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Kinetic, equilibrium and selectivity studies of heavy metal ions (Pb(II), Co(II), Cu(II), Mn(II), and Zn(II)) removal from water using synthesized *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent

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ABSTRACT

Batch-mode adsorption study was done for selected heavy metal ions (Pb(II), Co(II), Cu(II), Mn(II), and Zn(II)) using synthetic adsorbent (*C*-4-methoxyphenylcalix[4]resorcinarene **3**) to investigate the effect of different parameters such as contact time and pH. Selectivity of the adsorbent towards a mixture of heavy metals adsorbates was investigated. Results showed optimum agitation time of 30 min at pH 5.6 and initial concentration of 1 ppm for all investigated heavy metals. Different kinetic models of Santosa first-order, Lagergren pseudo-first-order and Ho pseudo-second-order were applied on the adsorption experimental data. Results proved that all adsorption processes were followed and pseudo-second-order kinetic model was adopted. The adsorption capacity of *C*-4-methoxyphenylcalix[4]resorcinarene towards the selected heavy metal ions was 95.00, 89.76, 89.58, 86.43, and 80.96% for Cu(II), Mn(II), Zn(II), Pb(II), and Co(II), respectively. Selectivity of adsorption was tested on a mixture of Cu(II), Mn(II), Zn(II), Pb(II), and Co(II) with an initial concentration of 1 ppm of each heavy metal and agitated time of 10 min with the adsorbent; removal percentage of each metal ion showed different values from each heavy metal alone as it was in decreasing order Cu(II) > Zn(II) > Co(II) > Mn(II) > Pb(II). The rate constant value for each heavy metal adsorption mechanism obtained from Ho pseudo-second-order model was in the order Co(II) > Zn(II) > Pb(II) > Mn(II) > Cu(II).

Keywords: Adsorption; Synthetic adsorbent; Atomic Absorption Spectroscopy; Adsorption selectivity; *C*-4-Methoxyphenylcalix[4]resorcinarene; Cu(II); Mn(II); Zn(II); Pb(II); Co(II)

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1. Introduction

Heavy metals are a group of metallic chemical elements that have relatively high density (at least five times greater than water density) and have toxic effect on environment. Their toxicity results from long-term, low-level exposure to common pollutants in our environment: air, water, food, and numerous consumer products. Heavy metals are not degradable, so their environmental studies have shown growing interest due to their harmful effects on human physiologies and other biological systems, especially when they exceed the tolerance levels and become ecotoxicological hazards [1,2].

Toxic heavy metals must be treated/removed from the environment when they exist above their threat level especially, when present in wastewater. Polluted wastewater, discharging its water into natural water, will constitute a great risk for the aquatic ecosystem, while the direct discharge to the sewerage system may affect negatively the subsequent biological wastewater treatment [3]. Various methods were done for the removal of heavy metals from aquatic system. These methods include coagulation, flotation, ion exchange, chemical precipitation, reverse osmosis, evaporation, and adsorption. The adsorption process is a process that results from a physical attraction, which holds molecules of the adsorbate at the surface of a solid by the surface tension of the solid. Adsorption has advantages over other methods because of simple design, and can involve low investment in terms of initial cost, land requirement, and simple removal of the adsorbent from aqueous media after treatment [4,5].

Heavy metals adsorption was investigated using different adsorbent materials of both natural polymers such as clay, soil, coal, and synthetic polymers origins [6]. Many studies showed that a type of synthetic chemical compound called *C*-4-methoxyphenylcalix[4]resorcinarene is a good adsorbate for many heavy metal ions from aqueous solutions at different pH, contact times, and initial metal concentration [7–13]. In continuation to our previous research on design and preparation of different types of calix[4]arenes for host–guest chemistry and environmental applications [14–17], herein, we report the adsorption properties of new type of synthesized *C*-4-methoxyphenylcalix[4]resorcinarene **3** as an adsorbent surface for selected heavy metals (Pb(II), Co(II), Cu(II), Mn(II), and Zn(II)). Kinetic, equilibrium, and selectivity studies were conducted on the adsorbent and on those selected heavy metals.

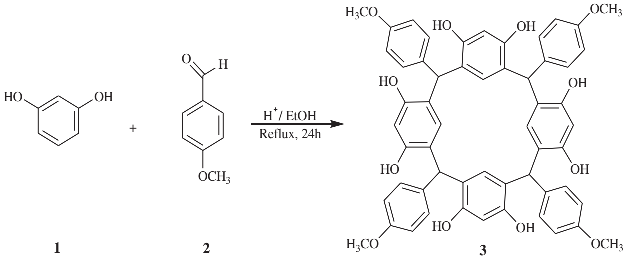

Fig. 1. Synthetic route for *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3.**

2. Materials and methods

2.1. Synthetic adsorbent *C*-4-methoxyphenylcalix[4]resorcinarene 3

Adsorbent **3** was prepared using a previously reported procedure [14–17] as shown in Fig. 1. A solution of 4-methoxybenzaldehyde **2** (1 g; 7.35 mmol) in ethanol (15 mL) was added dropwise to an ice-cooled solution of resorcinol **1** (0.8 g; 7.72 mmol) in a mixture of ethanol (15 mL) and catalytic amount of concentrated HCl (3 mL); after 30 min, a pink precipitate was formed and the reaction mixture was then refluxed with continuous stirring for 12 h. The precipitate was then filtered and washed with cold ethanol to produce adsorbent **3**.

