

Studies on Adsorptive Removal of Some Heavy Metal Ions by Calix[4]Resorcine

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Abstract

Removal of heavy metal ions (Mn(II), Cu(II), Co(II), Zn(II), and Pb(II)) from aqueous solutions was carried out using C-4-hydroxyphenylcalix[4]resorcinarene as adsorbent surface. The effect of various parameters, such as solution pH, contact time and temperature on the adsorption capacity of C-4-hydroxyphenylcalix[4]resorcinarene for the selected heavy metal ions, was investigated and optimized. The experimental data were investigated using three kinetic models: Santosa first order, Lagergren pseudo second order and Ho pseudo second order. Ho pseudo second order model described the adsorption process with high correlation coefficient (R^2) compared to the other two models. The selectivity of the adsorbent toward a mixture of heavy metal ions was studied and revealed that the removal percentage of the heavy metal ions in a mixture is ranked differently from the separate heavy metal ions. Three adsorption equilibrium isotherm models - Freundlich, Langmuir and Temkin - were applied on the adsorption experimental data. It was found that the Langmuir model well described the adsorption process much better than the other isotherm models. In addition, the thermodynamic parameters of the adsorption processes for the heavy metal ions were calculated and found to be as follows: negative ΔH° indicating exothermic processes; negative ΔG° indicating spontaneous processes.

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Keywords: C-4-Hydroxyphenylcalix[4]resorcinarene, adsorption, heavy metal ions, kinetic, isotherm, atomic absorption spectroscopy.

1. Introduction

Organic and inorganic pollutants are discharged into the environment from different sources, especially industrial wastes. Heavy metal ions, such as (Pd, Cu, Cd, Zn, Ni, etc.), are considered one of the main sources of water pollutants (Samiey et. al., 2014; Tuama and Mohammed, 2014). Most of the heavy metal ions are highly toxic, non-biodegradable and easily accumulative to toxic levels. The bio-accumulation of these ions in human bodies may damage or reduce the central nervous system, or may cause a kidney and a liver damage (Ahmad et. al., 2013). According to the World Health Organization (WHO), the regular limits of specific heavy metal ions in drinking water should not exceed 0.01, 2.0, 0.007, 0.003 and 5.0 mg/L for Pd, Cu, Ni, Cd and Zn, respectively (W.H.O., 1996). Therefore, such heavy metal ions must be removed from wastewater before discharging it into the ecosystem.

Among the various contaminants, which are found in water, heavy metal ions require special techniques for their removal, due to their toxicity, even though the environment has low concentrations (Harris, 1996). Several methods, such as precipitation (Esalah et. al., 2000), solvent extraction (Lertlapwasin et. al., 2010), coagulation/flotation (Rubio et. al., 2002; Ghurye et. al., 2004), ultrafiltration (Yurloval et. al., 2002), reverse osmosis (Greenlee et. al., 2009; Benit and Ruiz, 2002), electrochemical treatment (Emamjomeh and Sivakumar, 2009), and ion-exchange methods (Mahmoud and

Hoadley, 2012) investigated wastewater treatment. However, most of these techniques are very expensive, with a low efficiency and are inapplicable to treat low concentration levels of heavy metal ions in wastewater (Tuama and Mohammed, 2014).

The adsorption technique is a well-known separation method which is considered to be a promising alternative for environmental control (Ren et. al., 2008) and is considered to be an economic and efficient method for the removal of pollutants from water pollutant. In addition, the adsorbent can be regenerated by a suitable desorption procedure (Pan et. al., 2009). Different kinds of conventional and non-conventional adsorbents, such as activated carbon (Uzun and Güzel, 2000), zeolites (Biskup and Subotic, 2004; Cincotti et. al., 2006), clays (Gier and Johns, 2000; Koppelman and Dillard, 1977), polymers and agricultural wastes (O'Connell et. al., 2008; Dang et. al., 2009; Zewail and El-Garf, 2010) were used for the removal of heavy metal ions.

Recently, macromolecules have attracted the attention of chemists due to their use as baskets for trapping molecules or ions (Gutsche, 1988). The unique geometry of calixarenes, which are a family of macrocyclic oligophenols, and the presence of active sites - mainly OH groups - will allow them to form host-guest complexes with neutral molecules and ions (Kunsagi et. al., 2005). A number of calix[n]arene derivatives, such as calix[4]arene (Tabakci et. al., 2006), calix(aza)crown and its oligomeric analog (Akkus et. al.,

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2009), calix[6]-Na-hexasulphonate (Kunsagi et. al., 2005) etc, were successfully shown to adsorb-toxic heavy metal ions. In addition, calix[n]arene derivatives can be also used to adsorb dye waste (Ming et. al., 2011).

The present study is focused on the investigation of the adsorption efficiency of the synthesized C-4-hydroxyphenylcalix[4]resorcinarene as adsorbent surface for the heavy metal ions (Mn(II), Cu(II), Co(II), Zn(II), and Pb(II)). Moreover, isotherm models, kinetic modeling, thermodynamic, and selectivity studies of the adsorption of the selected heavy metal ions onto C-4-hydroxyphenylcalix[4]resorcinarene were carried out, calculated and presented.

