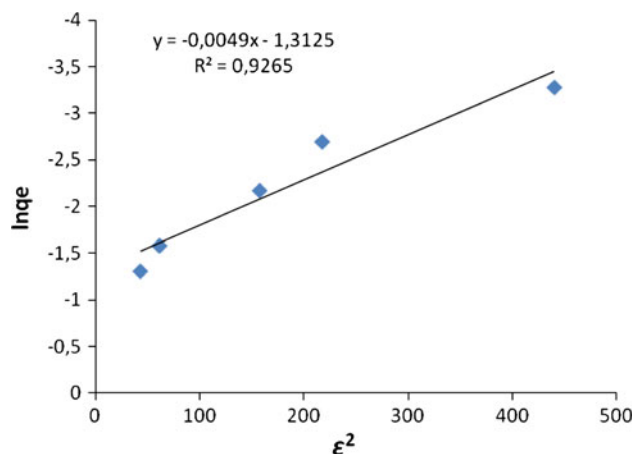
$$\ln q_e = \ln q_m - k\varepsilon^2 \quad (5)$$

where ε (Polanyi potential) is $[RT \ln(1 + 1/C_e)]$, q_e is the amount of solute adsorbed per unit weight of TR-CL[4]P (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 ε^2 it is possible to generate the value of q_m from the intercept, and the value of K from the slope (Fig. 11).

The constant K gives an idea about the mean free energy E (kJ mol⁻¹) of sorption and can be calculated using the relationship;

$$E = (-2K)^{1/2} \quad (6)$$

The typical range of bonding energy for ion-exchange mechanisms is 8–16 kJ mol⁻¹. In the case of $E < 8$ kJ mol⁻¹, physical forces such as van der Waals and

**Fig. 11** The D–R sorption isotherm

hydrogen bonding may affect the sorption mechanism [51]. If this value is between 8 and 16 kJ mol⁻¹, the sorption process can be explained by ion exchange. E value is calculated to be 10.2041 for Cu (II) ion. Therefore, it is possible to say that adsorption mechanism of Cu (II) metal ion can be explained with an ion-exchange process. D–R isotherm for Cu (II) was presented in Fig. 11 and some parameters calculated from the isotherm are listed in Table 2.

Thermodynamic parameters

The determination of the standard Gibbs free energy, ΔG° is very important to predict the spontaneity of the occurred adsorption while the entropy, ΔS° is used to describe the degree of freedom of the molecules in the system. On the other hand, the enthalpy represented by ΔH° is useful to decide if the process is either exothermic or endothermic. These thermodynamic parameters were determined using the following Equation;

$$\Delta G^\circ = -RT \ln K_d \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (9)$$

where ΔG° = change in free energy, kJ mol⁻¹; ΔH° = change in enthalpy, kJ mol⁻¹; ΔS° = change in entropy, J mol⁻¹K⁻¹; T = absolute temperature, K; R = gas constant = 8.314×10^{-3} ; K_d = equilibrium constant.

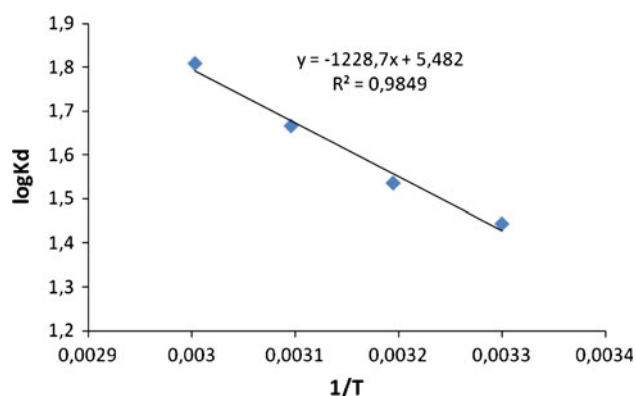


Fig. 12 $\log K_d$ – $1/T$ graphs for the sorption of Cu (II) onto TR-CL[4]P. (pH 6.0; t : 30 min; $C_0 = 1.0 \times 10^{-4}$ mol L $^{-1}$; sorbent: 0.025 g)

Table 3 Thermodynamic parameters for the sorption of Cu(II) ion onto TR-CL[4]P

Metal	ΔH° (kJ mol $^{-1}$)	ΔS° (kJ K $^{-1}$ mol $^{-1}$)	T(K)	ΔG° (kJ mol $^{-1}$)	R^2
Cu	23.53	0.105	303	–8.285	0.9849
			313	–9.335	
			323	–10.385	
			333	–11.435	

When $\log K_d$ is plotted against $1/T$, a straight line with slope $\Delta H^\circ/2.303RT$ and intercept $\Delta S^\circ/2.303R$ is obtained (Fig. 12) and the values of ΔH° and ΔS° were obtained from the slope and intercept of the van't Hoff plots. The obtained thermodynamic parameters for the sorption process for Cu(II) ion are given in Table 3. As it can be seen from Table 3, positive ΔH° value for Cu(II) sorption represent the endothermic nature of the sorption process. Negative values of ΔG° indicate the spontaneous nature of the reaction. The reaction is favored and getting easier at higher temperatures. The positive value of ΔS° suggests the increased randomness at the solid–solution interface during the adsorption of Cu (II) ion on silica. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. Enhancement of adsorption capacity at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface [52, 53].

Conclusions

In the present study, the synthesis and use of TR-CL[4]P with tripod structure as a novel sorbent were discussed.

TR-CL[4]P sorbent was prepared with immobilization onto APS of the aldehyde pointed calix[4]arene derivative. The prepared new sorbent was used for sorption of Cu(II) ion in aqueous solution and the results showed that TR-CL[4]P is effective sorbent towards Cu (II) ion. Therefore, for Cu(II) sorption, some optimum conditions were determined. Maximum Cu(II) removal was obtained at 30 °C, 30 min and pH 6 for TR-CL[4]P and the batch sorption capacity was found as 17.80 mg/g.

The characteristics of the sorption process of Cu(II) ion on the prepared sorbent were evaluated by using the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption isotherms. In the isotherm studies, it was determined that the experimental data follow better Freundlich isotherm model than that Langmuir. From the D–R adsorption isotherms, it was concluded that ion-exchange process was playing an important role in the sorption of Cu(II) ion onto TR-CL[4]P. Thermodynamic parameters indicated that the sorption process would be spontaneous and endothermic. Consequently, TR-CL[4]P may be used as an effective, and alternative sorbent for removal of metal ions from aqueous solutions.

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