2.2. Reagents and glassware

All glassware and polyethylene bottles were initially cleaned with soap, washed thoroughly with tap water, distilled water, and socked with 1% HNO_3 (v/v) overnight to remove any heavy metal ions contamination. Heavy metal ions solutions of different concentrations were prepared by diluting a stock solution of initial concentration 1,000 ppm of the metal ions Pb(II), Cu(II), Co(II), Mn(II), and Zn(II) in aqueous nitric acid to desired concentrations. The pH adjustment was carried out by slow addition of NaOH and/or HNO_3 solutions into the metal ions solutions followed by stirring until the desired pH was reached. The solvents used in this study were analytical reagent grade and were used as purchased. Resorcinol was purchased from BDH chemicals Ltd., Poole, England. Ethanol and concentrated hydrochloric acid were purchased from Aldrich chemical company. 4-Methoxybenzaldehyde (4-Anisaldehyd) was purchased from Fluka (USA).

2.3. Apparatus and instrumentation

pH measurements were done using glass electrode pH meter model pH 525 (WTW®, Weilheim, Germany). The pH meter was calibrated based on pH 4, pH 7, and pH 10 buffer solutions at 25˚C according to standard method [18]. 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, 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.

Standard solutions of heavy metal ions Cu(II), Mn(II), Zn(II), Pb(II), and Co(II) were prepared in order to obtain a calibration curve for each heavy metal ion solution. Fig. 2 shows the linear calibration curve for the selected heavy metal ions used in this study.

2.4. Effect of pH

The adsorption experiments were conducted by adding 0.1 g of the *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3** into 100 mL of metal ion solution with an initial concentration of 1 ppm. The adsorption of Pb(II), Co(II), Cu(II), Mn(II), and Zn(II) was investigated at pH = 3.0, 5.6, 7.0, and 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 in the filtrate.

2.5. Effect of contact time

The effect of contact time on the adsorption process was investigated by running agitation time in the range of 2–30 min. A 0.1 g in the *C*-4-methoxyphenylcalix[4]resorcinsrene adsorbent **3** was added into 100 mL of a metal ion-containing solution with initial concentration of 1 ppm. The acidity of sample solution was adjusted to optimum pH determined earlier from the experimental results. The contents of the flask were agitated at 25˚C for different time intervals of 2, 5, 7, 10, 15, 20, 25, and 30 min. The residual concentrations of metal ion in the blank and solution samples were determined using AAS. Blank solution serves as a controller of the occurrence of metal ions, which were precipitated after treatment.

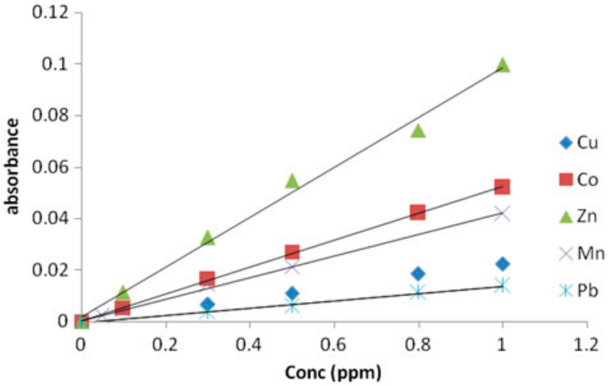

Fig. 2. Linear calibration curves for selected heavy metal ions Cu(II), Mn(II), Zn(II), Pb(II), and Co(II).

2.6. Selectivity and competition study

An accurate weight (0.1 g) of *C*-4-methoxyphenylcalix[4]-resorcinarene adsorbent **3** was mixed and shacked with 100 mL of an aqueous solution containing a mixture of heavy metal ions with an initial concentration of 1 ppm of each metal at an optimum pH. Blank experiments were simultaneously carried out without the adsorbents. 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.

Table 1
Standard parameters used in determination of different heavy metal ions using AAS (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

2.7. Data analysis

The uptake of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) ions was calculated from the mass balance, which was stated as the amount of metal ions adsorbed onto the *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3**. The amount of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) ions that is removed from the solution is expressed by Eq. (1) [18].

$$q_e = (C_i - C_e)/S \tag{1}$$

where q_e is the heavy metal ions concentration adsorbed at equilibrium (mg of 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 Eq. (2).

$$S = m/V \tag{2}$$

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 Eq. (3).

$$\%\,\text{adsorption} = (C_i - C_e)/C_i \times 100\% \tag{3}$$

3. Results and discussion

Adsorption of Pb(II), Cu(II), Co(II), Mn(II), and Zn(II) under different pH and contact time conditions was done to determine the maximum adsorption percentage of these heavy metal ions and to determine the kinetic mechanism of this study. The investigated conditions were as follows:

