



Synthesis of Piperdinomethylcalix[4]arene Attached Silica Resin for the Removal of Metal Ions from Water: Equilibrium, Thermodynamic and Kinetic Modelling Studies



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ARTICLE INFO

Received: 01 March 2020

Revised: 05 April 2020

Accepted: 19 April 2020

Available online: 21 April 2020

ABSTRACT

Toxic metal pollution is one of the most persistent environmental problems globally. This study deals with the synthesis of the *p*-piperdinomethyl calix[4]arene attached silica (PAS) resin and to investigate their metal ions removal efficiency from water. In batch adsorption experiment PAS resin shows good adsorption efficacy for the Cu²⁺ and Pb²⁺ metal ions. To examine the adsorption mechanism and validate the experimental adsorption data the isotherm models were applied and adsorption of the Cu²⁺ and Pb²⁺ metal ions follow Freundlich isotherm model very well with good correlation coefficient. However, the adsorption energy calculated from the D-R isotherm was at the range of 9-14 KJ/mole which describes the ion exchange nature of resin. Furthermore, breakthrough capacity of column was calculated from online adsorption as 0.027 and 0.041 mmol/g⁻¹ for Cu²⁺ and Pb²⁺, respectively. Furthermore, thermodynamics and kinetic study revealed that, the adsorption process spontaneity and endothermic that follows the pseudo 2nd order kinetic equation with good regression coefficient.

KEY WORDS

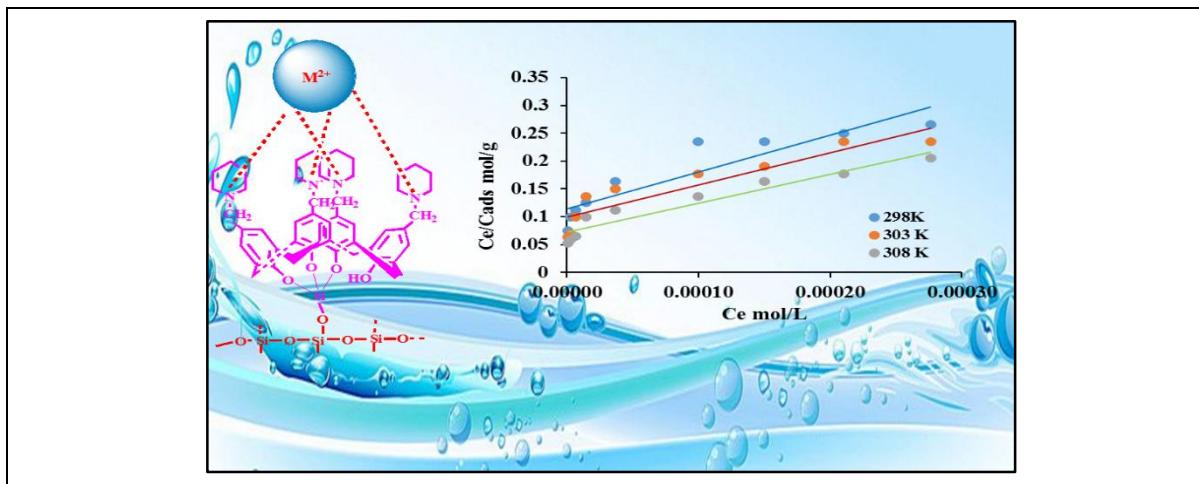
Batch adsorption

Toxic metal ions

Calix[4]arene

Online adsorption

GRAPHICAL ABSTRACT



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Introduction

Clean and pure water is very important and vital for human life. According to the literature 1.8 billion people drink polluted water resulting in the death of about a million of peoples specially children in every year. Water contains different types of contaminations such as water-soluble or insoluble, organic or inorganic toxic substances [1,2]. However, if such toxic polluted water is consumed by human beings or other water living organism, causing many dangerous health effects [3-5]. Among the different water pollutants, heavy metal ions have got important and extensive attention due to their non-degradable nature. They enter into body by oral source and accumulated into body tissues causing irritations, cancer or other infections [6]. Therefore, it became necessary for the industrial sector that the effluents should be treated to reduce the metal ion concentration level in water.

Removal of the metal ions *via* adsorption is one of the vital areas of the current research related to the adsorbents design as well as their binding sites due to their wide applications in separation science [7-11]. Among the most important adsorbents, the calixarenes are the familiar class of cyclic oligomers having three dimensional structures and can bind with guest species such as cations, anions, and neutral molecules [12]. Furthermore, synthetic chemists have made attempts to introduce the different moieties onto both rims of calixarenes as to design the receptors, which should have ability to transport particular ions. Therefore, in literature, different examples of the calixarenes have been observed, which are used as hosts or complexing agents for cations and anions [13-17]. Consequently, due to the role of different ions in chemical, physical, and biochemical processes, this field of study have got much more attention and interest for the

development of synthesis of such cavitands. Moreover, electron donating groups such as nitrogen, oxygen, and sulfur containing functional groups onto calix[4]arene upper rim are applicable and efficient extractants for cations [18,19]. Due to the flexible nature and ease of functionalization, calixarenes have been immobilized onto solid polymeric matrices to introduce a new class of selective adsorbent which have very high adsorption capacities. In our previous studies, such calixarene based adsorbent materials have been used for the remediation of polluted sites [18,20,21]. Keeping in view, the potential of these compounds, this study elaborate the synthesis of *p*-piperidinomethyl calix[4]arene derivative (**3**) immobilized on silica as support that has been used for batch and online column adsorption of metal ions from water.

