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Investigation of heavy metal ions adsorption behavior of silica-supported Schiff base ligands

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ABSTRACT

Schiff base-modified silica gel particles have been shown to be selective and efficient adsorbents for heavy metal ions Cu(II) and Pb(II). This potential was examined as a function of various parameters influencing the adsorption process. The adsorbents were able to be used for multiple adsorption–desorption processes. The analysis of temperature dependency of the process revealed that the adsorption of ions is controlled by positive entropy changes. The isotherm of adsorption process was studied using various models including Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms. Kinetics data were described by pseudo-second-order model, which allowed suggesting a chemisorption mechanism for the adsorption processes.

Keywords: Bulk silica particles; Schiff base ligands; Heavy metals; Thermodynamics; Isotherms; Kinetics

1. Introduction

The pollutions created by heavy metals are serious environmental problem in the world [1]. This provokes the removal of these metals from wastewater being the subject of extensive fundamental as well as industrial research activities [2]. In addition, the recovery of some heavy metals from secondary sources is important from economical point of view [3].

Among many types of solid-phase extractors [4–11], silica gel presents the advantages such as no swelling, fast kinetics, good mechanical as well as the thermal and chemical stability [12]. Chemical modifications of silica surface by immobilization of functional groups have been reported for concentration of metal ions [13,14].

Schiff base ligands bearing nitrogen/oxygen donor atoms have been shown to exhibit interesting ionophoric properties toward heavy metal ions, in particular, for Cu(II) and Pb(II) ions [15–19]. These properties have been examined using this group of ligands as modifier of octadecyl discs for separation–concentration of trace amount of metal ions [20], as phase transfer agents of metal ions in liquid–liquid extraction [21], and cloud point extraction [22], as mobile carrier agent in transport of metal ions through liquid membranes [15],

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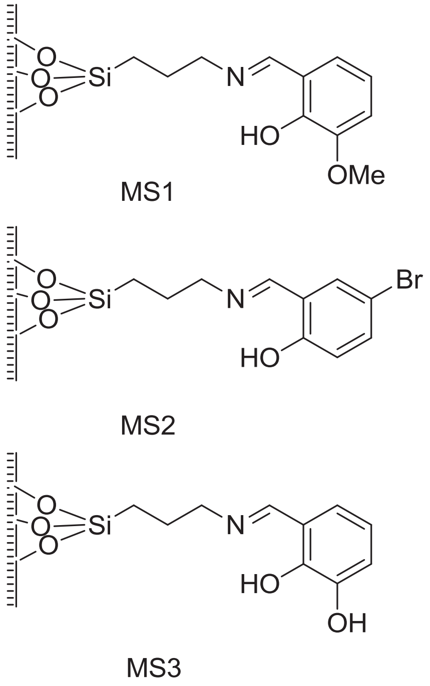
and also as sensory molecules for preparation of cation-selective electrodes [16].

Recently, we have reported the ionophoric properties of some Schiff base receptors [15,16] and their application as modifier of silica nanoparticles for removal of actinide and lanthanide ions from water samples [23]. The potential of these ligands toward metal ions provokes us to study the application of silica-supported Schiff base ligands as adsorbents for removal of heavy metal ions, Cu(II), Pb(II), Zn(II), Cd (II), Co(II), and Ni(II), from water solutions. The studied Schiff bases were 3-methoxy salicylaldimine propyle triethoxysilane, 5-bromo salicylaldimine propyl triethoxysilane, and 3-hydroxy salicylaldimine propyl triethoxysilane, which their corresponding sorbents were abbreviated as MS1, MS2, and MS3 (Fig. 1). The influence of parameters affecting the adsorption process was investigated and discussed. In addition, this study was concerned on the assessment and interpretation of thermodynamics, isotherms, and kinetics of the adsorption process.

2. Material and methods

2.1. Materials

Chemicals used for the synthesis of the Schiff bases were methanol, toluene, aminopropyltriethoxysilane, 2-hydroxy-3-methoxy benzaldehyde, 5-bromo-2-hydroxy benzaldehyde, and 2,3-dihydroxy benzaldehyde purchased from Merck Chemical company. Hydrochloric acid (Fluka), nitric acid (Merck), sulfuric acid (Merck), and silica particles (Merck) were used as received. Stock solutions of the heavy metal ions (1,000 mg/L) were prepared from their corresponding nitrate salts (Merck or Fluka). The stock solutions were standardized by complex formation titration [24]. The working solutions were prepared by appropriate dilution of the stock solutions with distilled water.



MS1

MS2

MS3

Fig. 1. Studied modified silica particles.