3.1. Effect of pH

Determination of the optimum pH solution of the adsorption of heavy metal ions on adsorbent **3** is an important study in evaluating the interactions between heavy metal ions and *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3**. 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 this study was investigated at pH

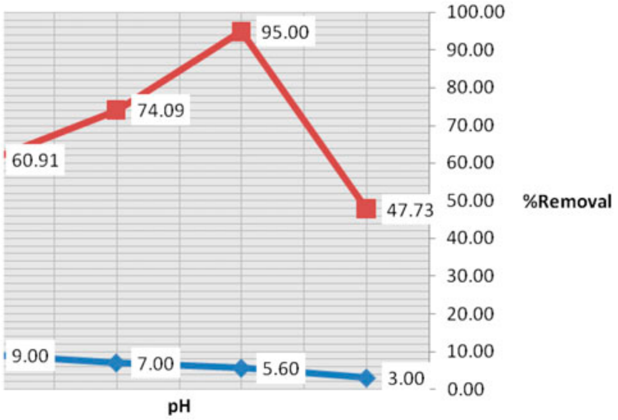

Fig. 3. pH effect on the adsorption of Cu(II) on *C*-4-methoxyphenylcalix[4]resorcinarene **3**; conditions: initial concentration 1 ppm; time = 30 min; *T* = 298 ± 1 K.

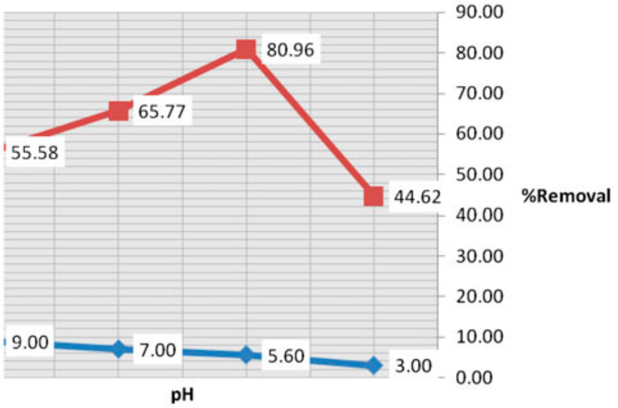

Fig. 4. pH effect on the adsorption of Co(II) on *C*-4-methoxyphenylcalix[4]resorcinarene **3**; conditions: initial concentration 1 ppm; time = 30 min; *T* = 298 ± 1 K.

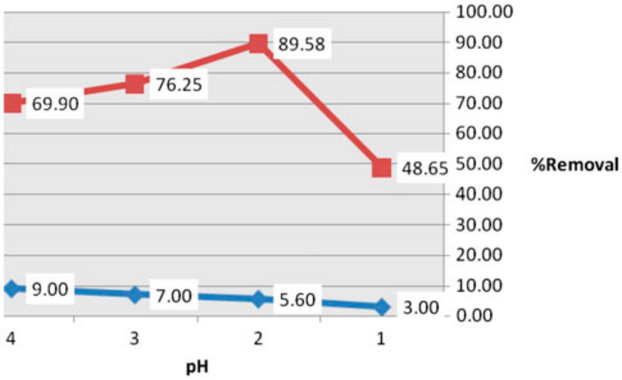

Fig. 5. pH effect on the adsorption of Zn(II) on *C*-4-methoxyphenylcalix[4]resorcinarene **3**; conditions: initial concentration 1 ppm; time = 30 min; *T* = 298 ± 1 K.

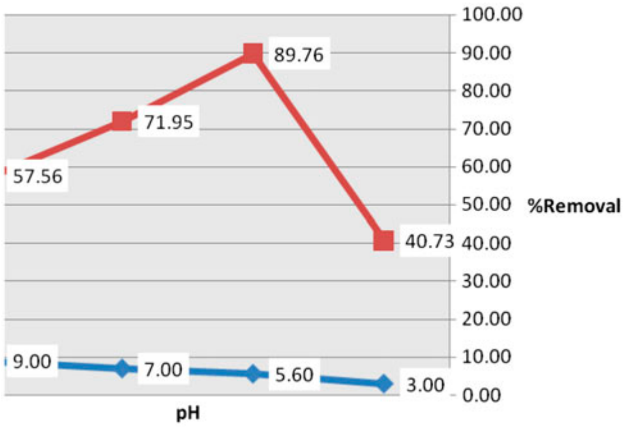

Fig. 6. pH effect on the adsorption of Mn(II) on *C*-4-methoxyphenylcalix[4]resorcinarene **3**; conditions: initial concentration 1 ppm; time = 30 min; *T* = 298 ± 1 K.