Experimental

Chemical

All the chemicals used during the synthesis were of analytical grade and GR grade. Fluka chemical company (Germany) provides silica gel with (230–400 mesh). The thin layer technique was performed by using pre-coated silica gel plates (SiO_2 , Merck PF254). All the metal solutions were prepared in deionized water.

Instrumentation

All the synthesized compounds were confirmed by the FTIR spectroscopy which was recorded by using the Thermo Nicllet 5700 FT-IR spectrometer (WI. 53711, USA). The surface of material was characterized using scanning electron microscopic (SEM, JSM-6380 Perkin Elmer, Shelton, CT06484, USA). All the metal solution were analyzed using the Cary 100 UV-VIS spectrophotometer and verify by Perkin-Elmer atomic absorption spectrophotometer (AAS) Model Analyst 700

(Norwalk, CT). A quaternary pump, HPLC-DAD spectra system SCM 1000 (model Q Grade-A 0024752 Thermo Finnigan) with vacuum degasser and rheodyne manual injector system (20- μ L loop) was used for online adsorption of metals.

Synthesis

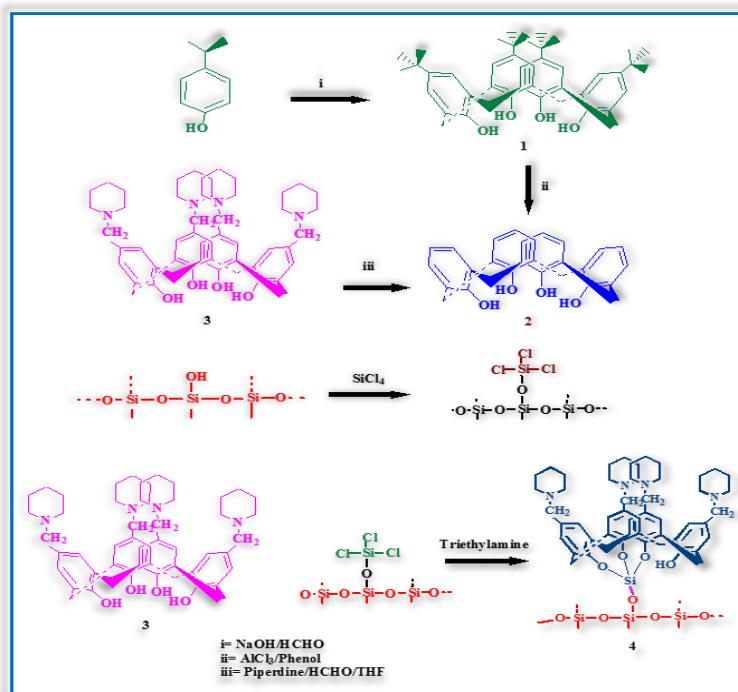
The compound **1** to **3** have been synthesized by [22,23] while the compound **4** was synthesized using the modified method [24].

Synthesis of piperidinomethylcalix[4]arene appended PAS silica resin

5 g of silica powder was added to 250 mL of (0.1 M) HCl solution and refluxed for 4 h to activate the silica surface. After reflux, the silica was washed with double distilled water and dried in oven for 5 h, then 250 mL SiCl₄ (0.1 M) in pre-dried CH₂Cl₂ was added into silica powder. After that, 1.5 mL of triethylamine was added that resulted in a cloudy mixture which was kept at room temperature for about more than 12 h. The

solvents were removed using a rotatory evaporator to get white powder of silica and placed on hot plate with stirrer and added 1.5 g of *p*-piperidinomethylcalix[4]arene (**3**) which was already dissolved in 60 mL tetrahydrofuran (THF) and the reaction mixture was continue refluxed followed by addition of 5 mL of triethylamine. The reaction mixture was monitored with the passage of time by using FT-IR spectroscopy technique and after the three days it was confirmed that the reaction has completed. Furthermore, in order to remove the unattached *p*-piperidinomethylcalix[4]arene (**3**) and some other possible impurities from PAS resin, the material was filtered and subsequently washed with 200 mL CHCl₃, 200 mL methanol, 200 mL water, and again with 200 mL CHCl₃ at the end of the reaction. Finally, gravimetric analysis method was performed to check the amount of *p*-piperidinomethylcalix[4]arene (**3**) attached onto silica surface. It has been found that the maximum amount of *p*-piperidinomethyl calix[4]arene (**3**) chemically attached onto the silica is 0.48×10^{-4} mmol/g⁻¹.

