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Efficient adsorption of heavy metal ions onto diethylamine functionalized calix[4]arene based silica resin

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Water might be contaminated by different metal ions, resulting in different water-borne diseases in human and aquatic life. This research study aimed at synthesizing the diethylamine functionalized calix[4]arene based silica (DFCS) resin for the effective removal of heavy metals such as Cd²⁺, Pb²⁺, and Hg²⁺ from water. The DFCS resin was characterized using the FTIR spectroscopy and SEM techniques. The efficiency of the DFCS resin for the removal of metal ions was evaluated by performing equilibrium studies under the optimized conditions. Moreover, the experimental data were subjected to isotherm models; however, the Freundlich model was best-fit one as compared to the Langmuir model. The energy calculated from the D-R model was 10.3, 9.7 and 9.2 KJ/mol for Cd²⁺, Pb²⁺, and Hg²⁺, respectively, suggesting that the ion exchange process is involved. The thermodynamic values revealed that the reaction is spontaneous and exothermic, following the pseudo second-order kinetic model equation.

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KEYWORDS

Calix[4]arene based resin; metal ions; thermodynamic and kinetic modelling.

Introduction

Toxic metal ions found in industrial effluents, municipal and urban waste water are very harmful to human beings and aquatic life. Development of urbanization and industrialization are major cause for increasing the level of metal ions in waterways [1,2]. The toxic metal ions released from the industries and municipal waste water are accumulated into soil [3]. Toxic metal ions present in wastewater are in very trace level, but they have a toxic effect on the living beings due to their non-degradable nature. Once an entrance into the body through water source, they may create dermal irritation, bacterial and viral infections by altering, removing or

impairing the enzyme function. They act as an enzyme mimic by targeting the DNA or other biomolecule site and remove essential minerals and inhibit its functioning [4-8]. Such type of harmful actions are the major cause of lung cancer, bladder, kidney failure diseases and irregularity in blood composition [3,9,10]. Therefore, due to the hazardous nature of the metal ions at very low level, it is important to remove them from wastewater. In this regard, different methods and techniques have been applied to remove these toxic metal ions; however, the adsorption is the most common and simple technique to remove these toxic metal ions. In adsorption process, many low cost natural and synthetic adsorbents are used such as lignin and chitosan, while in synthetic

adsorbents crown ethers, cyclodextrins and other polymeric based resins are widely used [11-15].

Nowadays, the third generation compounds of supramolecular chemistry known as calixarenes are also used as adsorbents. The calixarenes are cyclic oligomers containing two rims, which can be modified by different functional groups to bind with neutral or ionic species. Previously, different studies have been carried out on calixarenes application; for example, piperidine based calix[4]arene silica resin has been applied for the removal of reactive blue 19 dye from water [16]. Calix[4]arene tetraester and calix[6]arene hexaester derivatives exhibit significant selectivity toward Na^+ and Pb^{2+} , respectively [17,18]. In the present study, the diethylamine functionalized calix[4]arene based silica resin was synthesized and applied as an adsorbent for the removal of metal ions.

Experimental procedure

Reagents and chemicals

The chemicals used in reactions were of analytical grade. Silica gel was purchased from Sigma Aldrich. 4-*tert*-butylphenol, toluene, formaldehyde used for the synthesis of calix[4]arene were obtained from Sigma Aldrich. Diethylamine and chloroform was purchased from the Merck. All the metal nitrate solutions were prepared with deionized water.

Instrumentation

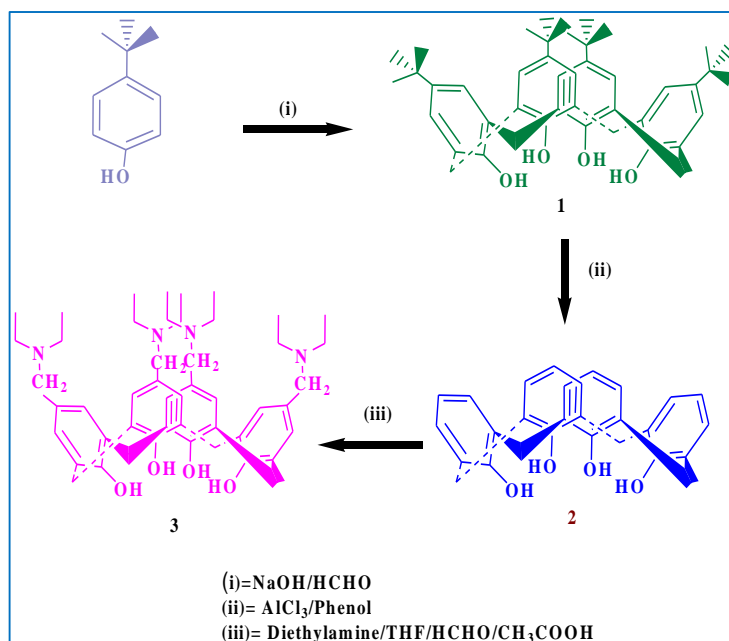
Melting points were determined on a Gallenkamp apparatus model (MFB.595. 010M England) in a sealed capillary. The CHNS study was performed to know the elemental

composition of *p*-diethylaminomethylcalix[4]arene and DFCS resin by using elemental analyzer (model Flash EA 1112, 20090-Rodano, Milan, Italy). The confirmation and characterization of all the synthesized compounds have also been performed by FTIR spectroscopy (Thermo Nicolet 5700 FT-IR spectrometer) as KBr pellets. The surface morphology of DFCS resin was performed using the scanning electron microscopic (SEM, model JSM-6380). The Cd^{2+} and Pb^{2+} metal ions concentration was determined and confirmed by atomic absorption spectroscopy (Perkin Elmer model Analyst 700; Norwalk, CT, USA), while the concentration of Hg^{2+} ions was determined by CVAAS method [19,20]. The pH meter (wtw 786 meter) was used to measure the pH. Batch adsorption study was performed using A Gallenkamp thermostat automated mechanical shaker (model BKS 305-101, UK).