2. Experimental

Apparatus and instrumentation

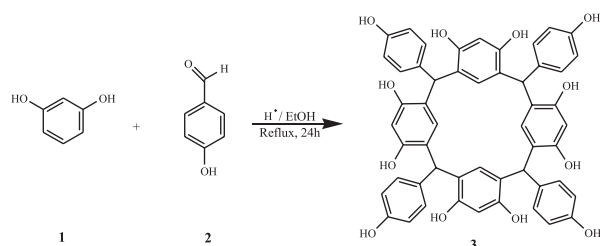
The pH measurements were done using glass electrode pH meter model pH 525 (WTW®, Weilheim, Germany). The pH meter was calibrated using pH 4, pH 7 and pH 10 buffer solutions at 25°C according to a standard method (Andrew et. al., 2005). Heavy metal ions concentrations were measured using an Atomic Absorption Spectrophotometer (AAS) Model AA-6200 (Shimadzu®, Kyoto, Japan). The AAS was equipped with a hollow cathode lamp and a 10 cm long slot-burner head and air/acetylene flame. The operating conditions adjustments in the spectrophotometer were carried out according to the standard guidelines of the manufacturer. The hollow cathode lamp and emission wavelength, slit width, the correct coefficient for the calibration straight line, the working linear range and detection limit were determined for each heavy metal ions. The optimum parameters for AAS used to determine the concentrations of different heavy metals are listed in Table 1. Figure 1 shows the linear calibration curve for each heavy metal ion used in the present study. Standard solutions of each heavy metal ion were prepared in order to obtain these calibration curves for the five heavy metal ions used in this study.

Table 1. Standard parameters used in determination of different heavy metal ions using Atomic Absorption Spectrophotometer (Shimadzu, AA-6200)

Heavy metal ion	Wave length (nm)	Slit width (nm)	Flow of fuel (L/min)	Lamp current (mA)	Flame description
Pb(II)	217.0	0.7	2.0	12	Air-Acetylene
Cu(II)	324.7	0.7	1.8	6	Air-Acetylene
Mn(II)	280.1	0.2	2.0	10	Air-Acetylene
Zn(II)	213.9	0.7	2.0	8	Air-Acetylene
Co(II)	240.7	0.2	2.2	12	Air-Acetylene

Adsorbent

As illustrated in scheme 1, C-4-hydroxyphenylcalix[4]resorcinarene 3 adsorbent was synthesized according to the previously published method (Weinelt and Schneider, 1991).



Scheme 1. Preparation of C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3

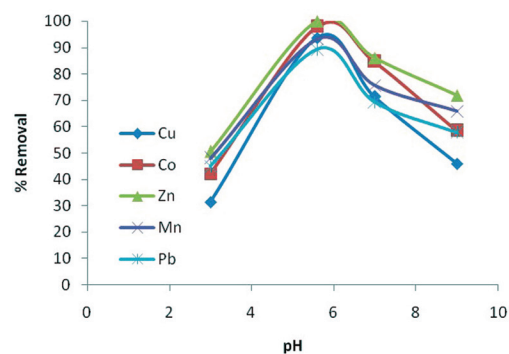


Figure 1. Linear calibration curves for selected heavy metal ions Cu(II); Mn(II); Zn(II); Pb(II); and Co(II)

Effect of pH

The adsorption experiments were carried out at different pH values. A 0.1 g sample of the C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3 was added to a 100 mL of each heavy metal ion solution with initial concentration of 1 ppm. The adsorption was investigated at pH = 3.0; 5.6; 7.0, 9.0. The mixtures were mechanically agitated at room temperature for 30 min. The solid adsorbent was filtered and the absorbance of the filtrate was measured using AAS spectrometry to determine the final heavy metal ion concentration.

Effect of contact time

The effect of the contact time on the adsorption efficiency was investigated by running a different agitation time in the range of 2–30 min. A 0.1 g sample of the C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3 was added into 100 mL of each metal ion solution with initial concentration of 1 ppm at the measured optimum pH. The contents of the flask were agitated at 25°C for time intervals of 2, 5, 7, 10, 15, 20, 25, 30 min. The residual concentration of the heavy metal ion in the blank and solution samples was determined using AAS. Blank solution serves as a controller for the presence of the heavy metal ion, which was precipitated after treatment.

Selectivity and competition study

A 0.1 g sample of the C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3 was added to a 100 mL of an aqueous solution containing a mixture of heavy metal ions with initial concentration of 1 ppm of each heavy metal ion at optimum pH. After shaking in a thermostatic system (25°C) for 10 min; the adsorbent was filtered and the concentration of the heavy metal ions in the filtrate was determined using AAS through dilution with distilled water.

Data Analysis

The removal of the selected heavy metal ions used in this study was calculated from the mass balance, which was stated as the amount of metal ions adsorbed onto the C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3. The amount of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) that is removed from the solution is expressed by Equation (1) (Al-Ghezawi et. al., 2010):

$$q_e = (C_i - C_e)/S \quad (1)$$

where q_e is the heavy metal ion concentration adsorbed at equilibrium (mg of heavy metal ion per g of adsorbent), C_i is the initial concentration of metal ions in the solution (ppm), C_e is the equilibrium concentration or final concentration of metal ions in the solution (ppm), S is the dosage (slurry) concentration and it is expressed by the following Equation (2):

$$S = m/V \quad (2)$$

where (V) is the initial volume of metal ion solutions used and m is the mass of adsorbent. The adsorption percentage is calculated using the following Equation (3):

$$\% \text{ adsorption} = [(C_i - C_e) / C_i] \times 100 \% \quad (3)$$

3. Results and Discussion

Adsorption of the selected heavy metal ions Pb(II), Cu(II), Co(II), Mn(II), and Zn(II) under different pH and contact time was investigated to determine the maximum adsorption percentage of these heavy metal ions and to determine the kinetic mechanism applied for this study:-