2.2. Apparatus

^{1}H NMR measurements were performed on a FT-Bruker (AVC 250 MHz) spectrometer and data were referenced relative to residual protonated solvents (7.26 ppm for $CDCl_3$). FT-IR spectra were recorded on a Thermo-Nicolet-is10 FT-IR spectrometer. The pH adjustments were performed by a Metrohm (model 780) digital pH-meter equipped with a combined glass electrode. An Ika magnetic stirrer (MR 3001K) was used for mixing adsorbent and aqueous solutions. Temperature of the experiment vessels was controlled using a Julabo MP5 thermostat water circulator. A flame atomic absorption spectroscopy (Varian 220AA) was applied for metal ions determination under manufacturer's recommended conditions. A furnace (Exiton, model Atash-1200) was used for activating the surface of silica particles, before their modification. Separation of the sorbent and aqueous phase mixtures was assisted by a high-speed centrifuge (Sigma 3–30K). Distilled water was passed through a filter (TKA-Gen Pure), before using in the experiments.

2.3. Preparation of the adsorbents

Condensation of aminopropyltriethoxysilane with 2-hydroxy-3-methoxy benzaldehyde, 5-bromo-2-hydroxy benzaldehyde, and 2,3-dihydroxy benzaldehyde in methanol produced 3-methoxy salicylaldimine propyle triethoxysilane (L^1), 5-bromo salicylaldimine propyl triethoxysilane (L^2), and 3-hydroxy salicylaldimine propyl triethoxysilane (L^3), respectively. Characterization of the prepared Schiff base ligands was performed by ^{1}H NMR and FT-IR spectroscopic methods. Modification of silica particles was realized according to the procedure reported previously [25]. Refluxing the prepared Schiff bases L^1, L^2, and L^3 with silica particles in toluene resulted in modified silica particles MS1, MS2, and MS3, respectively. Elemental analysis of the prepared adsorbents revealed that the amounts of grafted imine resulted from loading of 3-methoxy salicylaldimine, 5-bromo salicylaldimine, and 3-hydroxy salicylaldimine ligands on silica particles were

0.46×10^{-3}, 0.58×10^{-3}, and 0.38×10^{-3} mol imine/g of silica, respectively. The FT-IR spectra of adsorbents are shown in Fig. 2. Spectroscopic data of the products were as follows: 3-methoxy salicylaldimine propyle triethoxysilane (L^1): ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.67 (t, 2H, CH_2–Si), 1.2 (t, 9H, CH_3), 1.8 (dd, 2H, CH_2), 3.5 (t, 2H, N–CH_2), 3.8 (q, 6H, O–CH_2), 4.0 (s, 3H, OCH_3), 6.70–7.2 (3H, CHAr), 8.20 (s, 1H, CH=N), 14.08 (br s, 1H, OH) ppm; FT-IR (KBr): ν = 3,416 (O–H), 2,926 (C–H), 1,632 (C=N), 1,467 (C=C), 1,255 (C–O) cm^{-1}. 5-bromo salicylaldimine propyl triethoxysilane (L^2): ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.65 (t, 2H, CH_2–Si), 1.2 (t, 9H, CH_3), 1.8 (dd, 2H, CH_2), 3.5 (t, 2H, N–CH_2), 3.82 (q, 6H, O–CH_2), 6.80–7.3 (3H, CHAr), 8.23 (s, 1H, CH=N), 13.62 (br s, 1H, OH) ppm; FT-IR (KBr): ν = 3,446 (O–H), 2,925 (C–H), 1,634 (C=N), 1,467 (C=C), 1,279 (C–O) cm^{-1}. 3-hydroxy salicylaldimine propyl triethoxysilane (L^3): ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.68 (t, 2H, CH_2–Si), 1.2 (t, 9H, CH_3), 1.85 (dd, 2H, CH_2), 3.57 (t, 2H, N–CH_2), 3.82 (q, 6H, O–CH_2), 6.51–6.92 (3H, CHAr), 8.11 (s, 1H, CH=N) ppm. FT-IR (KBr): ν = 3,419 (O–H), 2,925 (C–H), 1,634 (C=N), 1,464 (C=C), 1,235 (C–O) cm^{-1}. MS1 FT-IR (KBr): ν = 3,432 (O–H), 2,923 (C–H), 1,646 (C=N), 1,097, 472 (–O–Si) cm^{-1}. MS2 FT-IR (KBr): ν = 3,441 (O–H), 2,923 (C–H), 1,635 (C=N), 1,065, 474 (–O–Si) cm^{-1}. MS3 FT-IR (KBr): ν = 3,427 (O–H), 2,929 (C–H), 1,653 (C=N), 1,100, 467 (–O–Si) cm^{-1}.