Synthesis process

Synthesis of *p*-diethylaminomethylcalix[4]arene (3)

The compound **1** and **2** were synthesized by published methods [21-24], while *p*-diethylaminomethylcalix[4]arene (**3**) given in (scheme 1) has been synthesized by following reported procedure with little modification [24-28]. 1 g of compound **2** was solubilized in THF with the addition of 0.5 mL of diethylamine, 0.2 mL HCHO and 1 mL CH_3COOH into the reaction flask for 4 h at 0 °C. The reaction has been confirmed by TLC, FTIR, and melting point. The synthesized compound was recrystallized with chloroform and methanol. The off-white 83% product was obtained.

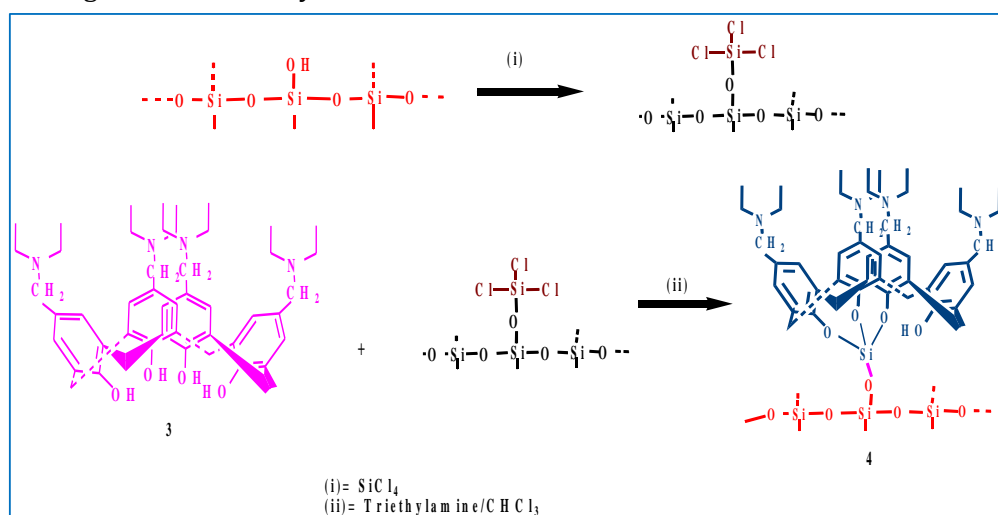


SCHEME 1 Synthesis route of *p*-diethylaminomethylcalix[4]arene (**3**)

Synthesis of DFCS resin (**4**)

The DFCS resin (**4**) was synthesized by the immobilization of compound **3** onto silica as given in (Scheme 2). The reaction was performed by following the reported method [16,29] after little modification. Compound **3** (2 g, 2.6 mmol) was dissolved in chloroform and added 5 g of silica already treated with

SiCl₄ and heated 36 h in inert environment. The reaction was monitored by FTIR spectroscopy technique. After confirmation, the surface of DFCS resin was characterized by scanning electron microscopy technique and amount of compound **3** attached onto silica surface was measured by gravimetric method, which was found to be 0.0034 mmol.g⁻¹.



SCHEME 2 Synthesis route of DFCS resin (**4**)

Adsorption procedure

The metal ions adsorption ability of the DFCS resin was assessed by batch adsorption

experiments under the optimized conditions such as DFCS dosage, pH effect, concentration, time, and temperature effect. The adsorption of metal ions was studied using DFCS resin

(0.01, 0.025, 0.05, 0.075, 0.1, 1.25, and 1.5 g) in their respective 10 mL aqueous solution (2.5×10^{-5} M). The pH was adjusted from 3 to 9 using NaOH (0.1 M) and HCl (0.1 M). Moreover, the temperature effect was examined at 25, 30, 35, 40, 45, and 50 °C along with the optimized values of pH and DFCS resin. During the adsorption isotherm experiments, the initial concentration has been varied from 2.5×10^{-5} to 2.5×10^{-7} M and finally all experiments were performed at pH 7 and 25 °C with the metal ions solution (2.5×10^{-5} M). The kinetic experiments have been performed by taking 0.1 g of the DFCS resin into Erlenmeyer flask (50 mL) containing 10 mL of metal ions solution (2.5×10^{-5} M) and at optimized pH 7. The DFCS resin was filtered off and remaining metal ions concentration have been checked by AAS. All the adsorption experiment data were repeated three times and average values were reported. The % adsorption and adsorption capacity q_e (mmol g^{-1}) of DFCS resin for metal ions were calculated by using the following Equation 1 and 2.

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

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

Where C_i and C_f and C_e (mol/L) are initial and equilibrium concentration of metal ions, respectively, and V (L) is the volume of the metal ions and m shows the mass (g) of DFCS resin.

Results and discussion

FTIR Study

All the synthesized compounds were characterized using the FTIR spectroscopy. In Figure 1, the spectrum (a) is of p-diethylaminomethylcalix[4]arene, which shows the characteristic peaks at 3361, 2919, 2663, 1606, 1434 and 1251 cm^{-1} for OH, C-H, C-C, C=C, C-O and C-N stretching frequencies, respectively, while the peak at 1043 cm^{-1} is OH bending frequency. The spectrum (b) has strong absorbance at 1095 cm^{-1} for Si-O-Si stretching. The peaks at 3454 and 1629 cm^{-1} are O-H stretching and O-H bending, respectively. The spectrum (c) is of DFCS resin, which have some new extra bands at 3361, 2979 and 1473 cm^{-1} for OH, C-H, and C=C groups of compound 3 that has been attached onto silica surface.