Scheme 1. Synthesis route of PAS resin



Batch adsorption

Batch adsorption method was performed to check the removal efficiency of the PAS resin for the Cu²⁺ and Pb²⁺ metal ions. During the batch adsorption experiments, the pH of the metal nitrate solution and dosage of the PAS resin were optimized. The pH values were adjusted from 3 to 9 using the NaOH (0.1 M) or HCl (0.1 M). During the adsorption isotherm experiment, the initial concentration of the metal ions solution varied from 1×10⁻³ to 1×10⁻⁶ M and experiment was performed at pH 7. Moreover, the temperature effect was examined at 298, 303, and 313 K at the optimized values of pH and PAS resin dosage. The kinetic studies were conducted by 20 mg of PAS resin at different interval of time and different temperature (298, 303 and 313 K) at the solution with the pH of 7. The PAS resin was filtered off and remaining metal ion concentration was analyzed using the AAS. All the adsorption experiment data were repeated three times and the mean values were reported. The % removal of the metal ions was calculated using the Equation 1.

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i and C_f (mol/L⁻¹) are the initial and final concentration of metal ions, respectively.

Dynamic adsorption procedure

Column packing

First, the empty stainless-steel column (15 × 3 mm I.D.) was washed carefully with the de-ionized water, aqueous HCl, NaOH solution, and methanol to remove the possible impurities which may be presented inside the column. After that the PAS silica resin was packed in column by using the slurry

column packing technique using the peristaltic pump.

Online adsorption

The four steps are involved in on-line solid phase extraction procedure that is given below, while the data was recorded at 300 nm.

Step 1: This step involves the conditioning of PAS silica resin packed column with acetonitrile and water (30:70) mixture of for 10 min.

Step 2: The solutions of selected metal nitrates with appropriate concentrations were passed through the column at the flow rate of 0.5 mL/min⁻¹. The loading of the metal solution was continued until the PAS silica resin packed column was at about saturation or saturated.

Step 3: The washing of unloaded metal ions took place in this step for this the de-ionized water was passed through the column at flow rate of 0.5

mL min⁻¹ for about 10 min.

Step 4: This step is related with unloading of metal ion from the PAS silica resin packed column with appropriate stripping agent at a flow rate of 1 mL/min⁻¹. During this step, all the solutions leaving towards the detector were collected and subjected to AAS for quantitative analysis.

Results and discussion

Characterization of PAS resin

The PAS resin was characterized using the FTIR spectroscopy and scanning electron microscopy (SEM).

FTIR study

Several peaks indicated the presence of different functional groups in the compound. In Figure 1, the spectrum (a) is of silica characterized by the presence of peaks at 3440 and 1631 cm⁻¹ for OH and Si-O, characteristic peaks respectively while the peak 1105 cm⁻¹ is OH bending peaks. The spectrum (b) is of *p*-piperdinomethyl calix[4]arene (**3**). The peaks observed at

3400 cm⁻¹, 3100 cm⁻¹, 2926 cm⁻¹, 1600 cm⁻¹, 1460 cm⁻¹ and 1257 cm⁻¹ indicates OH, =C-H, -C-H, C-C, C-O and C-N stretching respectively. The spectrum (c) is of PAS resin which shows the some additional peaks as compared to silica. These additional peaks analyzed at 3400, 2932, 1629, 1440, and 1332 cm⁻¹ are the characteristic peaks of OH, =C-H, C-C, C-O and C-N stretching respectively. The peak observed at 1101 cm⁻¹ is of OH bending frequency. These additional new peaks on silica clearly shows that *p*-piperdinomethyl calix[4]arene (**3**) is successfully attached on silica.

Figure 1. FTIR spectrum (a) pure silica (b) *p*-piperdinomethyl calix[4]arene and (c) PAS resin