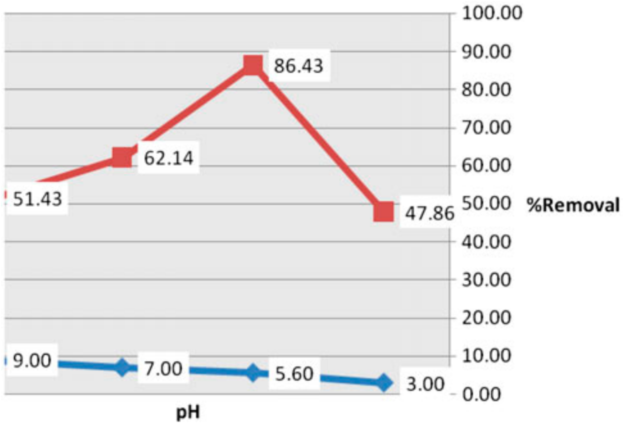

Fig. 7. pH effect on the adsorption of Pb(II) on *C*-4-methoxyphenylcalix[4]resorcinarene **3**; conditions: initial concentration 1 ppm; time = 30 min; *T* = 298 ± 1 K.

ranging from 3 to 9. Figs. 3–7 show the relationship between the amount of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) adsorbed under different pH values. It was found that metal ions adsorption capacity reached its maximum value at pH 5.6 for all investigated heavy metal ions onto the adsorbent **3**. *C*-4-methoxyphenylcalix[4]resorcinarene **3** contains eight phenolic-OH groups that may act as the active binding sites. Under acidic conditions (pH 3), hydroxyl (–OH) groups on *C*-4-methoxyphenylcalix[4]resorcinarene **3** will be protonated so that these active sites tend to be positively charged. Thus, in highly acidic solutions, most likely, electrostatic repulsion interactions between the adsorbent and the adsorbate will occur due to similar positive characters. In other words, there was 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 number of protons in solution decreased with increasing pH, so the adsorption competition between H^+ and Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) is further reduced, resulting in escalating adsorption of heavy metal ions by *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3**. Moreover, at pH 7, the deprotonation of the phenolic hydroxyl group of *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3** converts them into negatively charged phenoxide ions. Since the phenoxide ions of compound **3** 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 percent removal of the heavy metal ions by the adsorbent.

3.2. *Effect of contact time*

Removal percentage of heavy metal ions with agitating time is a necessary parameter for determination of adsorption equilibrium and to determine the adsorption rate constant based on the adopted kinetic model. Removal percentage for the selected heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) with time using *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3** is shown in Fig. 8. The optimum adsorption contact time that leads to maximum removal percentage for the selected heavy metal ions Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) was 30 min for all of them. When the adsorption equilibrium is reached, increasing contact time does not affect the amount of the adsorbed heavy metal ions. At initial adsorption

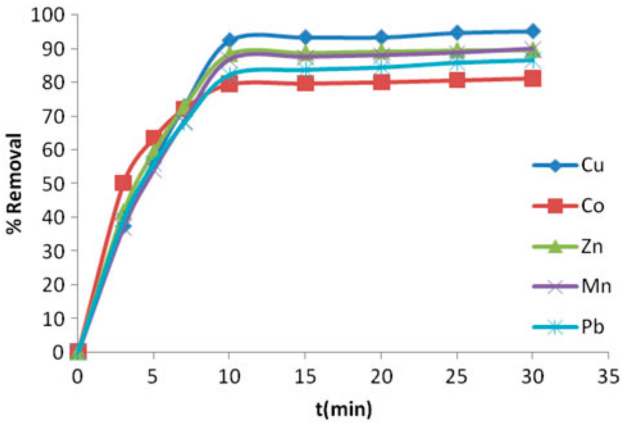

Fig. 8. Effect of contact time on the adsorption of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) on *C*-4-methoxyphenylcalix[4]resorcinarene **3**; conditions: initial concentration 1 ppm; pH 5.6; *T* = 298 ± 1 K.