2.4. Adsorption procedure

The adsorption experiments were carried out in stoppered plastic vessels using 0.1 g of one of the adsorbents in 20 mL of the solution containing Cu, Pb, Co, Ni, Zn, and Cd ions (20 mg/L). After the mixture was magnetically stirred for 50 min, the phases were separated by centrifugation. Then, the concentration of the cations remaining in the aqueous phase was measured by flame atomic absorption spectroscopy. The amounts of uptake and desorption percentage of the cations were calculated by following equations:

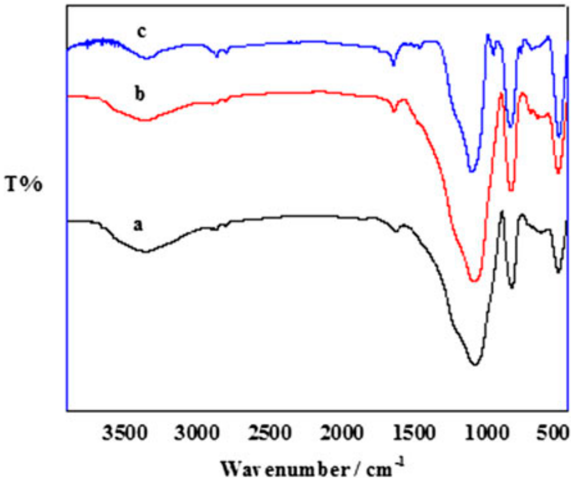


Fig. 2. FT-IR spectra of the studied adsorbents (a) MS1, (b) MS2, and (c) MS3.

$$\text{Uptake }\% = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

$$\text{Desorption }\% = \frac{m_d}{m_a} \times 100 \qquad (2)$$

In these equations, C_0 and C_e are the initial and equilibrium concentration of ions (mg/L), respectively; m_d and m_a (mg) are the desorbed and adsorbed mass of ions, respectively.

3. Results and discussion

3.1. Effect of aqueous solution pH

Because of the acidic nature of hydroxyl group of the Schiff base ligands, it is assumed that the pH of aqueous solutions plays a key role on the uptake efficiency of the prepared adsorbents. This parameter was examined by carrying out the adsorption experiments of the metal ions as a function of the aqueous phase pH (Fig. 3). By increasing the aqueous phase pH, a significant increase in the copper uptake was observed. A similar effect was found in the removal of lead ions by MS1 and MS3. This was attributed to a decrease in the competition of H^+ and metal cations for the active sites of the adsorbents. These results are in agreement with an ion exchange mechanism for the removal of the ions by the studied Schiff base-modified silica particles.

In order to clarify the role of modification on the adsorption characteristics of silica particles, the removal of the studied metal ions by the unmodified silica particles (S) was also examined. It was found that practically no adsorption of the metal ions was observed by the unmodified silica particles. This revealed the significant role of the Schiff base modification on the adsorption characteristics of the silica particles.

All the studied sorbents showed selective removal toward copper ions. However, a significant selectivity toward copper ions with respect to the other examined ions was presented by MS2. Except for Cu^{2+} and Pb^{2+} ions, under selected experimental conditions, the studied adsorbents were not capable to remove other

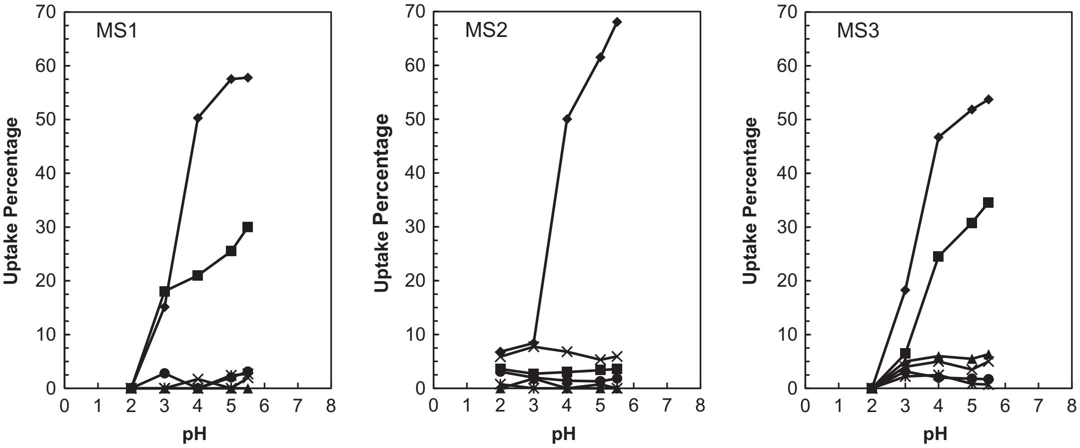


Fig. 3. Effect of pH on the sorption of Cu (♦), Pb (■), Zn (▲), Cd (×), Co (✳), Ni (●) ions by MS1, MS2, and MS3. Concentration of the metal ions 20 mg/L; adsorbent dose 0.05 g; contacting time 60 min; temperature 25˚C.

heavy metal ions, regardless to the applied aqueous phase pH. A comparison of the removal percentage of copper ions by the adsorbents at pH 5 allows considering the capacity order of them as MS2 > MS1 > MS3. This order is in accordance with the amount of grafted Schiff base ligands on the silica matrix (see Section 2.3). In addition, the extraction of lead ions at lower pH region by MS1 with respect to MS3 demonstrates the higher acidic nature of the hydroxyl group of the Schiff base grafted on MS1.