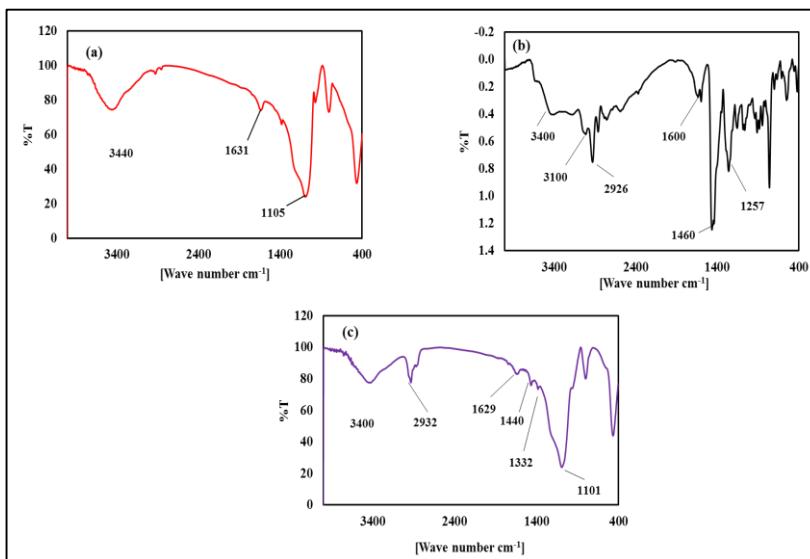
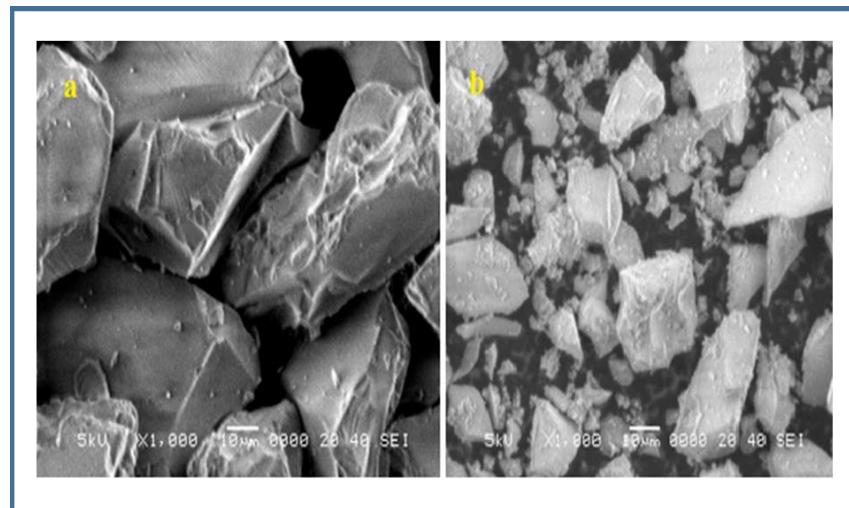


Figure 2. SEM images of (a) pure silica (b) is PAS resin



Scanning electron microscopy (SEM) analysis

Surface properties of the adsorbent such as surface area, porosity and roughness or smoothness present are characterized by the scanning electron microscopy (SEM) technique. Therefore, the silica and PAS silica resin were characterized by SEM technique (Figure 2). Figure 2a shows the pure silica which has very clean surface and shows smooth morphology, while in the case of image (b) has the roughness and unclear surface. The roughness observed onto silica surface proves that the *p*-piperdinomethyl calix[4]arene is attached on the silica surface.

Metal selectivity

PAS silica resin with coordination binding sites have proved that it possesses good capability to form stable complexes with metal ions such as Cu^{2+} , Pb^{2+} , Ba^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Mg^{2+} and Cs^+ . Consequently, adsorption of different metal ions on the PAS silica resin was performed and shown in Figure 3. It was deduced that, Cu^{2+} and Pb^{2+} are possible targets of PAS resin. Other metals were also under the influence of the soft binding sites but less than that of Cu^{2+} and Pb^{2+} . The order of removal decreased as $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ba}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cs}^+ > \text{Mg}^{2+}$.

PAS resin dosage

To check the dosage effect of the PAS resin onto the percentage removal of the metal ion, different amount of PAS resin were taken format the range of 10-50 mg. Figure 4

illustrates that, the maximum adsorption percentage was obtained by using 30 mg of PAS resin. Further enhancing the PAS resin demonstrated no significant increase in the adsorption percentage therefore all other parameters were performed by using 30 mg of PAS resin.

Adsorption isotherms

The adsorption isotherm models describe the phenomenon of adsorbate and the adsorbent surface in the form of monolayer/multilayer, energy variations, also pressure at constant temperature, mechanism and predication of adsorption process. The experimental data was subjected towards the Langmuir model shown in Equation 2.

$$\left(\frac{C_e}{C_{ads}} \right) = \left(\frac{1}{Qb} \right) + \left(\frac{C_e}{Q} \right) \quad (2)$$

Figure 3. Selectivity of different metals ions on PAS resin (1×10^{-4} mol/L, 60 min contact time)