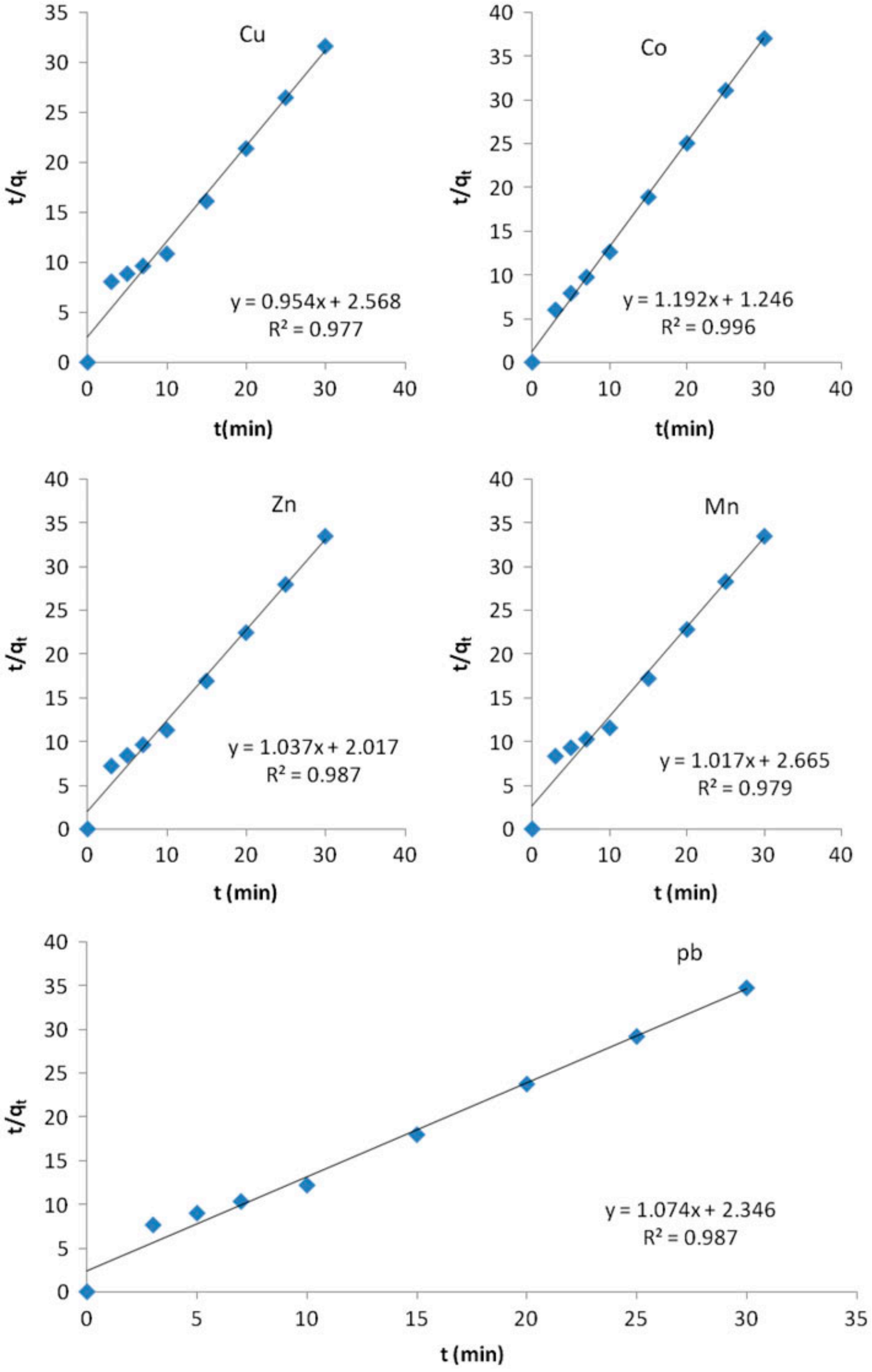

Fig. 9. Pseudo-second-order kinetics of selected heavy metal ions adsorption on the *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3.**

stage, the surface of the adsorbent was empty, so the absorption of heavy metal ions by the adsorbent was rapid. Later, adsorption rate decreases with time, indicating saturation on the active sites of the adsorbent.

3.3. Adsorption kinetic modeling

Several models can be used to express the mechanism of solute sorption onto an adsorbent. In order to investigate the mechanism of sorption, Santosa et al.