3.2. Adsorbent dose

Amount of the adsorbent is among the parameters conventionally investigated for achieving maximum removal efficiency in an adsorption process, which depends on the adsorbent capacity and the active sites found on an adsorbent. To examine this parameter, a series of experiments were performed by applying different doses of the adsorbents in the range 0.025–0.2 g (Fig. 4) for the removal of Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} ions from its single component aqueous phase adjusted at pH 5. Application of more adsorbent dose results that the ligating group available for interaction with metal ions increases, consequently redounds to increase the metal ions sorption. It was found that using >0.1 g of the adsorbents MS1, MS2, and MS3, a quantitative removal of copper ions can be achieved. Although, an amount of >0.2 g of MS1 and MS3 allows a quantitative elimination (~90%) of lead ions. The lower efficiency of MS2 inhibits the removal of these ions to be more than 50% using the same amount of this adsorbent. The results obtained by MS2 show also its potential for removal of other examined ions using higher amount of this adsorbent. This investigation showed that using 0.2 g of MS2, it is possible to reduce about 56% of zinc ions, 30% of cobalt, 24% of cadmium and nickel ions from aqueous phase. Also using 0.2 g of MS1 and MS3, it could be possible to remove zinc ions from aqueous solution up to 35 and 22%, respectively.

3.3. Time dependency of the processes

Investigation of the effect of contacting time of the adsorbents with sample solutions on the removal efficiency of chemical species is important because this investigation determines the time required for achieving an equilibrium condition, on one hand, it allows describing the kinetics of the adsorption process (see Section 3.9), on the other hand. To assess the effect of this parameter, the adsorption of metal ions from aqueous solutions, adjusted at pH 5, using 0.075 g of the modified silica particles MS1, MS2, and MS3 was carried out as a function of contacting time in the range 3–120 min (Fig. 5). Equilibrium condition for the adsorption of copper ions was achieved after 30, 90, and 50 min using MS1, MS2, and MS3, respectively. This indicated the kinetic of the copper adsorption on MS1 is more rapid with respect to the other studied adsorbents. The more rapid adsorption of lead ions on MS1 with respect to MS3 was also concluded. The results found in this investigation showed a shaking time of 60 min is sufficient for a maximum adsorption of the metal ions.

3.4. Initial metal ions concentration

This variable was tested by removal of the studied metal ions from aqueous solutions (pH 5) contacting

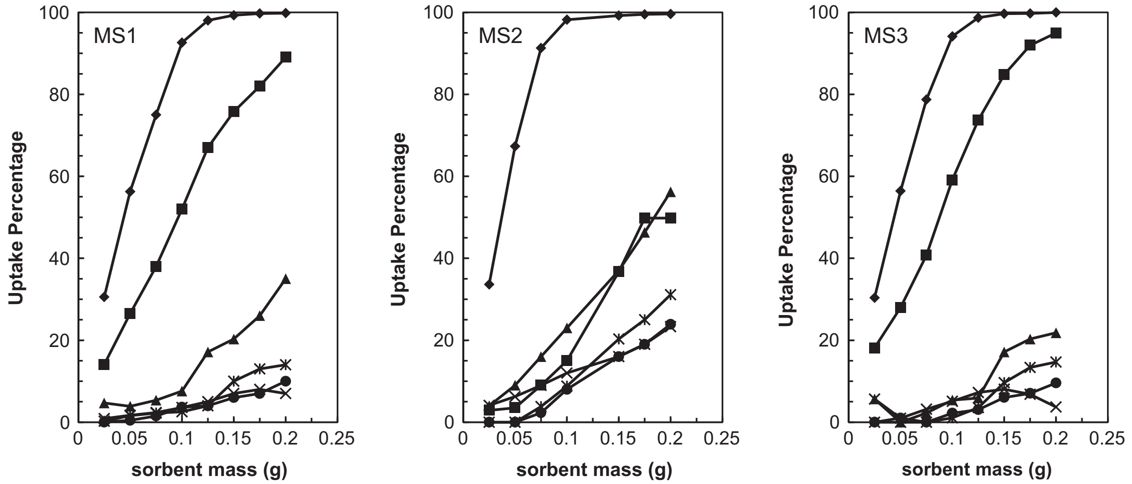


Fig. 4. Effect of adsorbent dose on their efficiency for removal of Cu (♦), Pb (■), Zn (▲), Cd (×), Co (✳), Ni (●) ions by MS1, MS2, and MS3. Concentration of the metal ions 20 mg/L; solution pH 5; contacting time 60 min; temperature 25˚C.