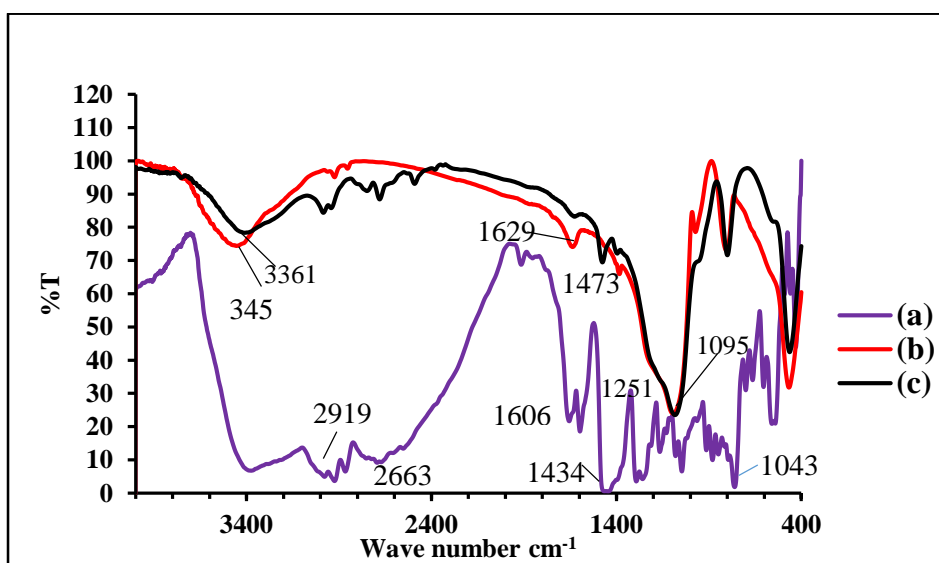


FIGURE1 FTIR Spectrum (a) of p-diethylaminomethylcalix[4]arene (b) silica (c) DFCS resin SEM Analysis

Surface morphology of the DFCS resin was characterized using the SEM technique. Figure 2 reveals the SEM images of the pure silica and DFCS resin. Figure 2-a shows the pure silica, which is smooth and crystalline; while Figure

2-b demonstrates the DFCS resin, which is rough and amorphous. This clearly shows that the roughness is due to the attachment of compound 3 onto pure silica.

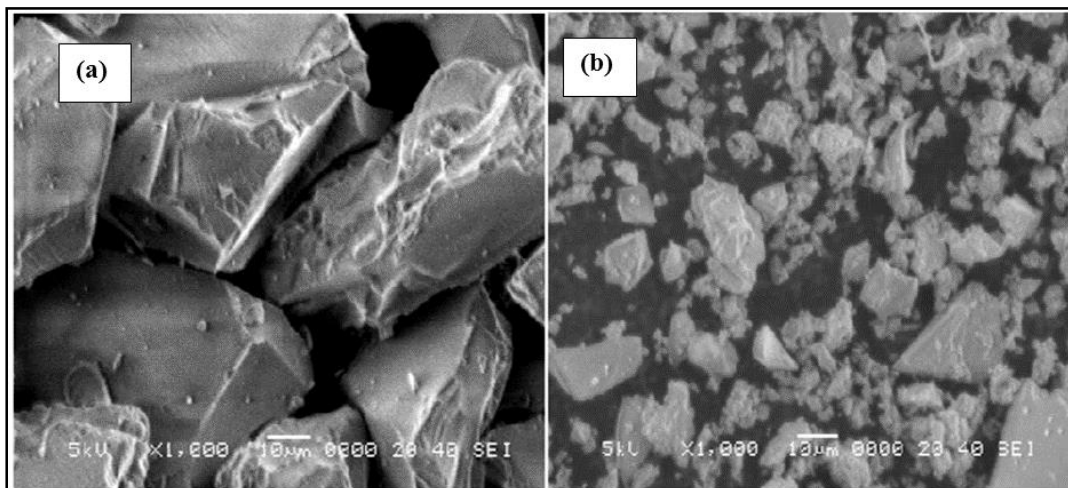


FIGURE 2 SEM images of (a) pure silica and (b) DFCS resin

Metal selectivity

The DFCS resin has ability to form complexes with different metal ions such as Cu^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+} , and Hg^{2+} . The DFCS resin has nitrogen moieties containing calixarene compound at its surface, which act as soft

coordinate centres for metal ions. The % adsorption of different metal ions on DFCS resin is demonstrated in Figure 3. As seen in Figure 3, the DFCS resin binds with Cd^{2+} , Pb^{2+} and Hg^{2+} more efficiently as compared to other metal ions may be due to their comparable ionic size and charge.