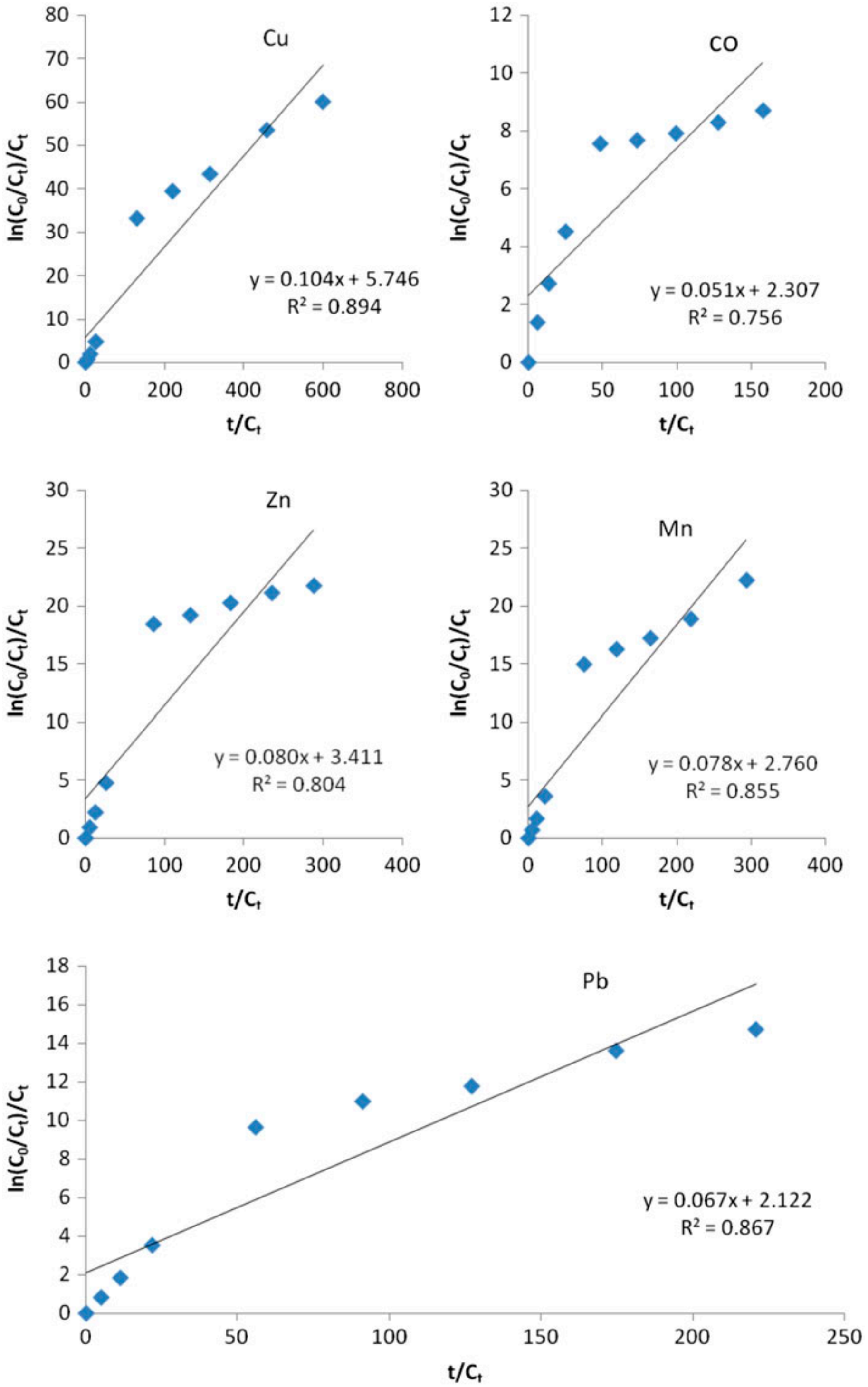

Fig. 10. First-order-kinetic of selected heavy metal ions adsorption on *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3.**

[19] made a kinetic equation model of a single metal ion adsorption on the adsorbent with an overview of the concentration of adsorbate in the liquid phase. Mathematical equation for a single ion condition can be indicated by Eq. (4).

$$\ln (C_0/C_a)/C_a = k_1 t/C_a + K \qquad (4)$$

where C_0 is the initial metal concentration (mg/L), C_a is the concentration of metal ions in solution at time t