Effect of pH

In the adsorption process, the pH of the solution may affect the adsorbent surface charge, the distribution of metal species, and the level of dissociation of functional groups on the active sites of adsorbent. The effect of pH on the adsorption of heavy metal ions in the present study was investigated at different pH ranging from 3 to 9. Figure 2 shows the effect of solution pH on the amount of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) adsorbed onto C-4-hydroxyphenylcalix[4]resorcinarene 3. It was found that the heavy metal ions adsorption capacity reached its maximum value at pH = 5.6 for all investigated heavy metal ions onto adsorbent 3. C-4-hydroxyphenylcalix[4]resorcinarene 3 contains 8 phenolic-OH groups that may serve as active binding sites. At pH = 3, hydroxyl (-OH) groups of the C-4-hydroxyphenylcalix[4]resorcinarene 3 will be protonated to make these active sites positively charged. Thus, in highly acidic solutions electrostatic repulsion interactions between the adsorbent and the adsorbate will most likely occur due to similar positive characters. In other words, there was an adsorption competition between the proton (H^+) and metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II)) that causes the least amount of metal ions adsorbed by the resorcinarene.

The concentration of protons in the solution decreases with increasing pH so the adsorption competition between H^+ with Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) is reduced, resulting in an escalating adsorption of heavy metal ions by C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3. Moreover, at pH=7 the deprotonation of the phenolic hydroxyl group of C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3 converts them into negative charged phenoxide ions which are huge and labile, other competitive smaller anions (anions accompanied with the transitions metal cations used) will selectively chelate to the heavy metal ions, thus resulting in reduction of % removal of the heavy metal ions by the adsorbent.

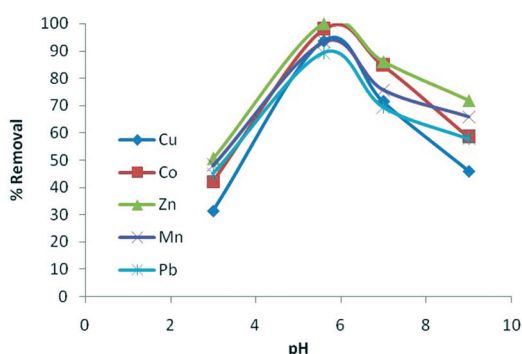


Figure 2. Effect of solution pH on the adsorption of the selected heavy metal ions on C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3

Effect of contact time

Investigating the uptake amount of the heavy metal ions vs. agitating time is a necessary parameter for determining the adsorption equilibrium and the adsorption rate constant based on the kinetic model adopted. The removal percentage of the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) vs. agitating time using C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3 is shown in Figure 3. The optimum contact time that leads to the maximum adsorption of each heavy metal ion was 30 min. When the adsorption equilibrium is reached, increasing contact time will not affect the amount of adsorbed heavy metal ions. At initial adsorption stage, the surface of the adsorbent was empty, so the adsorption of heavy metal ions onto the adsorbent surface was rapid. Later, the adsorption rate decreased with time, indicating that the saturation on the active sites of the adsorbent is reached.

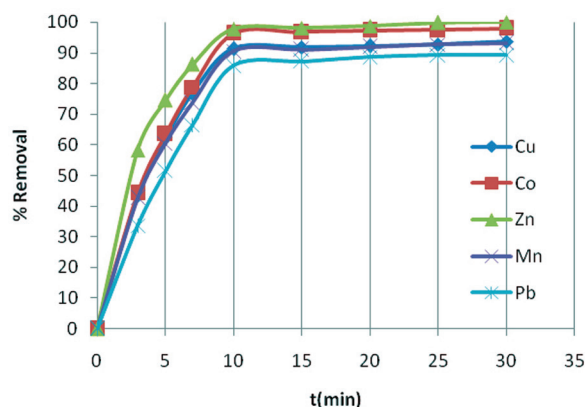


Figure 3. Effect of contact time on the amount of heavy metal ions onto C-4-methoxyphenylcalix[4]resorcinol 3; conditions: initial concentration 1 ppm; pH 5.6; T = 298±1 K

Adsorption kinetics

Several models are available to understand and rationalize the mechanism of heavy metal ions sorption onto the adsorbent. In order to investigate the mechanism of sorption, Santosa et. al. (2007) introduced a kinetic equation model for a single heavy metal ion adsorption onto the adsorbent surface with an overview of the concentration of adsorbate in the aqueous phase. Mathematical equation for such single ion adsorption is expressed by equation (4):

$$\ln (C_0/C_t)/C_t = k_1 t/C_t + K \quad (4)$$

where C_0 is the initial metal concentration (mg/L), C_t is the concentration of heavy metal ions in solution at time t (mg/L), t is the contact time (min), k_1 is the first-order rate adsorption constant (min^{-1}), and K is adsorption-desorption equilibrium constant (mg/L^{-1}).

The approach to the second order kinetics model is reviewed based on the concentration of adsorbate in solid phase (the adsorbent). In order to distinguish the kinetic equation based on the concentration of solution and adsorption capacity of the adsorbent, Lagergren's (Lagergren, 2007) first order and Ho's (Ho and McKay, 2000) second order rate equations are called pseudo-1st order and pseudo-second order, respectively. The pseudo 1st order equation is generally expressed by equation (5) (Lagergren, 2007):

$$\log (q_e - q_t) = \log q_e - k_1 t \quad (5)$$

and the pseudo 2nd order kinetic model, which was reviewed by Ho and McKay (2000), is expressed by equation 6:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

where q_e and q_t (mg.g^{-1}) are the adsorption capacities at equilibrium and contact time t , while k_1 and k_2 are the rate constants of pseudo-1st order and pseudo-second order adsorption, respectively.