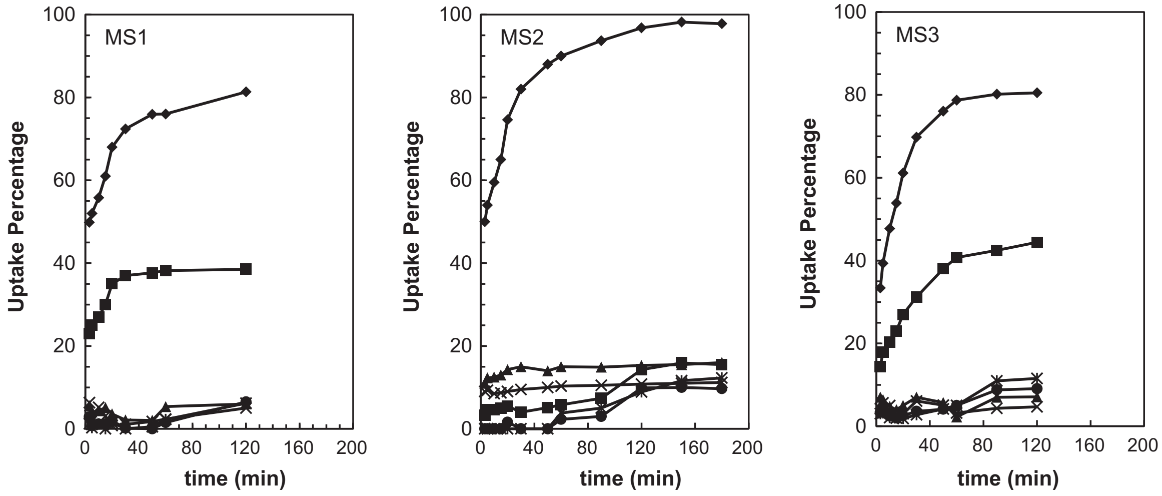


Fig. 5. Variation in adsorption uptake of Cu (♦), Pb (■), Zn (▲), Cd (×), Co (✳), Ni (●) ions by MS1, MS2, and MS3 as a function of contacting time. Concentration of the metal ions 20 mg/L; adsorbent dose 0.075 g; solution pH 5; temperature 25˚C.

with 0.15 g of the adsorbents for 60 min (Fig. 6). The capacity of the process can be monitored by evaluating the amount of maximum adsorbed metal ions ($q_{\max}$). The determined $q_{\max}$ for copper adsorption by MS1, MS2, and MS3 varies as 4.7, 4.93, and 6 mg copper per g of the adsorbent, respectively. This value was 2.27 and 3.33 mg lead per g of the adsorbent for MS1 and MS3, respectively.

It is seen that the adsorption capacity of the lead ions increases with initial ion concentration up to 50 mg/L using MS1. Beyond this concentration, a decrease in the adsorption percentage of the ions was observed. Although at this stage of the study we cannot give an explanation for such results, a similar attitude was also observed in the adsorption of cadmium and lead ions onto amine-functionalized SBA-15 materials [26] and europium ions onto some modified mesoporous silica SBA-15 materials [27].

3.5. Desorption process

The stability of the studied adsorbents and their potential for multiple uses were examined by performing a series of adsorption experiments as follow.

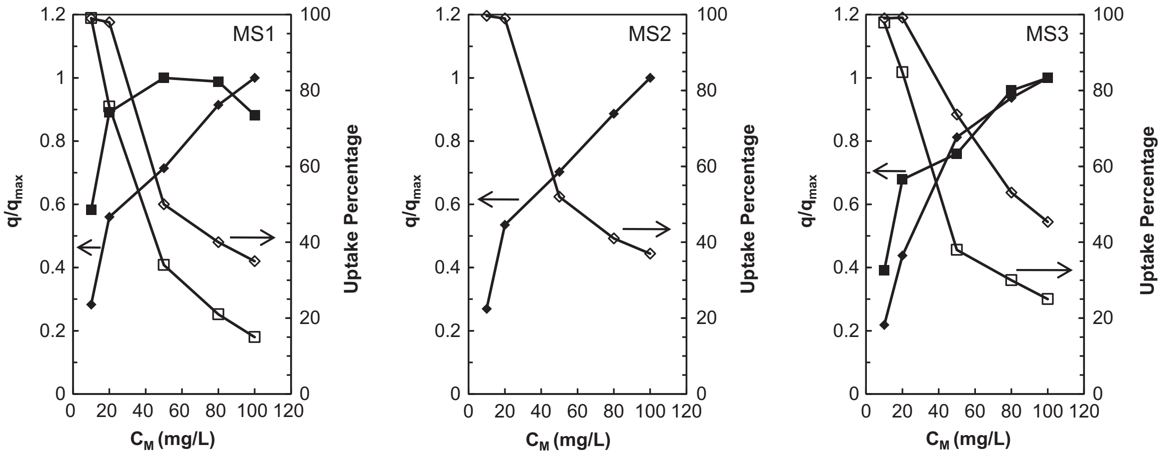


Fig. 6. Relative adsorption to the maximum capacity (q/q_{max}) and uptake percentage of copper (♦) and lead (■) ions by the studied adsorbents as a function of initial concentration in the aqueous phase. Adsorbent dose 0.15 g; solution pH 5; contacting time 60 min; temperature 25°C.