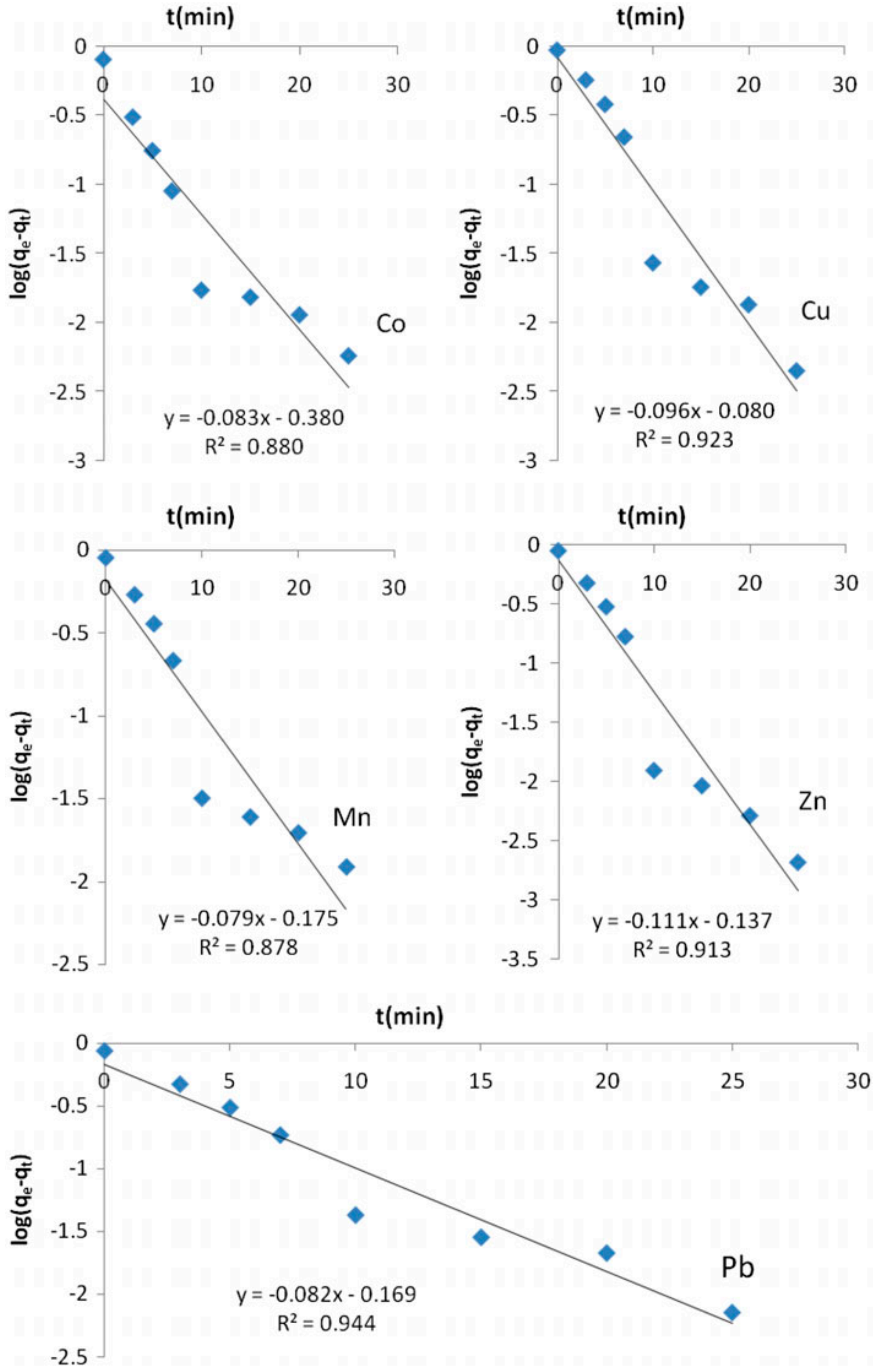

Fig. 11. Pseudo-first-order kinetic of selected heavy metal ions adsorption on the *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3.**

(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 the solid phase (the adsorbent). In order to distinguish the kinetic equation based on the concentration of solution and adsorption capacity of the adsorbent,

Table 2
Kinetic modeling and its adsorption parameters of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) onto *C*-4-methoxyphenylcalix[4]resorcinarene **3**

Kinetic models	Rate constant, k		Correlation coefficient, R^2
First order of Santosa	Cu(II)	0.104 (min^{-1})	0.894
	Co(II)	0.051 (min^{-1})	0.756
	Zn(II)	0.080 (min^{-1})	0.804
	Mn(II)	0.078 (min^{-1})	0.855
	Pb(II)	0.067 (min^{-1})	0.867
Pseudo-first-order of Lagergren	Cu(II)	0.096 ($\mathrm{mg\,g}^{-1}\,\mathrm{min}^{1}$)	0.923
	Co(II)	0.083 ($\mathrm{mg\,g}^{-1}\,\mathrm{min}^{1}$)	0.880
	Zn(II)	0.111 ($\mathrm{mg\,g}^{-1}\,\mathrm{min}^{1}$)	0.913
	Mn(II)	0.079 ($\mathrm{mg\,g}^{-1}\,\mathrm{min}^{-1}$)	0.878
	Pb(II)	0.082 ($\mathrm{mg\,g}^{-1}\,\mathrm{min}^{-1}$)	0.944
Pseudo-second-order of Ho & Mc Kay	Cu(II)	0.354 ($\mathrm{g\,mg}^{-1}\,\mathrm{min}^{-1}$)	0.977
	Co(II)	1.14 ($\mathrm{g\,mg}^{-1}\,\mathrm{min}^{-1}$)	0.996
	Zn(II)	0.533 ($\mathrm{g\,mg}^{-1}\,\mathrm{min}^{-1}$)	0.987
	Mn(II)	0.388 ($\mathrm{g\,mg}^{-1}\,\mathrm{min}^{-1}$)	0.979
	Pb(II)	0.491 ($\mathrm{g\,mg}^{-1}\,\mathrm{min}^{-1}$)	0.987

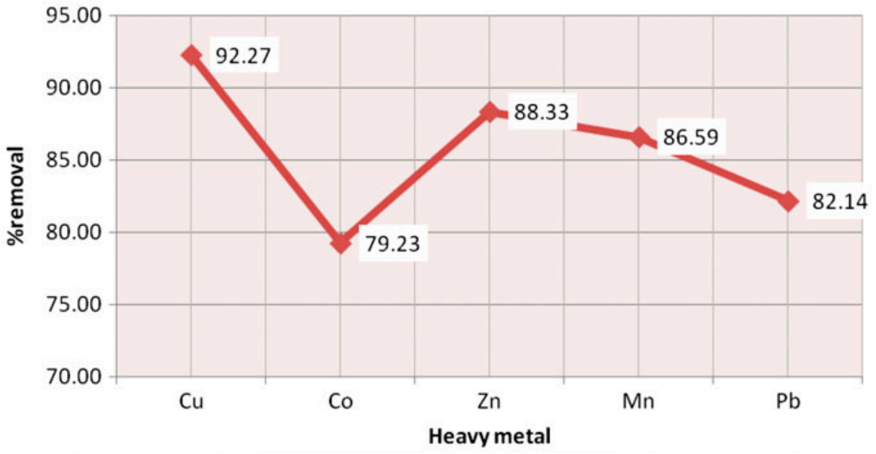

Fig. 12. Adsorption efficiency of *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3** towards individual heavy metal ions.