The rate constant (k_1) was determined from the slope of the plot of $\log(q_e - q_t)$ vs. t and k_2 was obtained from the plot of t/q_t vs. t . The time-dependent experimental adsorption data presented in Figure 3 were used for kinetic modeling. In order to study the adsorption kinetics of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) onto C-4-methoxyphenylcalix[4]resorcinarene adsorbent 3, the 1st order heavy metal ion adsorption of Santosa et. al. (2007) pseudo-1st order of Lagergren (2007) and pseudo-2nd order of Ho and McKay (2000) models, were applied and used to process and treat the experimental adsorption data.

Based on Figure 4, the plotted curve has the highest level of linearity comparing with the 1st order heavy metal ions adsorption showed in Figure 5 and pseudo-1st order adsorption showed in Figure 6. The results obtained from the kinetic study, including the rate constant value for each heavy metal ion adsorption kinetic, are presented in Table 2. Thus, it can be concluded that the adsorption of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) onto C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3 follows pseudo-2nd order kinetic model.

Table 2. Kinetic modeling and adsorption parameters of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) onto C-4-hydroxyphenylcalix[4]resorcinarene

Kinetic models	Rate constant k		Correlation coefficient, R^2
1 st order of Santosa	Cu (II)	0.094 (min^{-1})	0.859
	Co (II)	0.134 (min^{-1})	0.905
	Zn (II)	0.226 (min^{-1})	0.957
	Mn (II)	0.093 (min^{-1})	0.877
	Pb (II)	0.080 (min^{-1})	0.871
Pseudo 1 st order of Lagergren	Cu (II)	0.085 ($\text{mg.g}^{-1} \text{min}^{-1}$)	0.870
	Co (II)	0.105 ($\text{mg.g}^{-1} \text{min}^{-1}$)	0.896
	Zn (II)	0.109 ($\text{mg.g}^{-1} \text{min}^{-1}$)	0.942
	Mn (II)	0.093 ($\text{mg.g}^{-1} \text{min}^{-1}$)	0.930
	Pb (II)	0.112 ($\text{mg.g}^{-1} \text{min}^{-1}$)	0.957
Pseudo 2 nd order of Ho & McKay	Cu (II)	0.519 ($\text{g.mg}^{-1} \text{min}^{-1}$)	0.988
	Co (II)	0.458 ($\text{g.mg}^{-1} \text{min}^{-1}$)	0.986
	Zn (II)	0.760 ($\text{g.mg}^{-1} \text{min}^{-1}$)	0.995
	Mn(II)	0.473 ($\text{g.mg}^{-1} \text{min}^{-1}$)	0.987
	Pb(II)	0.335 ($\text{g.mg}^{-1} \text{min}^{-1}$)	0.973

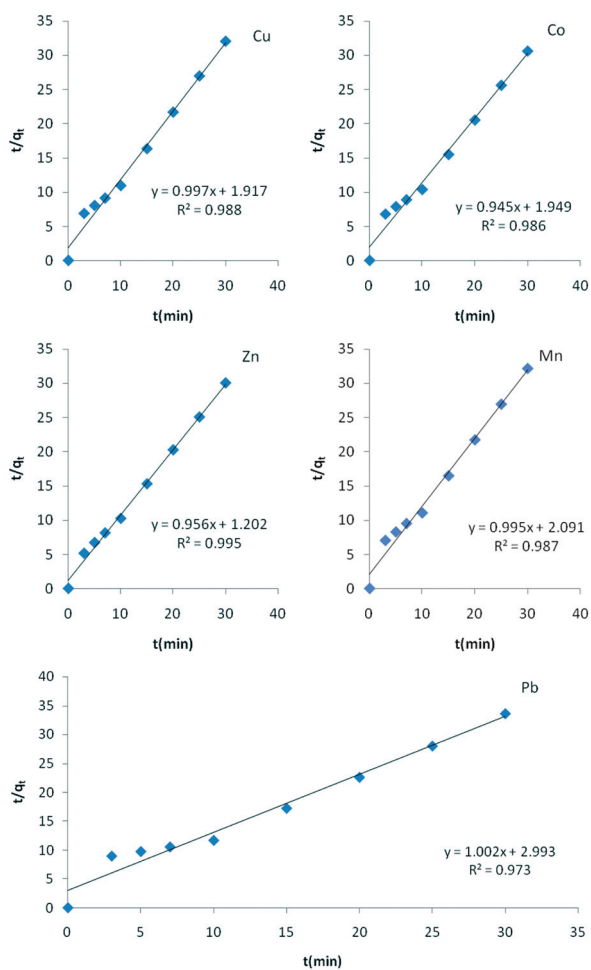


Figure 4. Pseudo second order kinetics of selected heavy metal ions adsorbed onto the C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3