In these experiments, 20 mL aqueous solutions containing 20 mg/L of copper and lead ions adjusted at pH 5 was contacted with 0.2 g of the adsorbents. The mixture was stirred magnetically for 60 min. The phases were then separated and the metal ions remained in the aqueous phase were determined. The results showed the removal of 100 percent of copper with the all studied adsorbents, 89, 50, and 95 percent of lead ions by MS1, MS2, and MS3, respectively. The loaded adsorbents were then washed two times with distilled water, and were dried at 110°C. The adsorbed ions were stripped from the surface of adsorbents by 5 mL of nitric, hydrochloric, and sulfuric acid solutions (Table 1). This investigation showed that a solution of nitric acid (5 mL, 0.1 mol/L) is able to strip quantitatively the copper ions from MS1 and MS2 and lead ions from MS1. For a complete desorption of copper and lead ions from loaded MS3, the stripped adsorbent in the first step was contacted with a second 5 mL solution of 0.1 mol/L nitric acid. Under such conditions, all the adsorbed metal ions were transferred to the aqueous phase.

Although the effect of type of the acid used as strippant cannot be described by considering just a cation exchange mechanism for the adsorption–desorption processes of a cation on acidic sites of the adsorbents, the dependency of the stripping efficiency on the type of acid used in such processes has been reported elsewhere [28–30]. In addition, the results shown in Table 1 signify that the stripping efficiency of the acids depends also on the type of the applied adsorbent.

In order to examine the stability of the adsorbents after desorption of the adsorbed metal ions by acid solutions, FT-IR spectra of the studied adsorbents before using in the adsorption and after stripping process with nitric acid solution were compared. This comparison confirmed the stability of the adsorbents during adsorption/desorption processes.

Table 1
Results of the desorption of the adsorbed copper and lead ions by various strippants[a]

	MS1		MS2		MS3	
Strippant (0.1 mol/L)	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}
HNO_3[b]	99.8	95.1	97.8	–	88.4	80.5
HNO_3[c]	–	–	–	–	12.5	20.0
HCl	54.6	70.0	86.0	–	88.8	83.6
H_2SO_4	63.8	47.3	100.0	–	85.7	6.0

[a] The values are in comparison with 100% of the copper and lead ions loaded onto the adsorbents. Standard deviation < ±1.6%.

[b] First stripping by 5 mL of nitric acid.

[c] Second stripping by 5 mL of nitric acid.

The separated silica particles were used repeatedly for the experiments described above. It is found that no significant decrease in the adsorbents efficiency (<5%) was observed using them for three adsorption–desorption cycles.

3.6. Applications

The applicability of the studied adsorbents was tested by their application for removal of copper and lead ions from water samples. To this end, a series of adsorption–desorption experiments, under optimized conditions, were done using three water samples including tap water and well water samples from University of Zanjan Campus (Zanjan-Iran) and a sample prepared by molten snow. The samples were first digested by nitric acid solution and then copper and lead ions (20 mg/L) were spiked to them. A volume of 20 mL of the samples adjusted at pH 5 was stirred, for 60 min, with 0.2 g of each of the adsorbents, at room temperature. These experiments were performed three times. It was found that a quantitative removal of copper ions can be achieved under selected conditions by all the studied adsorbents. This investigation revealed also the possible removal of quantitative lead ions by MS1 and MS3 adsorbents (Table 2).

3.7. Thermodynamics of the process

As other equilibria, adsorption process can be influenced by temperature. Verification of the effect of temperature on equilibria allows evaluating the thermodynamic functions ΔG°, ΔH°, and ΔS° [31]. The corresponding distribution coefficient (K_d) of adsorption processes is determined using Eq. (3):

$$K_\mathrm{d} = \frac{q_\mathrm{e}}{C_\mathrm{e}} \tag{3}$$

Here q_e defines the quantity of analyte adsorbed onto the adsorbent (mg/g) and C_e is the concentration of metal remained in the solution at equilibrium condition (mg/L).