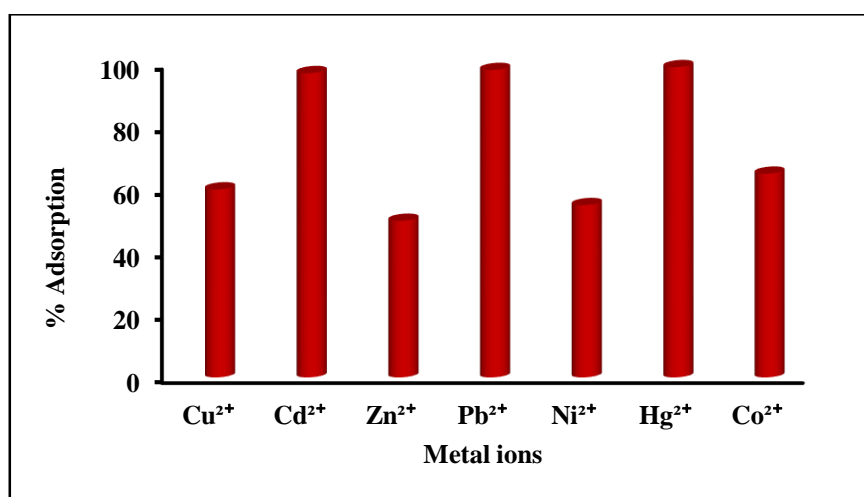


FIGURE 3 The % adsorption of different metal ions (Conc: 2.5×10^{-5} M)

Adsorbent dosage

During the adsorption of metal ions; the DFCS resin dosage was optimized, which is one of

the most effective parameter to check the binding and adsorption capacity. The graph was plotted between the adsorption percentages versus the DFCS resin

dosage (Figure 4). The % adsorption enhanced with increasing the DFCS resin dosage and the maximum 98% adsorption was achieved at the appropriate dose of 0.1 g, further high

doses of DFCS resin show no significant increase in % adsorption. Therefore, the optimized dosage of the DFCS resin for the removal of metal ions was found to be 0.1 g.

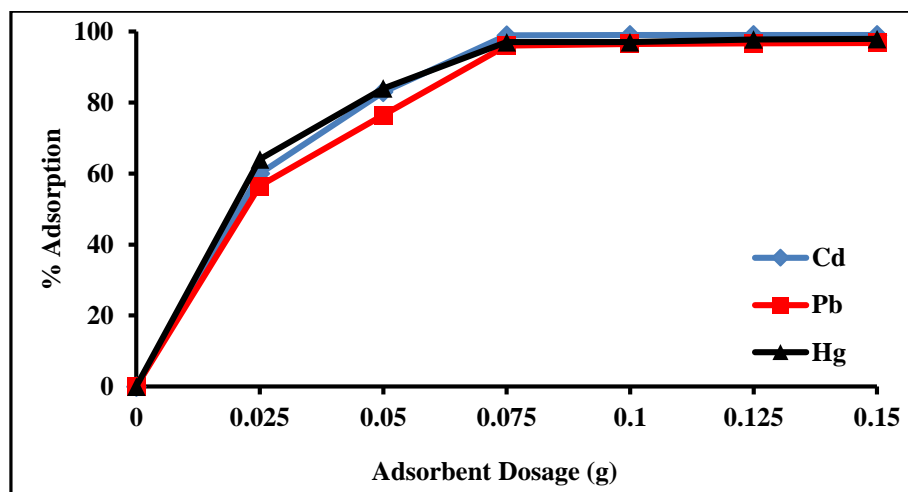


FIGURE 4 The effect of DFCS resin dosage (10 mL of metal ion solution 2.5×10^{-5} M, 60 min. contact time)

pH effect

The pH effect on the adsorption of metal ions by DFCS resin is discussed (Figure 5). The pH of solution affects the adsorbent surface and the interaction between the adsorbent and metal ions. It has been noted that by increasing the pH of solution from 3 to 9, the adsorption percentage increases and 98.9 % adsorption was achieved at pH 7; while the

minimum adsorption percentage was observed at low pH due to the protonation of amine moieties onto DFCS resin surface that reduces the binding sites for the interaction of metal ions. The pH above 7 shows no significant increase in the adsorption percentage, therefore a neutral condition is favourable for adsorption of metal ions by DFCS resin.

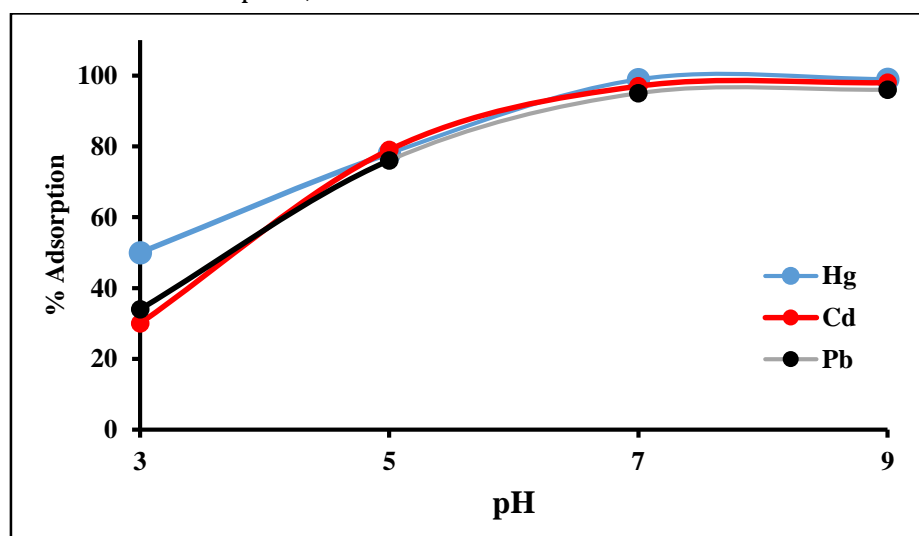


FIGURE 5 The effect of pH on the adsorption metal ions by DFCS resin

Isotherm models

Figure 6 demonstrates the adsorption of the metal ions on DFCS resin as a function of solution concentration (2.5×10^{-7} to 2.5×10^{-5} mol/L). By increasing the concentration, the adsorption capacity of the DFCS resin (mmol/g) gradually enhanced and became constant at 2.5×10^{-5} mol/L, when there was almost no further any adsorption capacity enrichment. This observation indicated that the metal ions bind with the respective sites. Therefore, the maximum adsorption capacity of DFCS resin for Cd^{2+} , Pb^{2+} and Hg^{2+} was found to be 0.42, 0.51 and 0.53 mmol/g, respectively. The analysis of the experimental data is important to describe the adsorbate and adsorbent interactions. Equations 3-5 were

used to calculate the Langmuir and Freundlich models.