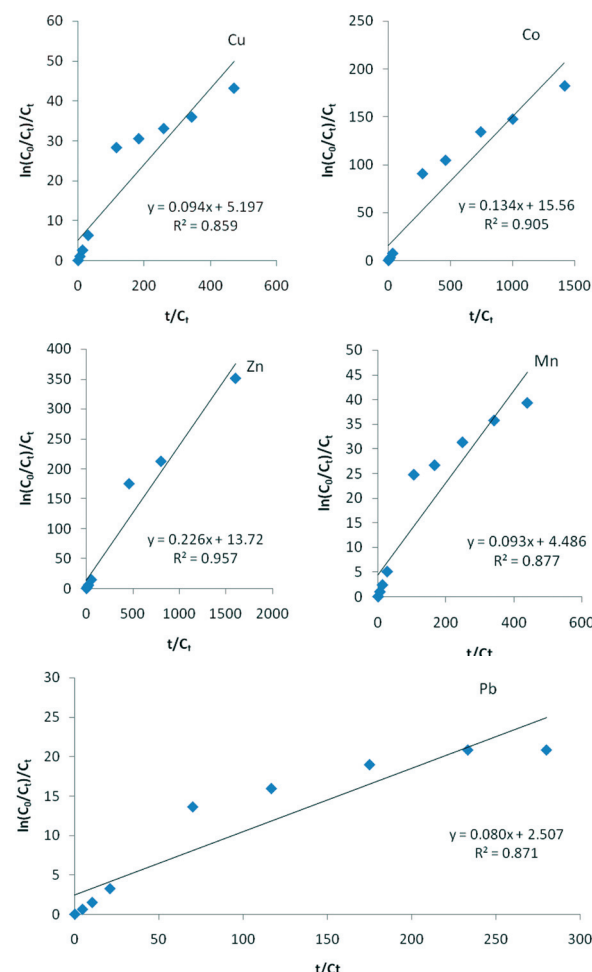


Figure 5. First order kinetics of selected heavy metal ions adsorption onto C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3

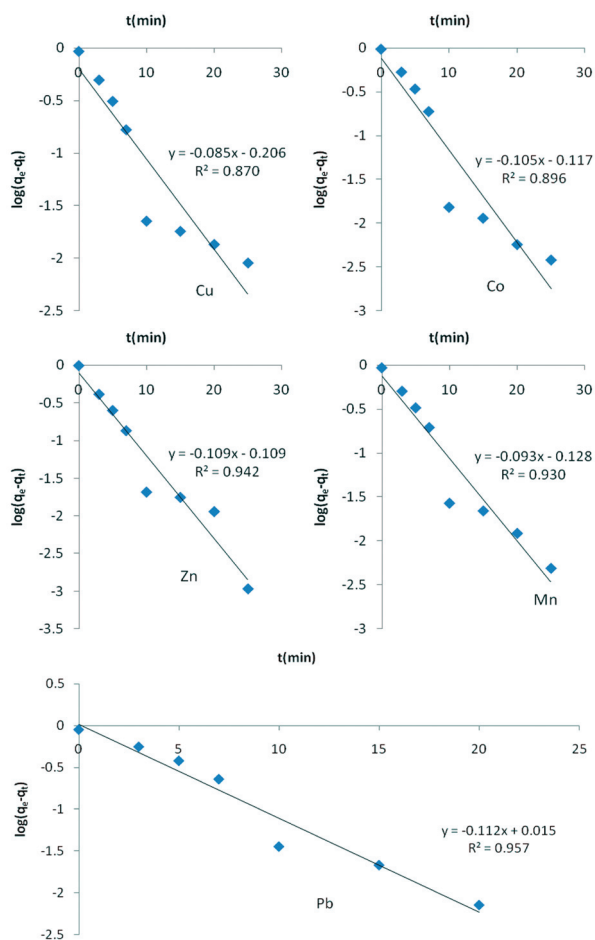


Figure 6. Pseudo first order kinetics of selected heavy metal ions adsorption onto the C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3

Selectivity and competition study

The adsorption selectivity experiments of adsorbent 3 towards a mixture of heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) were conducted at pH = 5.6 and shaking time of 10 min. The adsorption efficiency of C-4-hydroxyphenyl-calix[4]resorcinarene 3 against separate heavy metal ions is shown in Figure 7 with a removal capacity in the order: Zn(II) > Co(II) > Cu(II) > Mn(II) > Pb(II), and with a removal percentage of 97.81%, 96.35%, 91.36%, 90.49%, 85.71%, respectively. On the other hand, the removal percentage of a mixture of heavy metal ions was affected and differed from those of the separated heavy metal ions. The removal percentage of a mixture of initial concentration of 1 ppm was Zn(II) > Cu(II) > Co(II) > Mn(II) > Pb(II), with a percentage removal 33.13%, 24.10%, 18.08%, 15.12%, 7.86%, respectively, as illustrated in Figure 8.

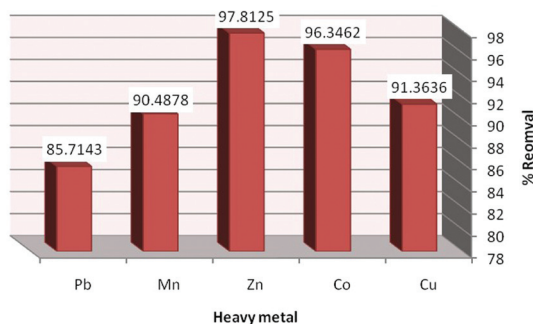


Figure 7. Adsorption efficiency of C-4-hydroxyphenylcalix[4]resorcinarene adsorbent 3 towards separate heavy metal ions

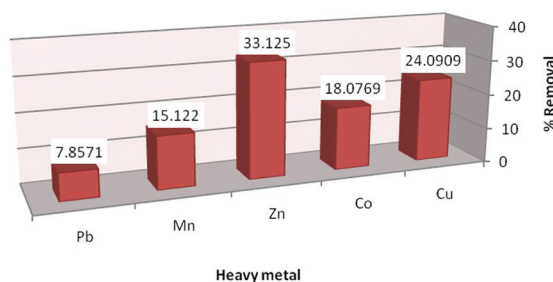


Figure 8. Selectivity of C-4-hydroxyphenylcalix[4]resorcinarene 3 towards a mixture of heavy metal ions

Effect of temperature

The temperature effect on the adsorption of the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) onto C-4-hydroxyphenylcalix[4]resorcinarene 3 was studied by performing the adsorption experiments at temperatures of 298, 303, 308, and 318 K. The influence of temperature on the adsorption of the heavy metal ions on C-4-hydroxyphenylcalix[4]resorcinarene 3 at optimum pH and contact time is illustrated in Figure 9.