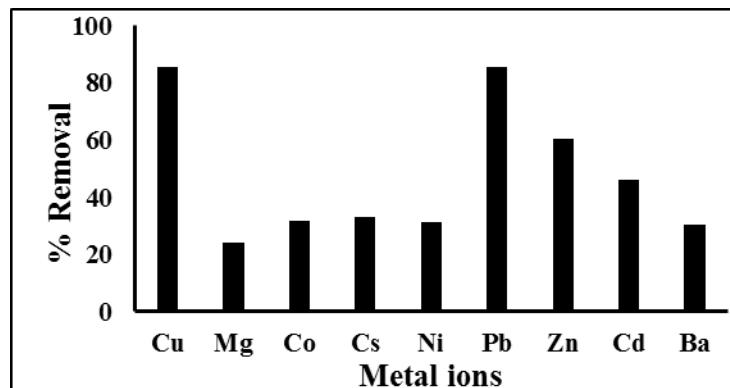
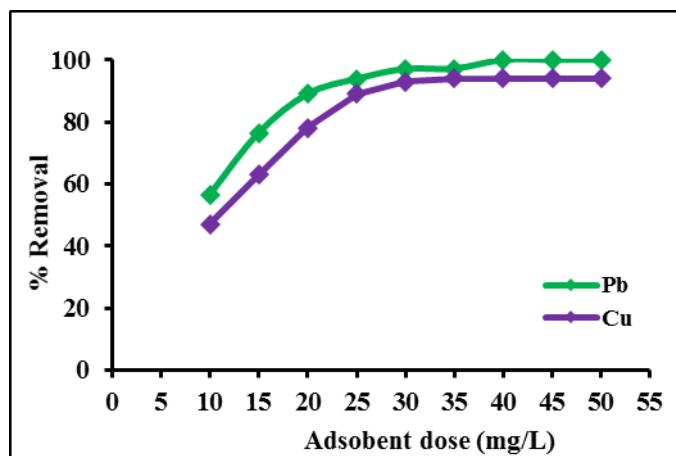


Figure 4. Effect of PAS resin dosage on the adsorption of Cu^{2+} and Pb^{2+} metal ions



Where C_{ads} is the adsorbed amount of adsorbate, C_e is the metal ion equilibrium concentration, and Q is the amount of metal ions adsorbed to form to monolayer, where b is the Langmuir model constant value. In Figure 5, the graph is plotted in between C_e/C_{ads} mmol/g versus C_e mol/L, from the slope and intercepts the values b Langmuir constant and value of Q can be calculated as shown in Table 1.

The R_L is a constant and it is a characteristic of this model and can be obtained using the Equation 3.

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

Freundlich isotherm model is a non-ideal heterogeneous reversible adsorption isotherm model demonstrated in Equation 7.

$$\log C_{ads} = \log A + \left(\frac{1}{n} \right) \log C_e \quad (4)$$

Where A is a Freundlich constant, which describes adsorption capacity, n is the energy or intensity of adsorption, and C_e is the metal ion equilibrium concentration.

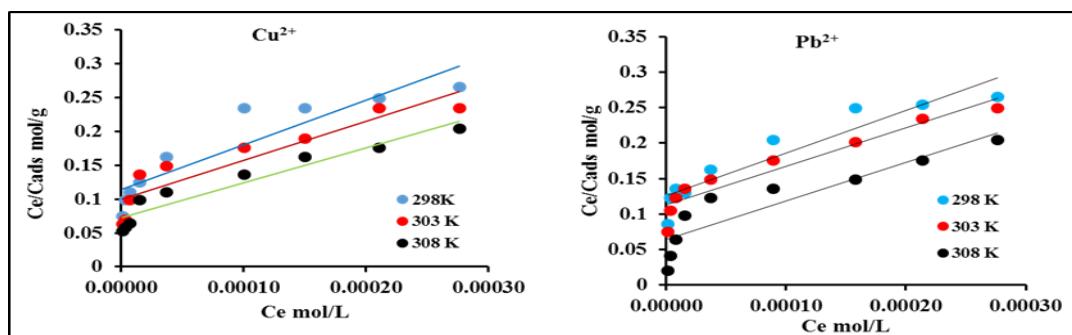


Figure 5. Langmuir isotherm (Conc. 1.60×10^{-5} to 1.3×10^{-3} mol/L, 30 mg PAS resin, per 10 mL of adsorbate with 60 min shaking time at 298-308 K)

Table 1. Langmuir isotherm parameters

Metal ions	Temperature (K)	Q (mmol/g)	b	R_L	R^2
Cu^{2+}	298	1.51	576.4	0.1-0.99	0.900
	303	1.57	635.4	0.12-0.99	0.901
	308	1.58	860.3	0.2-0.99	0.908
	298	1.62	479.8	0.5-0.99	0.902
Pb^{2+}	303	1.78	509.0	0.78-0.99	0.908
	308	1.81	1033.2	0.9-0.99	0.903

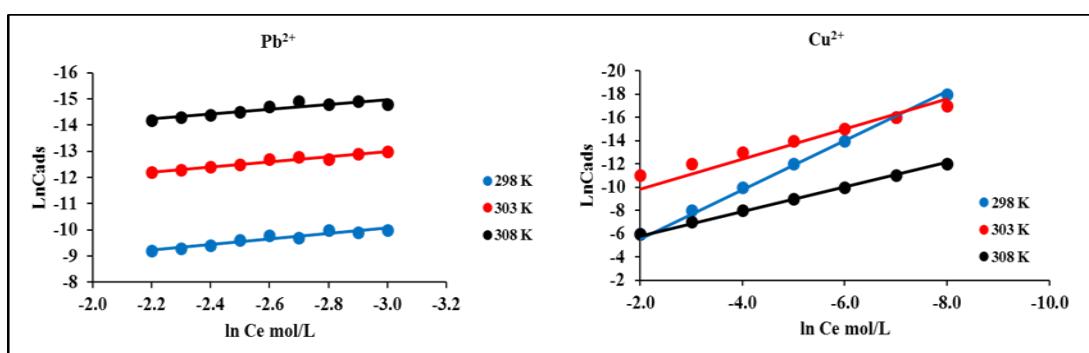


Figure 6. Freundlich isotherm (Conc. 1.60×10^{-5} to 1.3×10^{-3} mol/L, 30 mg PAS resin, per 10 mL of adsorbate with 60 min shaking time at temperature range from 298-308 K)