Lagergren's first-order and Ho's second-order rate equations have been called pseudo-first-order and pseudo-second-order, respectively. The pseudo-first-order equation is generally expressed by Eq. (5) [20]:

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

and the pseudo-second-order kinetic model which was reviewed by Ho and Mckay [21] and expressed by Eq. (6):

$$t/q_t = 1/K_2 q_e^2 + t/q_e \qquad (6)$$

where q_e and q_t ($\mathrm{mg\,g}^{-1}$) are the adsorption capacities at equilibrium and at contact time t, while k_1 and k_2 are the rate constants of pseudo-first-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 Fig. 8 were used for kinetic modeling. In order to study the adsorption kinetic of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) onto *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3**, the first-order metal adsorption of Santosa et al. [19], pseudo-first-order of Lagergren [20], and pseudo-second-order of Ho and Mckay [21]

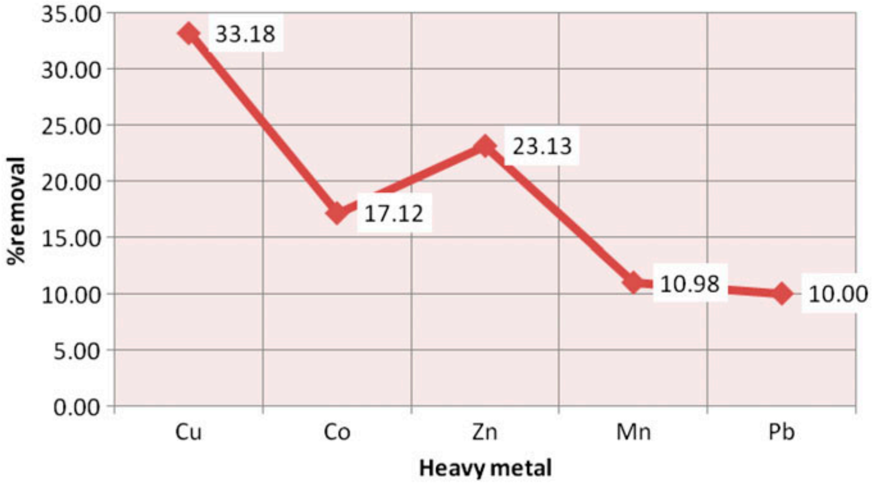

Fig. 13. Selectivity of *C*-4-methoxyphenylcalix[4]resorcinarene **3** towards a mixture of heavy metal ions.

models were applied and used to process the experimental adsorption data. Based on Fig. 9, the resulting curve has the highest level of linearity comparing with the previous determination of first-order heavy metal ions adsorption showed in Fig. 10 and pseudo-first-order adsorption showed in Fig. 11. The results of the kinetic study are presented in Table 2. Thus, it can be concluded that the kinetic pattern of Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) onto *C*-4-methoxyphenylcalix[4]resorcinarene adsorbent **3** follows pseudo-second-order kinetic model. Table 2 lists the rate constant value for each heavy metal adsorption mechanism. The adsorption rates for the heavy metals are ranked as: Co(II) > Zn(II) > Pb(II) > Mn(II) > Cu(II).

3.4. Selectivity and competition study

The selectivity of adsorbent towards a mixture of selected heavy metal ions Cu(II), Co(II), Zn(II), Mn (II), and Pb(II) was conducted at pH = 5.6 and shacking time of 10 min. The adsorption efficiency of *C*-4-methoxyphenylcalix[4]resorcinarene **3** against individual heavy metal ions is shown in Fig. 12 with removal capacity in the order: Cu(II) > Zn(II) > Mn(II) > Pb(II) > Co(II); and with a removal percentage of 92.27, 88.33, 86.59, 82.14, and 79.23%, 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 at an initial concentration of 1 ppm was Cu(II) > Zn(II) > Co(II) > Mn(II) > Pb(II); with a percentage removal of 33.18, 23.13, 17.12, 10.98, and 10.00%, respectively, as illustrated in Fig. 13.

4. Conclusions

In the current study, synthetic adsorbent surface **3** was prepared by one-step reaction through the acid-catalyzed condensation of resorcinol with 4-methoxybenzaldehyde. The prepared adsorbent surface was studied and proved to be a good adsorbent for selected heavy metal ions such as Cu(II), Co(II), Zn(II), Mn(II), and Pb(II) at an initial metal ion concentration of 1 ppm. Effect of the pH solution on the adsorption efficiency indicated that the optimum pH for heavy metal ions adsorption is 5.6 at contact time 30 min. The adsorption model of metal ions on the synthetic adsorbent surface **3** followed the pseudo-second-order kinetics. Adsorbent surface **3** trapped individual heavy metal ions with percent removal in the order of Cu(II) > Mn(II) > Zn(II) > Pb(II) > Co(II), while the selectivity of adsorbent **3** towards a mixture of 1 ppm of each metal ion is ranked as: Cu(II) > Zn(II) > Co(II) > Mn(II) > Pb(II). The adsorption rate constants for the adsorption of each heavy metal ions followed the order of Co(II) > Zn(II) > Pb(II) > Mn(II) > Cu(II). Future work in our laboratories will include studies of adsorption effects of other calixarenes derivatives, these, and other transition metal ions, including those of mercury.

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