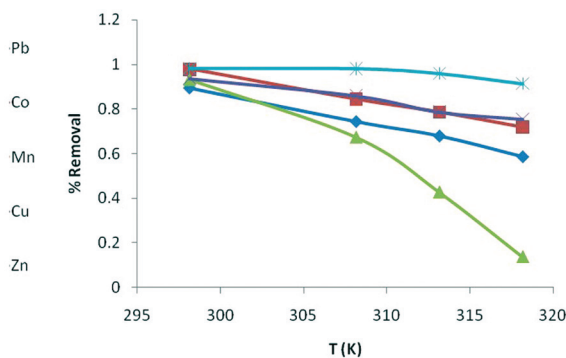


Figure 9. Temperature effect on the removal efficiency of the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II)

Adsorption isotherms

To understand the mechanism of the adsorption systems, the equilibrium adsorption isotherms were studied in details. The adsorption process was examined against different isotherm models, such as Langmuir, Freundlich, and Temkin.

The Langmuir isotherm

This isotherm model describes the adsorbate-adsorbent system, assuming that each adsorbate molecule occupies only one site, surface is homogenous and adsorption on surface is not delocalized (Thajeel, 2013). The linear form of the Langmuir isotherm equation is expressed as:

$$(C_e/q_e) = 1/q_{\max} b + (1/q_{\max})C_e \quad (7)$$

where $q_{\max}$ is the maximum metal ions uptake per unit mass of adsorbent (mg/g), b is the Langmuir constant (L/mg) which is related to the free energy of adsorption.

A plot of C_e/q_e vs. C_e gives a straight line with a slope of $1/q_{\max}$ and intercept of $1/q_{\max} b$ as shown in Figure 10. The calculated constants obtained from Langmuir isotherm are listed in Table 3. The characteristic of the Langmuir isotherm is expressed in terms of dimensionless equilibrium parameter (R_L) (Surchi, 2011) which is represented in equation 8 where $K = bM$ and M is the atomic mass of the selected heavy metal ion:

$$R_L = 1/(1 + KC_0) \quad (8)$$

The correlation coefficient (R^2) values for the heavy metal ions Pb(II), Co(II), Cu(II), and Zn(II) are high (0.981-0.999), which might be due to the fact that the adsorption of these heavy metal ions can be well described using the Langmuir isotherm model. In addition, the R_L values for the adsorption of the selected heavy metal ions are above 0 and below 1, which confirmed that the adsorption process is favorable for all the selected heavy metal ions. The relation between standard free energy (ΔG°) and the Langmuir constant (K) is given by the following equation 9 (T. J., 1997; Y. Liu, 2006)

$$\Delta G^\circ = -RT \ln K \quad (9)$$

Based on the data listed in Table 3, the ΔG° value for each heavy metal ion is calculated using equation 9 and presented in Table 3 for each heavy metal ion, and found to be negative, which confirmed that the adsorption process is spontaneous.

The Freundlich isotherm

This isotherm model assumes a heterogenous adsorption surface with sites that have different energies of adsorption and are not equally available (Freundlich, 1906; Tadjarodi et. al., 2013; Moradi et. al., 2012). It is more widely used but provides no information on the monolayer adsorption capacity and its linear equation form can be expressed as:

$$\log q_e = \log K + 1/n \log C_e \quad (10)$$

where K ($\text{mg}^{1-1/n} \text{L}^{1/n}$) and n (dimensionless) are the

Freundlich adsorption constants. These constants and correlation coefficients were calculated and presented in Table 4. The calculations were performed by plotting $\log q_e$ vs. $\log C_e$ as shown in Figure 11.

The Temkin isotherm

This linear form of Temkin isotherm equation (Chwdhury et. al., 2010) is given and presented in equations 11-12:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (11)$$

$$b_T = (RT) / (B_T) \quad (12)$$

where K_T is Temkin adsorption potential (L/g), B_T and b_T are Temkin constants, R is the universal gas constant and T is the temperature.

Figure 12 illustrates the plotting of q_e vs. $\ln C_e$. Table 5 listed K_T , B_T and b_T for each of the selected heavy metal ions. The Enthalpy change (ΔH°) and Entropy change (ΔS°) are related with the Gibbs free energy by equation 13 which can be expressed as:

$$\log K = \Delta S^\circ / 2.303 R - \Delta H^\circ / 2.303 RT \quad (13)$$

So plotting $\log K$ vs. $1/T$ will produce a straight line with slope equal to $-\Delta H^\circ / 2.303R$ and intercept equal to $\Delta S^\circ / 2.303R$. Figure 13 represents the plotting of $\log K$ vs. $1/T$ for each heavy metal ion used in this study. The calculated thermodynamic parameters obtained from Figure 13 are listed in Table 6.