As seen in Figure 6, the heterogeneous adsorption occurred on the adsorbent surface which is the clear indication towards the validation of the Freundlich model. The numerical values of A and n can be calculated from the slop and intercept of plot and values are presented in Table 2.

Dubinin–Radushkevich D-R adsorption isotherm model is shown in Equation 5, that evaluates the porosity, the apparent free energy and mechanism of adsorption.

$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2 \quad (5)$$

The characteristic property of Dubinin–Radushkevich model is ε i.e. the Polanyi potential [25] which can be expressed in Equation 6:

Table 2. Freundlich isotherm parameters

Metal Ions	Temperature(K)	A(mg/g)	n	R ²
Cu^{2+}	298	1.19	4.88	0.991
	303	5.07	4.62	0.994
	308	6.41	4.44	0.995
Pb^{2+}	298	3.11	5.61	0.992
	303	6.91	5.57	0.910
	308	7.01	3.17	0.998

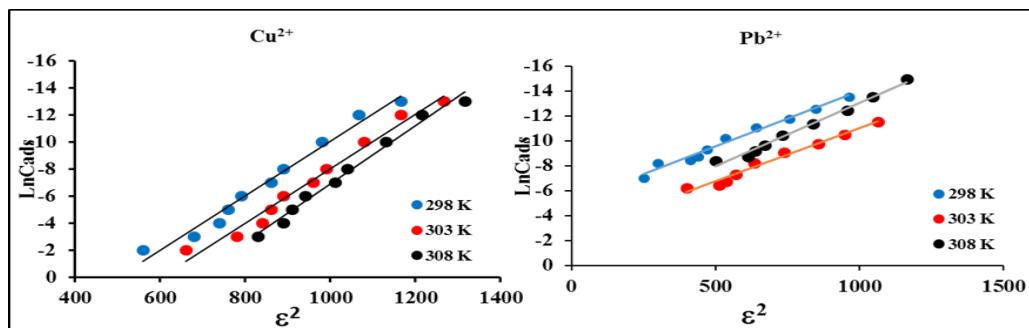


Figure 7. D-R isotherm (Conc. 1×10^{-5} to 1×10^{-3} mol/L, 30 mg PAS resin, per 10 mL of adsorbate with 60 min shaking time at temperature range from 298–308 K)

Table 3. D-R isotherm parameters

Metal Ions	Temperature (K)	Xm (mol/g)	E (kJ/mol)	R ²
Cu^{2+}	298	0.071	11.5	0.901
	303	0.790	10.7	0.992
	308	0.091	12.1	0.997
Pb^{2+}	298	0.034	9.08	0.985
	303	0.056	10.1	0.991
	308	0.080	10.5	0.981

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6)$$

Where R and T stand for gas constant temperature, respectively. The, E (kJ/mol⁻¹) is mean adsorption energy, calculated using the Equation 7:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (7)$$

The constant values of D-R model are given in Table 3, obtained from slop and intercept of Figure 7. The E value varies from 9.0 to 16.0 kJ/mol⁻¹ suggesting that the metal ions are adsorbed onto PAS resin predominantly by following the ion exchange phenomenon.

Thermodynamics study

The thermodynamic parameters such as the enthalpy change ΔH (kJ/mol⁻¹), entropy change ΔS (kJ/mol⁻¹/K⁻¹), and Gibbs free energy ΔG (kJ/mol⁻¹) can be calculated using the Equation 8 and 9.

$$\ln k_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

$$\Delta G = -RT \ln k_c \quad (9)$$

The graph that plotted between the $\ln k_c$ versus $1/T$ is shown in Figure 8, and the constant values of ΔH (kJ/mol⁻¹), and ΔS (kJ/mol⁻¹/K⁻¹) can be calculated from the slop and intercept (Table 4). The low value of ($-\Delta G$) clearly proves that the practicability of adsorption process and negative ($-\Delta G$) values by increasing in temperature describes the spontaneity of the process. The + value of enthalpy change ΔH verify that the adsorption process is endothermic and (ΔS) values suggest good affinity of Cu^{2+} and Pb^{2+} ions towards PAS resin.

Kinetic study

To examine the adsorption process, the kinetic study was performed by applying the pseudo 1st and 2nd order kinetic models (Equation 10 and 11).