The evaluated distribution coefficients allow determining the free energy changes (ΔG°) through the Gibbs–Helmholtz equation (Eq. (4)):

$$\Delta G^\circ = -RT \ln K_\mathrm{d} \tag{4}$$

Considering the relation between the free energy changes with enthalpy (ΔH°) and entropy changes (ΔS°):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

It is possible to determine the thermodynamic parameters ΔG°, ΔH°, and ΔS°, using the plots of $\ln K_\mathrm{d}$ vs. T^{-1} via Eq. (6):

$$\ln K_\mathrm{d} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

In order to verify the influence of temperature on the process, the removal of copper and lead ions (20 mg/L) from aqueous solutions by the modified silica particles (0.075 g) was examined in the range 293–343 K. The results revealed that the adsorption efficiency increases with temperature. The corresponding thermodynamic values are presented in Table 3. These values reveal that all the adsorption processes are endothermic and are controlled by entropy changes. The positive enthalpy change is a consequence of the dehydration of the metal ions during the adsorption process. This dehydration process needs much energy surpasses the heat released from the adsorption reaction.

It is worth of note that when ΔG° has positive value, this means that the reaction is non-spontaneous under standard conditions, which, however, may not

Table 2
Results of the application of the adsorbents for removal of copper and lead ions from water samples[a]

	Well water		Tap water		Molten snow	
Adsorbent	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}	Cu^{2+}	Pb^{2+}
MS1	100.0 (±0.02)	91.3 (±1.7)	100.0 (±0.3)	93.3 (±1.1)	100.0 (±0.5)	97.6 (±0.9)
MS2	97.9 (±0.3)	–	98.8 (±0.2)	–	97.7 (±0.1)	–
MS3	99.4 (±0.02)	96.1 (±0.1)	98.9 (±0.5)	95.9 (±0.2)	99.5 (±0.2)	96.3 (±0.2)

[a] Experimental conditions: aqueous phase, 20 mL of the samples injected by 20 mg/L of copper and lead ions; pH 5; adsorbent dose 0.2 g; stirring time 60 min; temperature 25˚C.

Table 3
Thermodynamic functions (in kJ/mol) for the adsorption of copper and lead ions by the studied sorbents at 298 K[a]

Adsorbent	Metal ion	ΔH°	$T\Delta S^\circ$	ΔG°
MS1	Cu^{2+}	3.9	2.8	1.1
	Pb^{2+}	44.7	39.6	5.1
MS2	Cu^{2+}	47.9	46.8	1.1
	Pb^{2+}	32.7	26.7	56.0
MS3	Cu^{2+}	4.5	3.4	1.1
	Pb^{2+}	23.8	20.0	3.8

[a]Standard deviation < ±0.6.

be verified in the experiments. Therefore, in place of ΔG°, the values of ΔG must be considered for estimating the spontaneity of the processes. The obtained results show that adsorption occurs spontaneously although ΔG° is positive. This is not a contradiction and it is noteworthy that same result was reported by other researchers [32].

3.8. Isotherms

Adsorption isotherm describes the relation of the adsorbed amount of an analyte onto an adsorbent, and its equilibrium concentration in the solution. This relation gives important information about the mechanism of adsorption and helps for designing efficient adsorbing systems [33]. In order to select a proper isotherm model for describing experimental data, the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) isotherms were examined [31,34–38].

The equation describing Langmuir isotherm is given below:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{7}$$

in which C_e is the equilibrium concentration of metal ions in solution (mg/L), q_e is the amount of metal ions adsorbed per unit mass of adsorbent under equilibrium conditions (mg/g), $q_{\max}$ is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant which is related to adsorption energy (L/mg). A plot of C_e/q_e vs. C_e allows determining $q_{\max}$ and K_L. For this isotherm, separation factor or equilibrium parameter (R_L) is a useful dimensionless parameter which indicates the possibility of the adsorption process to proceed. This parameter is expressed by Eq. (8):

$$R_L = \frac{1}{1 + K_L C_0} \tag{8}$$

A process is unfavorable if $R_L > 1.0$ or <0, $R_L = 1$ shows a linear favorable process, for the case R_L value lays between 0 and 1 ($0 < R_L < 1$) the process is favorable, and an irreversible process can be deduced if R_L equals zero [34].

The Freundlich isotherm is an empirical equation suitable for high and middle range of solute concentrations. The mathematical expression of Freundlich isotherm is shown by Eq. (9):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{9}$$

where K_F and n are Freundlich constants called the adsorption capacity and adsorption intensity, respectively. It is noteworthy that in this model n is greater than unity, and a smaller value of $1/n$ reveals a stronger interaction between adsorbent and solute.

The equation describing Temkin isotherm is given in Eq. (10):

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \tag{10}$$

where R is the gas constant (0.0083 kJ/mol K), T is the absolute temperature (K), b is the Temkin constant related to heat of adsorption (kJ/mol), and K_T is the Temkin isotherm constant (L/g). The parameters K_T and b can be estimated by drawing the variation of q_e as a function of $\ln C_e$.