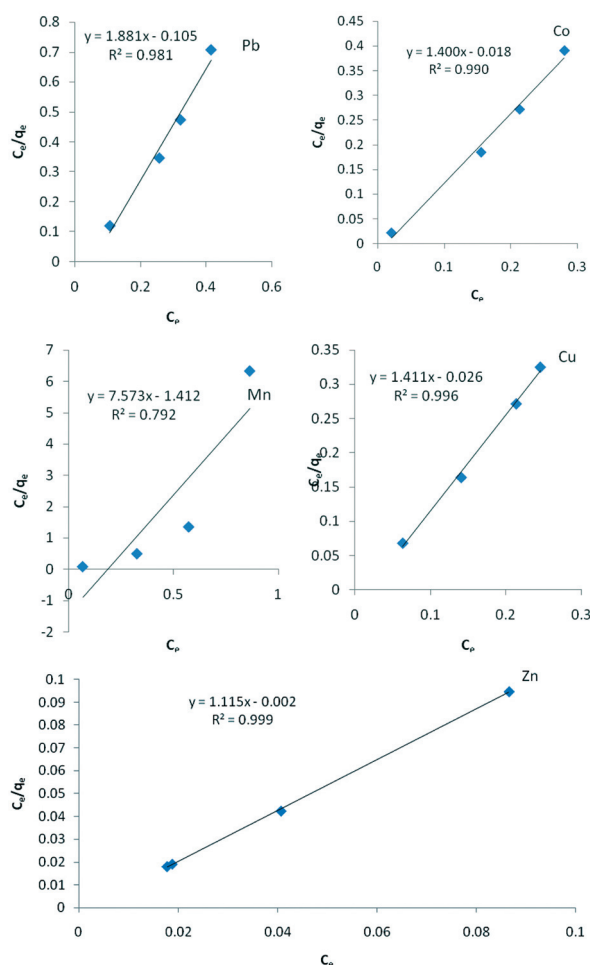


Figure 10. The linear Langmuir adsorption isotherms for the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II)

Table 3. The calculated Langmuir adsorption constants and thermodynamic parameters for the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) at 298 K

Heavy metal ion	$q_{\max}$ (mg/g)	b / K (L/mol)	R_L	ΔG° (KJ/mol)
Pb(II)	0.53	17.9 / 3708.8	2.7×10^{-4}	-20.37
Co(II)	0.71	78.25 / 4626.0	2.16×10^{-4}	-20.92
Mn(II)	0.13	5.45 / 299.4	3.33×10^{-3}	-14.13
Cu(II)	0.71	54.17 / 3442.3	2.90×10^{-4}	-20.19
Zn(II)	0.9	555.6 / 36330	2.74×10^{-5}	-26.03

Table 4. The calculated Freundlich adsorption constants and correlation coefficients for the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) at 298 K

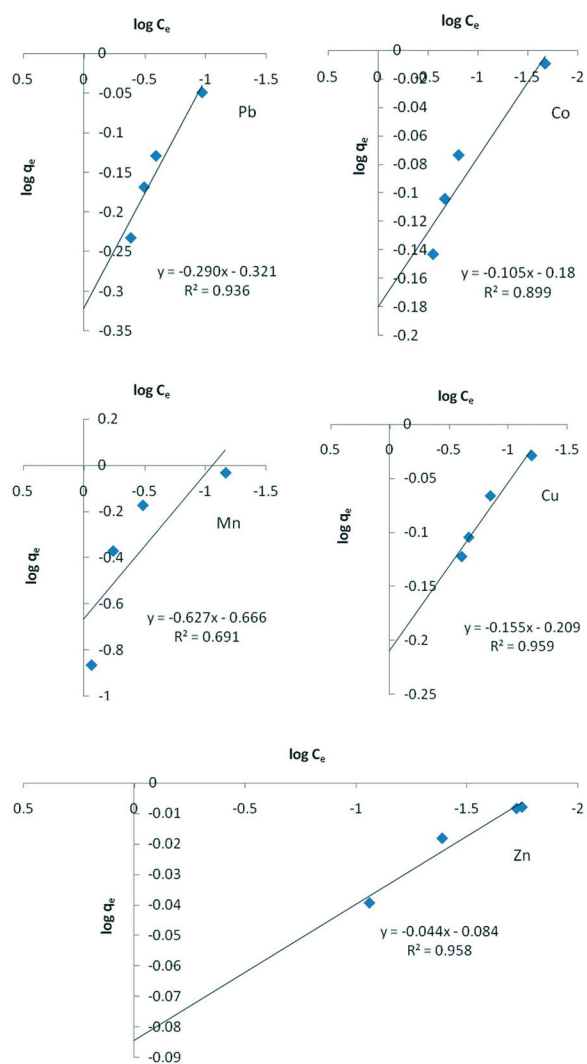
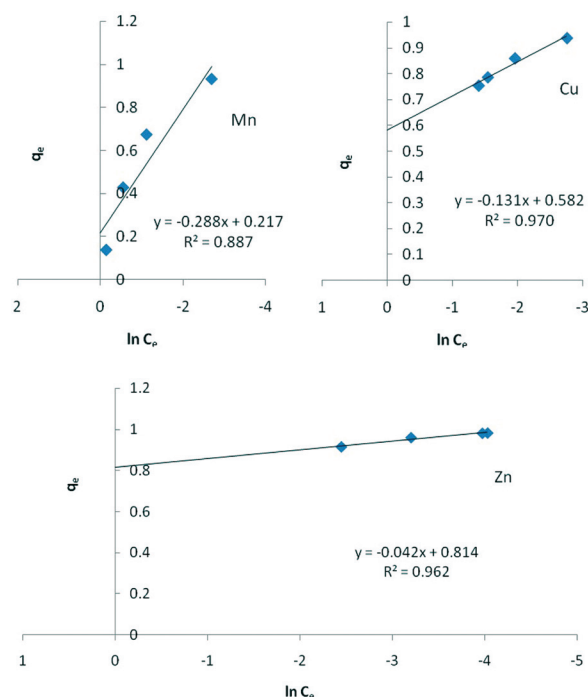
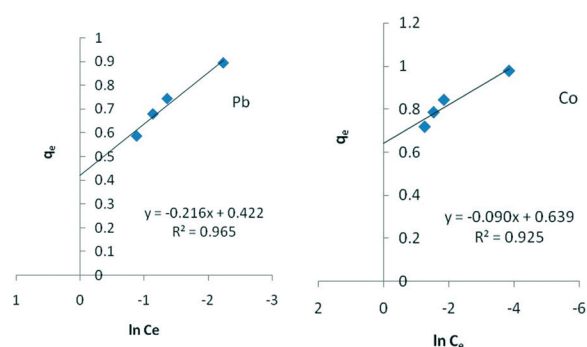
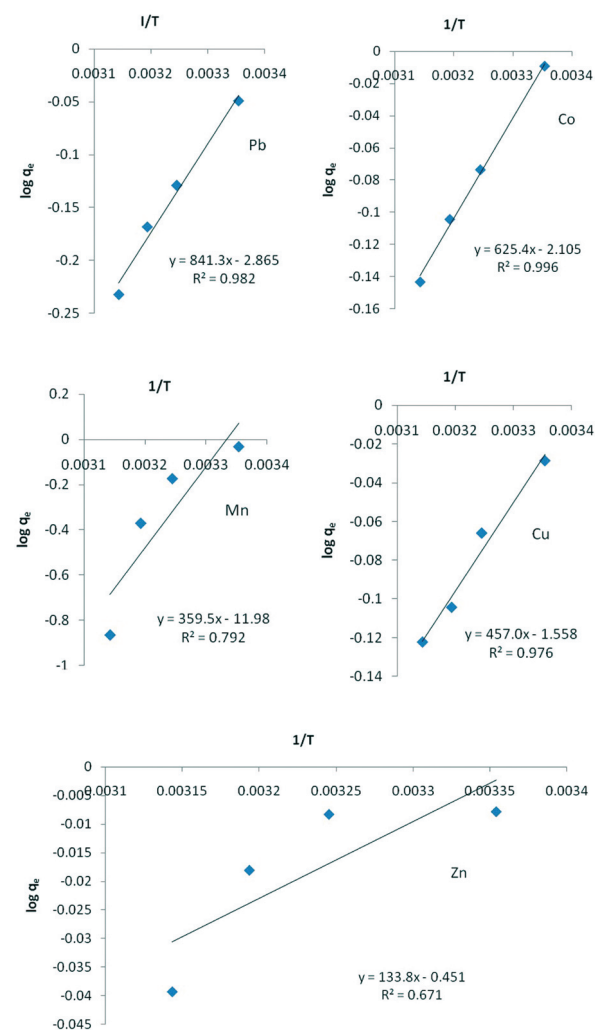
Heavy metal ion	K	n	R^2
Pb(II)	0.48	3.45	0.936
Co(II)	0.66	9.52	0.899
Mn(II)	0.22	1.59	0.691
Cu(II)	0.62	6.45	0.959
Zn(II)	0.82	22.73	0.958