$$\left(\frac{C_e}{C_{ads}}\right) = \left(\frac{1}{Qb}\right) + \left(\frac{C_e}{Q}\right) \quad (3)$$

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

$$R_L = \frac{1}{(1 + bC_i)} \quad (5)$$

Where C_{ads} shows the adsorbed amount of metal ions and C_e is the remaining amount of metal ion at equilibrium, Q is adsorption capacity during the monolayer formation, and b is Langmuir constant. In Equation 4, A is a constant shows the adsorption capacity, n is the energy or intensity of adsorption, and in Equation 5 R_L is an essential characteristic of the Langmuir model.

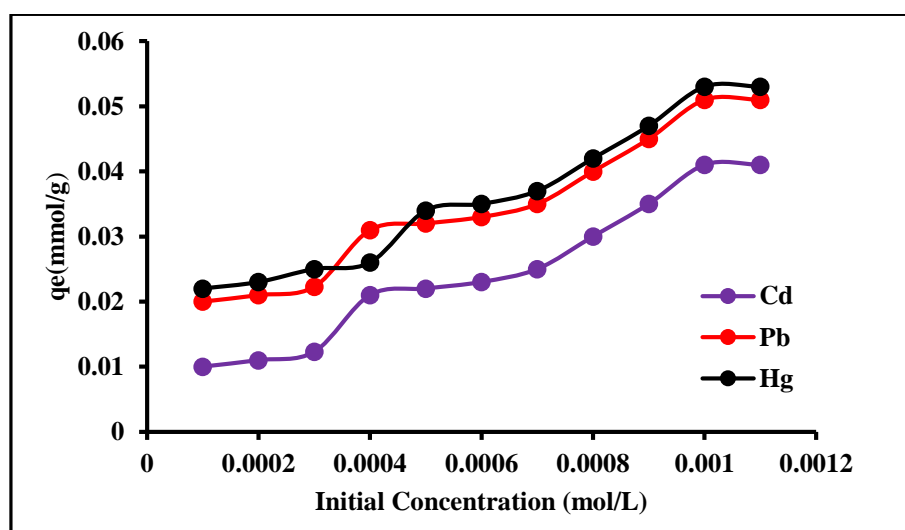


FIGURE 6 Effect of initial concentration on the adsorption of Cd^{2+} , Pb^{2+} and Hg^{2+} on DFCS resin at 0.1g of DFCS resin

The Langmuir model was applied and graph was plotted between the C_e vs C_{ads} mmol/g (Figure 7) b and Q values were obtained from the plot of C_e/C_{ads} mol.g⁻¹ versus

C_e mol/L and are shown in Table 1, which describes that the Langmuir model is not best fit one and does not form monolayer.

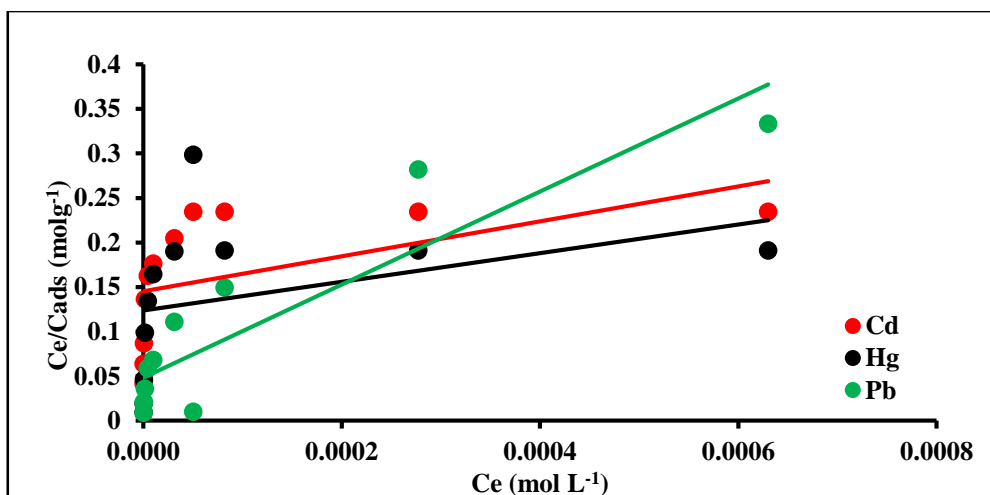


FIGURE 7 Langmuir isotherm (Conc. 2.5×10^{-5} to 2.5×10^{-7} mol/L) 0.1 g of DFCS resin 10 mL of metal solution at 25 °C

TABLE 1 Langmuir isotherm parameters

| Metals | Q (mol/g) | b | R_L | R^2 |
|------------------|-----------|------|-----------|-------|
| Cd^{2+} | 2.30 | 10.7 | 0.94-0.99 | 0.811 |
| Pb^{2+} | 6.96 | 10.2 | 0.91-0.99 | 0.782 |
| Hg^{2+} | 2.41 | 10.1 | 0.33-0.99 | 0.724 |

The adsorption on the surface as multilayer formation indicates the validation of Freundlich isotherm model. By applying Equation 4, the values of A and n can be obtained from the $\log C_{\text{ads}}$ (mol/g) versus $\log C_e$ (mol/L) (Figure 8). If the sorption intensity value $1 > n > 10$ the phenomenon is referred to cooperative in nature whereas, if $1 < n < 10$

indicates the chemisorption nature. This study reveals that the value of n is $1 < n < 10$ for Cd^{2+} , Pb^{2+} and Hg^{2+} (Table 2), showing that the chemisorption takes place. Furthermore, the value of (R^2) is higher in Freundlich than in Langmuir (Table 1 and 2), indicating the adsorption follows Freundlich isotherm.