Figure 8. Effect of Temperature on adsorption of metal ions on PAS resin

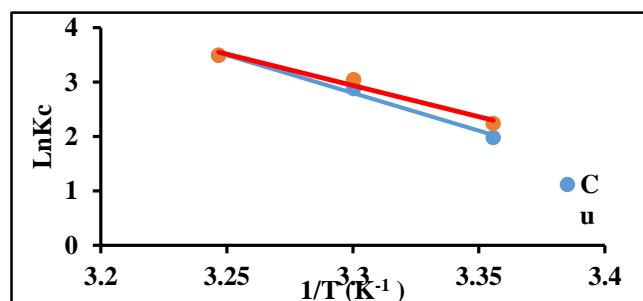


Table 4. Thermodynamic parameters for sorption of Pb^{2+} and Cu^{2+} on PAS resin

Metal Ion	ΔH (kJ/mol)	ΔS (kJ mol ⁻¹ K ⁻¹)	298 K	303 K	308 K
Cu^{2+}	0.05	0.180	-4.8 lnKc=1.98	-7.2 lnKc=2.89	-9.0 lnKc=3.50
Pb^{2+}	0.06	0.210	-5.4 lnKc=1.81	-7.6 lnKc=1.83	-9.1 lnKc=1.86

$$\ln(qe - qt) = \ln qe - k_1 t \quad (10)$$

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{qe} \right) t \quad (11)$$

Where qe and qt stand for the amount of metal ions (mg/g) at equilibrium and time, respectively. The k_1 and k_2 shows the pseudo first and second order rate constant respectively. Table 5 presents the constant values of the pseudo first and second order kinetic model which clearly explain that the adsorption mechanism followed by pseudo second order kinetic model very well with correlation coefficient values (R^2 0.99).

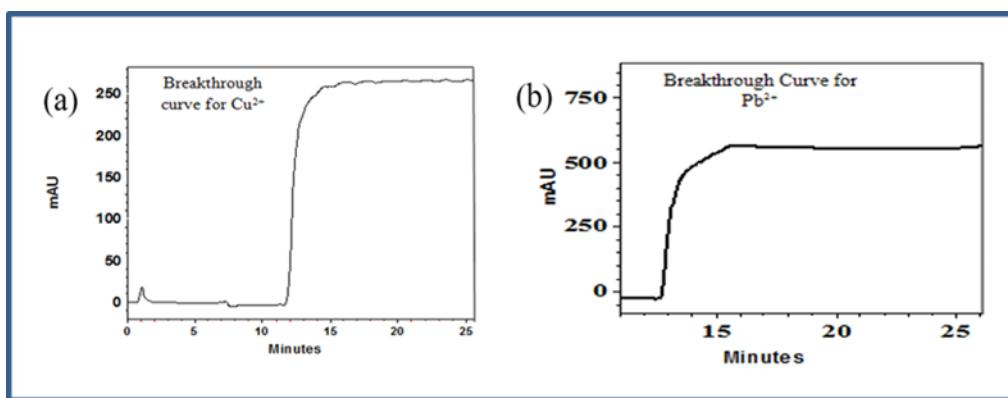
Column adsorption

Breakthrough capacity of column through online adsorption

The column study was carried out in a packed column to remove the metal ions by using the on-line adsorption technique. The breakthrough curve, *i.e.* plot of absorbance v/s time obtained as a response of HPLC Figure 9, was used to calculate breakthrough capacities of the packed column. The total capacity was found to be 0.029 and 0.044 mmol/g⁻¹ and breakthrough capacity were 0.027 and 0.041 mmol/g⁻¹ for the Cu^{2+} and Pb^{2+} , respectively.

Table 5. Pseudo 1st and 2nd order kinetic parameters Cu²⁺ and Pb²⁺ at different temperatures

Temperature	Pseudo First Order Kinetic Model			Pseudo Second Order Kinetic Model		
	Cu ²⁺	K ₁ /min ⁻¹	qe (mmol/g)	R ²	K ₂ /g/mol ⁻¹ min ⁻¹	qe (mol/g)
298	7.3	954	0.971	100.1	0.064	0.991
303	7.1	933	0.983	111.3	0.065	0.989
308	6.9	923	0.975	112.7	0.066	0.979
Pb ²⁺						
298	6.9	951	0.997	59.2	3.70	0.983
303	6.8	922	0.822	140.4	7.21	0.985
308	6.7	922	0.962	135.7	7.40	0.984

**Figure 9.** The breakthrough curves (a) Cu²⁺ (b) Pb²⁺ ion

Atomic absorption spectroscopy (AAS) analysis of stripped fractions

This study was carried out by using the standard metal solutions with linear concentration range ($R^2=0.99$). The data obtained were used to perform all calculations. In detail, the fractions of both metal samples were stored during stripping and then were subjected to AAS for analysis, where the values of stripped/desorbed metal were calculated. It was revealed that about 95% and 98% of Cu²⁺ and Pb²⁺ ions, respectively, was stripped from the column. The higher efficiency in column agreement as compared to that of batch process may be due to the greater contact of metal ions with PAS resin. Whereas, the interaction of metal ions with PAS based resin can be elaborated on the basis of nature of each metal ion such as their softness and size of calix[4]arene moiety, coordination properties as well as ionic radii etc. Accordingly, the higher or

smaller desorption is a clue for the interaction between the metal ion and ligand. In addition, the binding sites and special characteristics of PAS may involve *p-p* interactions, hydrogen bonding, electrostatic interactions, and/or cation dipole interactions, which are responsible for different behavior with different metals ions.