Table 5. The calculated Temkin adsorption constants and correlation coefficients for the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) at 298 K

Heavy metal ion	K (L/g)	B_T	b_T	R^2
Pb(II)	0.14	-0.216	-1.15×10^4	0.965
Co(II)	8.25×10^{-4}	-0.090	-2.75×10^4	0.925
Mn(II)	0.47	-0.288	-8.6×10^3	0.887
Cu(II)	0.01	-0.131	-1.89×10^4	0.970
Zn(II)	3.83×10^{-9}	-0.042	-5.9×10^4	0.962

Table 6. The calculated thermodynamic parameters for the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) at 298 K

Heavy metal ion	ΔS° (J/mol)	ΔH° (KJ/mol)	ΔG° (KJ/mol)	R^2
Pb(II)	-54.86	-16.11	-20.37	0.965
Co(II)	-40.30	-11.97	-20.92	0.925
Mn(II)	-229.38	-6.88	-14.13	0.887
Cu(II)	-29.83	-8.75	-20.19	0.970
Zn(II)	-8.63	-2.56	-26.03	0.962

**Figure 11.** The linear Freundlich adsorption isotherms for the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II)**Figure 12.** The linear Temkin adsorption isotherms for the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II)**Figure 13.** The linear plotting of $\log K$ vs. $1/T$ for the heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II)

4. Conclusions

The adsorption experimental data obtained from the current study confirmed that C-4-hydroxyphenylcalix[4]resorcinarene 3 is an effective adsorbent for the removal of heavy metal ions (Mn(II), Cu(II), Co(II), Zn(II), and Pb(II)) from aqueous solutions. The adsorption capacity increases with the increase of the contact time until equilibrium is reached at contact time of 30 min. In addition, it has been found that the adsorption capacity increases with increasing the pH of the heavy metal ions solution with optimum results achieved at pH = 5.6; this is because the active binding sites (OH groups) become more negatively charged at higher pH values.

The experimental data for the adsorption of the selected heavy metal ions were adopted by Langmuir isotherm model ($0 < R_L < 1$) and followed pseudo second order kinetic model.

The calculated thermodynamic parameters values of Gibbs free energy (ΔG°) and heat of enthalpy (ΔH°) indicated that the adsorption processes were favorable, spontaneous, and exothermic. Future work could be extended to include studying the other adsorption variables, such as initial concentration of the heavy metal ion, amount of adsorbent, and other toxic heavy metal ions.

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