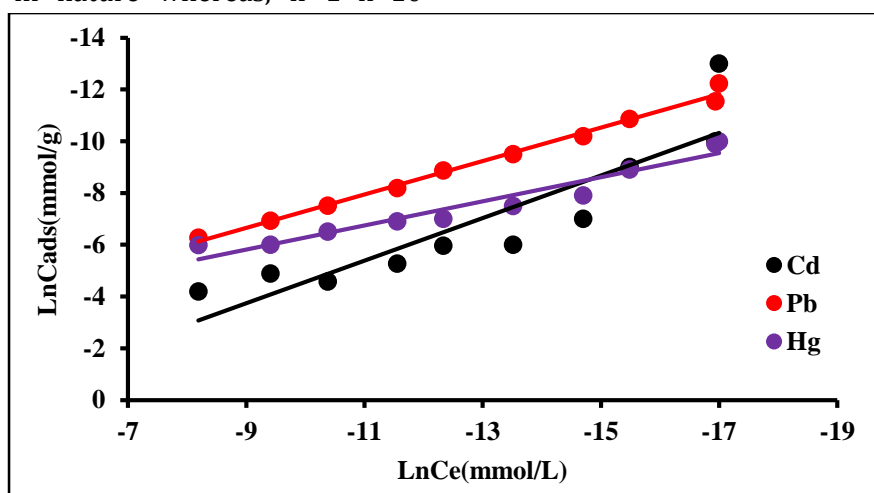


FIGURE 8 Freundlich isotherm (Conc. 2.5×10^{-5} to 2.5×10^{-7} mol/L), 0.1 g of DFCS resin per 10 mL of metal solution at 25 °C

TABLE 2 Freundlich isotherm parameters

| Metal | A (mg g ⁻¹) | n | R ² |
|------------------|-------------------------|------|----------------|
| Cd ²⁺ | 0.704 | 1.37 | 0.992 |
| Pb ²⁺ | 0.748 | 1.35 | 0.997 |
| Hg ²⁺ | 0.7033 | 1.51 | 0.990 |

Dubinin–Radushkevich adsorption isotherm model describes the nature of adsorption and estimate the energy utilized during adsorption process. D-R model constant values can be calculated using the Equation 6. While the Polanyi potential can be described well by utilizing the Equation 7 while the E (kJ/mol) values can be calculated by Equation 8.

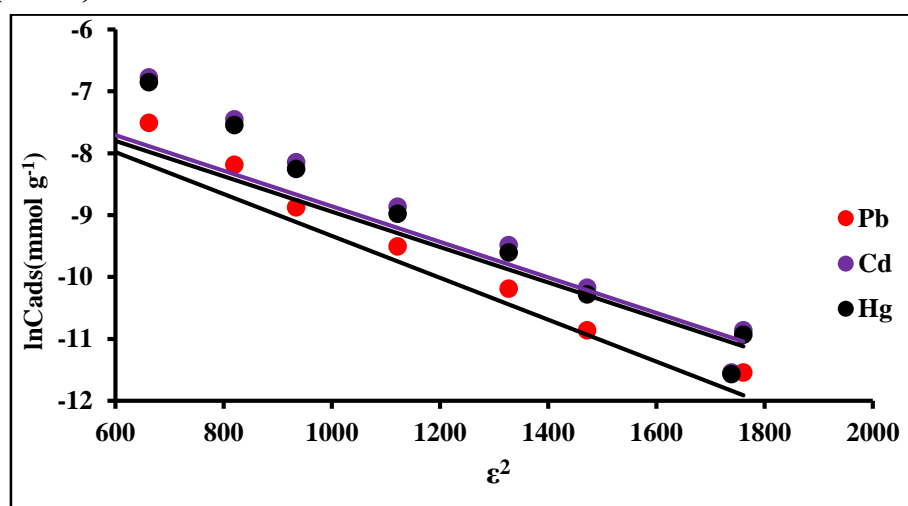
$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2 \quad (6)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

Where R is the gas constant, T is the temperature in Kelvin, and X_m is the adsorption capacity.

The graph has been plotted between Polanyi potential value vs $\ln C_{ads}$ (mmol.g⁻¹) which shows linear regression of metal ions on DFCS resin shown in (Figure 9). The constant values of this model are enlisted in Table 3.

**FIGURE 9** D-R isotherm (Conc. 2.5×10^{-5} to 2.5×10^{-7} mol/L), 0.1 g DFCS resin per 10 mL of metal ions at 25 °C)

The adsorption capacity (X_m) was calculated as 6.95, 8.56 and 9.80 mmol/g and (E) was found to be 10.7, 10.9 and 10.8 kJ/mol for the Cd²⁺, Pb²⁺ and Hg²⁺, respectively. The E

value is between 9.0 and 16.0 kJ/mol, suggesting that the metal ions are adsorbed onto DFCS resin mainly by ion exchange mechanism and is chemisorption in nature.