Stripped fractions V/S breakthrough capacities

A comparative study of the breakthrough capacities and concentration of stripped solutions calculated through AAS was carried out to elaborate the efficiency of the column. Figure 10 reveals that both the values (loaded and stripped solutions in (mmol/g⁻¹) are in good agreement suggesting the higher efficiency and reusability of the PAS silica resin.

Comparative study

Efficiency of the PAS resin is compared with different other adsorbent given in

Table 6, which shows that the resin has good efficiency over the other adsorbents.

Figure 10. The breakthrough/loading and stripping capacities of Cu^{2+} and Pb^{2+} ions on PAS resin

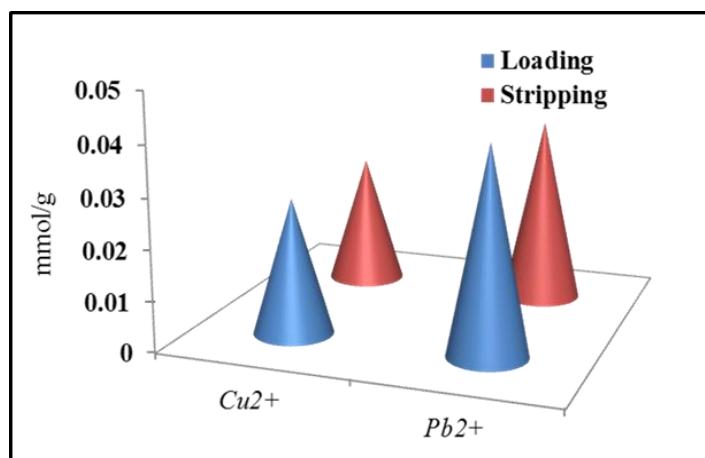


Table 6. Comparison of PAS resin with other adsorbents for adsorption of Pb^{2+} and Cu^{2+}

Adsorbent	Metal ion	% Adsorption	Reference
Nitroso-R salt impregnated magnetic Ambersorb 563	Pb^{2+}	98	26
	Cu^{2+}		
Mesoporous silica-supported bis(diazo-azomethine) compounds	Pb^{2+}	95–99	27
	Cu^{2+}		
Mucor pusillus immobilized Amberlite XAD-4 bio composites	Pb^{2+}	96–97	28
	Cu^{2+}		
Multiwall carbon nanotubes	Pb^{2+}	97	29
	Cu^{2+}	75	
PAS resin	Pb^{2+}	95	Present study
	Cu^{2+}	98	

Conclusion

This study discusses the synthesis and application of new PAS resin. FTIR and surface morphological results justified the successful attachment of compound (3) on the surface of silica. The synthesized resin was applied for the adsorption of different soft metal ions in batch as well as the column wise agreement using Online adsorption. The order of adsorption decreased as $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ba}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cs}^+ > \text{Mg}^{2+}$ and maximum adsorption was observed for Cu^{2+} and Pb^{2+} . The value of R_L suggested the favorability of Langmuir

isotherm. Whereas, the Freundlich adsorption isotherm model was found to be good correlation coefficient and it was best-fit for Cu^{2+} and Pb^{2+} . Furthermore, adsorption intensity value (n) from the Freundlich isotherm referred to good adsorption of metal ions on PAS resin. Also, the breakthrough capacity of column was also calculated from online SPE and was found to be 0.027 and $0.041 \text{ mmol/g}^{-1}$ for copper and lead, respectively. Finally, the break through and stripping capacities of the column were also compared which suggested the higher efficiency and reusability of the PAS resin. Kinetic and thermodynamic studies described that the

reaction was endothermic, following the pseudo second order kinetic model.

Acknowledgement

The authors would like to thank the National Centre of Excellence in Analytical Chemistry, University of Sindh, and Jamshoro for the financial support of this work.

Disclosure statement

No potential conflict of interest was reported by the author.

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How to cite this manuscript: Ranjhan Junejo, Shahabuddin Memon, Fatih Durmaz, Ayaz Ali Memon, Fakhar N. Memon, Nida Jalbani, Safia Sanam, Asif Ali Bhatti, Synthesis of Piperdinomethylcalix[4]arene Attached Silica Resin for the Removal of Metal Ions from Water: Equilibrium, Thermodynamic and Kinetic Modelling Studies, *Adv. J. Chem. A*, **2020**, *3*, S680–S691.