TABLE 3 D-R adsorption isotherm parameters

| Metals | X_m (mmol/g) | E (kJ/mol) | R ² |
|------------------|----------------|--------------|----------------|
| Cd ²⁺ | 6.95 | 10.7 | 0.991 |
| Pb ²⁺ | 8.56 | 10.9 | 0.990 |
| Hg ²⁺ | 9.80 | 10.8 | 0.993 |

Thermodynamics studies

Adsorption of metal ion on the DFCS resin was analyzed at various temperatures and it is noticed that the % adsorption increases with raise in temperature (Figure 9). Therefore, the graph has been plotted between $\ln k_c$ versus $1/T$ (Figure 10). From the graph, ΔH (KJ/mol), ΔS (KJ/mol /K) and listed in Table 4, which describes the thermodynamic phenomenon of adsorption process. The $(-\Delta G)$ values indicates

the feasibility and spontaneity of adsorption process at higher temperature. The small and negative $(-\Delta H)$ values shows the adsorption process takes place exothermally and very low values of ΔS describes the good affinity of metal ions towards DFCS resin.

$$\ln k_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (9)$$

$$\Delta G = -RT \ln k_c \quad (10)$$

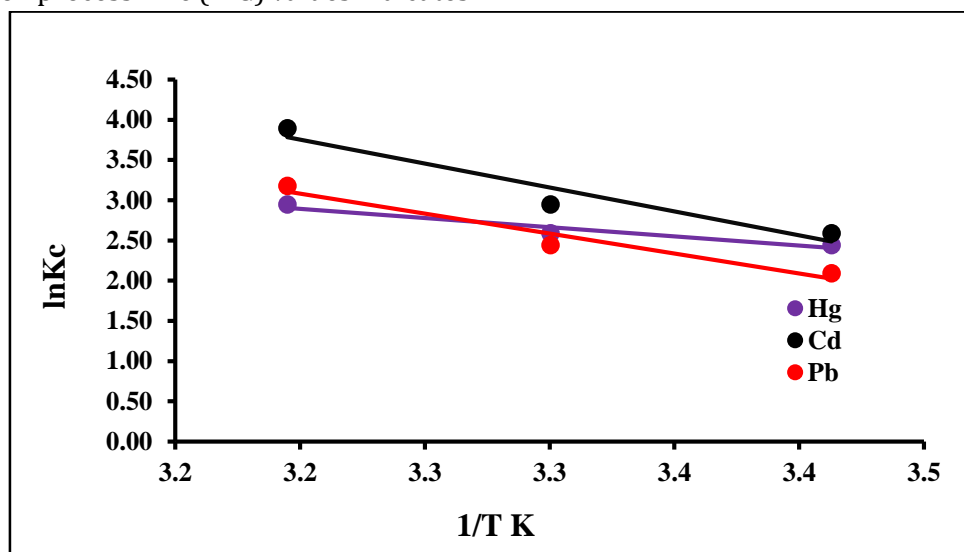


FIGURE 10 Graph of $\ln K_c$ vs $1/T$ for the Adsorption of Cd^{2+} , Pb^{2+} and Hg^{2+} on DFCS resin.

TABLE 4 Thermodynamic parameters for adsorption of Cd^{2+} , Pb^{2+} and Hg^{2+} on DFCS resin

| Metal | ΔH | ΔS | Temperature | ΔG | $\ln K_c$ |
|------------------|------------|------------|-------------|------------|-----------|
| Hg^{2+} | -0.01 | 0.08 | 293 | -5.9 | 2.4 |
| | | | 303 | -6.5 | 2.6 |
| | | | 313 | -7.6 | 2.9 |
| Pb^{2+} | -0.04 | 0.16 | 293 | -5.6 | 2.3 |
| | | | 303 | -5.0 | 2.0 |
| | | | 313 | -6.1 | 2.4 |
| Cd^{2+} | -0.04 | 0.19 | 293 | -7.3 | 2.9 |
| | | | 303 | -8.4 | 3.1 |
| | | | 313 | -10.1 | 3.8 |

Adsorption kinetic

The adsorption percentage of the Cd^{2+} , Pb^{2+} , and Hg^{2+} by DFCS resin is affected by the temperature and time which is shown in Figure 11. The % adsorption increased with raising the reaction temperature and time as the metal ions in solution travel faster at high

temperature and remains in contact with the passage of time. The kinetic study for the adsorption of the Cd^{2+} , Pb^{2+} , and Hg^{2+} metal ions on the DFCS resin were performed and the experimental data was subjected to the pseudo first order and pseudo second order kinetic equations. The kinetic parameters along with the correlation coefficient are

presented in Table 5. The values of the correlation coefficient for both the kinetic models were plotted at different temperatures. The values of the correlation coefficient of the pseudo first order kinetic model are less than that of pseudo second order kinetic model; therefore, the adsorption follows the pseudo second order kinetic model. Therefore, it is assuming that during

the adsorption process rate determining step is physio sorption in nature that governed by weak forces of attraction in between adsorbent surface and metal ions. The Pb^{2+} , Hg^{2+} and Cd^{2+} adsorption on DFCS resin at 298-313 K can be well described by pseudo second order kinetic equation. The values are tabulated in Table 5.

TABLE 5 Pseudo 1st and 2nd order kinetic parameters Cd^{2+} , Pb^{2+} and Hg^{2+} at different temperatures

| Temperature | Pseudo First Order Kinetic Model | | | Pseudo Second Order Kinetic Model | | |
|------------------------------------|----------------------------------|----------------|---------------|---|---------------|---------------|
| | $K_1 \text{ min}^{-1}$ | q_e (mmol/g) | R^2 | $K_2 \text{ g mol}^{-1} \text{ min}^{-1}$ | q_e (mol/g) | R^2 |
| Pb^{2+} | | | | | | |
| 293 | 0.013 | 213.9 | 0.246 | 197.4 | 0.00154 | 0.9910 |
| 303 | 0.0006 | 77.58 | 0.176 | 209 | 0.00023 | 0.9665 |
| 313 | 0.0006 | 8.178 | 0.245 | 2242 | 0.00167 | 0.9997 |
| Hg^{2+} | | | | | | |
| 293 | 0.0013 | 212.7 | 0.248 | 143.7 | 0.00183 | 0.994 |
| 303 | 0.0006 | 75.43 | 0.1391 | 162.9 | 0.00030 | 0.999 |
| 313 | 0.0006 | 7.830 | 0.1442 | 40060 | 0.0027 | 0.994 |
| Cd^{2+} | | | | | | |
| 293 | 0.0127 | 218.4 | 0.24 | 184.76 | 0.001472 | 0.990 |
| 303 | 0.0007 | 78.3 | 0.24 | 212.27 | 0.000235 | 0.966 |
| 313 | 0.0008 | 8.10 | 0.14 | 395.90 | 0.002563 | 0.996 |

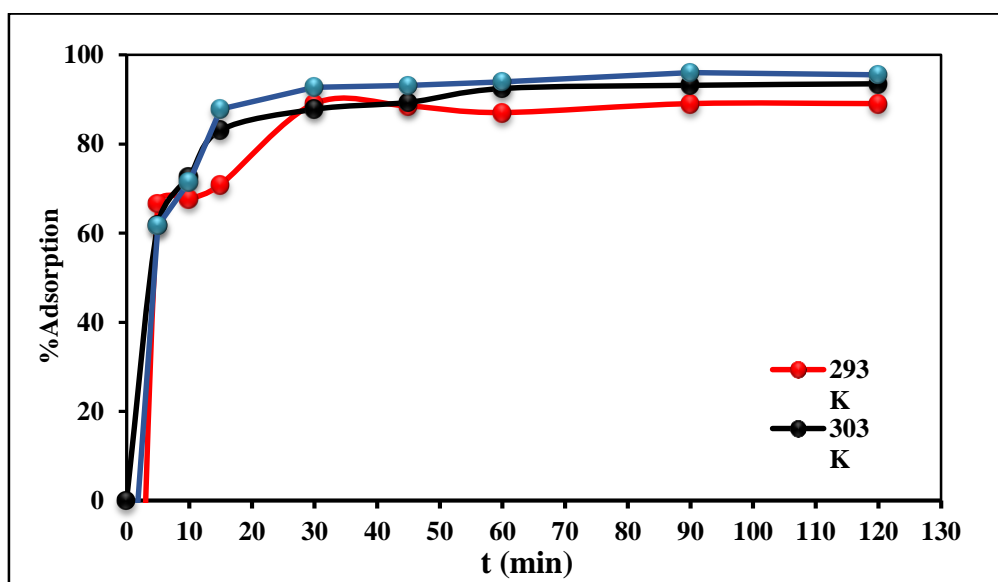


FIGURE 11 Effect of time and temperature on the removal of Cd^{2+} , Pb^{2+} and Hg^{2+} metal ion

Comparative study

The present study shows the maximum adsorption percentage of Cd^{2+} , Pd^{2+} and Hg^{2+} .

As seen in Table 6, different studies were compared with the current study.

TABLE 6 Comparison of DFCS resin with other adsorbents for Cd²⁺, Pb²⁺ and Hg²⁺

| Adsorbent | Metal ion | % Adsorption | Reference |
|---|--------------------------|--------------|------------------|
| Magnetic composite CoFe ₂ O ₄ -SiO ₂ (CF-S) | Cu, Mn, Cd, Pb | 90-95 | [30] |
| Fe-Mg (hydroxide)@GO | Pb, Cu, Ag, Zn and Cu | 95-99 | [31] |
| Graphene oxide-calcium-zinc (GO@CZ) Nanocomposite | Cr(III) and Cu(II) | 96-97 | [32] |
| Muscovite/phillipsitic zeolite | Hg, As | 80 | [33] |
| NiFe ₂ O ₄ coated sand | Pb ²⁺ | 90 | [34] |
| DFCS resin | Cd, Pb and Hg | 95-99 | Present study |

Conclusion

This study highlights the synthesis of *p*-diethylamine functionalized calix[4]arene silica (DFCS) resin for the effective removal of Cd²⁺, Pb²⁺ and Hg²⁺ from water. The batch adsorption studies were conducted to examine the ability of the DFCS resin for metal ion removal. The results demonstrate that the DFCS resin had a very good efficiency for the removal of these toxic ions under the optimized conditions. To validate the adsorption phenomenon, the isotherm models were applied and Freundlich model was found to be the best fit with good correlation coefficient values (R^2 0.99), which reveals that the resin has good multilayer adsorption capacity. Thermodynamic parameters such as ΔH (KJ/mol), ΔS (KJ/mol/K) and $(-\Delta G)$ describe that the adsorption is spontaneous and exothermic in nature and kinetic study helped to determine adsorption mechanism. The study may find its applicability in the fields of analytical and environmental sciences.

Acknowledgements

We are thankful to National Center of Excellence in Analytical Chemistry University of Sindh Jamshoro, Sindh-Pakistan, for his kind support and providing me environment for my research.

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How to cite this article: Ranjhan Junejo*, Shahabuddin Memon, Ismail Murat Palabiyik. Efficient adsorption of heavy metal ions onto diethylamine functionalized calix[4] arene based silica resin. *Eurasian Chemical Communications*, 2020, 2(7), 785-797.

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