The equation describing Dubinin–Radushkevich (D–R) isotherm is given by Eq. (11):

$$\ln q_e = \ln q_{\max} - K_{D\text{–}R}\varepsilon^2 \tag{11}$$

Here $K_{D\text{–}R}$ (in mol^2/J^2) is a constant which is related to the adsorption energy and ε is the Polanyi potential defined by Eq. (12):

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{12}$$

A plot of $\ln q_e$ variation as a function of ε^2 allows evaluating the parameters $K_{D\text{–}R}$ and $q_{\max}$. E is a parameter defined as the mean energy (kJ/mol) for bringing a mole of adsorbate from infinity to the surface of the adsorbent [35]. It can be calculated by Eq. (13):

Table 4
Parameters evaluated using various isotherms for the adsorption of copper and lead ions onto the studied adsorbents

		MS1		MS2	MS3	
Isotherm type	Parameter	Cu^{2+}	Pb^{2+}	Cu^{2+}	Cu^{2+}	Pb^{2+}
	$q_{\mathrm{max,exp}}$ (mg/g)	4.7	2.27	4.93	6.04	3.33
Langmuir isotherm	K_{L} (L/mg)	2.19	1.52	6.54	1.46	0.65
	$q_{\mathrm{max,cal}}$ (mg/g)	4.90	2.25	5.46	5.35	2.92
	R_{L}	0.02	0.03	0.01	0.03	0.07
	R^2	0.994	0.994	0.999	0.996	0.997
Freundlich isotherm	K_{F} ((mg/g)/(mg/L)$^{1/n}$)	3.47	1.64	4.42	3.35	1.60
	n	7.81	9.62	11.24	6.02	5.32
	$1/n$	0.128	0.104	0.089	0.166	0.188
	R^2	0.994	0.973	0.924	0.997	0.993
Temkin isotherm	K_{T} (L/g)	1,703.2	3,604.7	45,443.3	625.3	251.2
	b (kJ/mol)	5.1	12.16	5.83	4.56	7.11
	R^2	0.991	0.93	0.937	0.997	0.973
D–R isotherm	$K_{\mathrm{D\text{–}R}}$ (mol^2/kJ^2)	1.09 0.023	0.53	0.028	0.26 0.039	0.078
	$q_{\mathrm{max,cal}}$ (mg/g)	4.97 3.94	2.28	5.29	4.91 3.84	2.37
	E (kJ/mol)	23.19 23.19	23.84	15.81	18.51 18.51	18.56
	R^2	0.966 0.970	0.997	0.991	0.878 0.992	0.991

Table 5
Kinetic parameters evaluated using pseudo-first-order and pseudo-second-order models for interpreting the experimental data

		MS1		MS2	MS3	
Kinetic models	Parameter	Cu	Pb	Cu	Cu	Pb
	$q_{\mathrm{e,exp}}$ (mg/g)	4.34	2.04	5.24	4.28	2.37
Pseudo-first-order	$q_{\mathrm{e,cal}}$ (mg/g)	2.04	1.22	2.63	2.89	1.75
	$k_{1,\mathrm{ads}}$ (1/min)	0.048	0.094	0.028	0.05	0.03
	R^2	0.979	0.982	0.987	0.987	0.989
Pseudo-second-order	$q_{\mathrm{e,cal}}$ (mg/g)	4.44	2.16	5.43	4.57	2.71
	$k_{2,\mathrm{ads}}$ (g/mg min)	0.053	0.13	0.03	0.03	0.02
	h (mg/g min)	1.05	0.60	0.84	0.68	0.16
	R^2	0.998	0.997	0.998	0.996	0.998

$$E = \frac{1}{\sqrt{2K_{\mathrm{D\text{–}R}}}} \tag{13}$$

This parameter is used to estimate the type of adsorption process. If $E < 8$ kJ/mol, adsorption process is of a physical nature, whereas, if value $E > 8$ kJ/mol, the adsorption process can be explained by ion exchange mechanism.

Based on the descriptions noted above, the parameters related to the Langmuir, Freundlich, Temkin, and D–R isotherms have been determined and shown in Table 4. Comparison of the evaluated R^2 values corresponding to the tested isotherms allowed considering the Langmuir isotherm for interpreting the adsorption data of copper and lead ions by MS1, MS2 (for copper ions), and MS3. The adsorption of copper ions onto MS2 obeyed well from the Langmuir and D–R isotherms. The variation of $\ln q_e$ vs. ε^2 based on D–R isotherm presented two linear ranges. The R^2 value of the second linear range permits considering this model to be valid for the adsorption of copper ions onto MS3 in this region. Except for the copper ion adsorption onto MS3 at the first linear range presumed by D–R isotherm and lead ion adsorption at Temkin isotherm, the investigation of the adsorption of these ions on MS3 reveals all the studied isotherms

Table 6
Comparison of the adsorption capacity of MS1, MS2, and MS3 with that of some other adsorbents reported in the literature

Adsorbent	Ions	Adsorption capacity (mg/g)	Refs.
SDS-PVC-BHABDI[a]	Cu^{2+} Pb^{2+}	2.6 2.2	[45]
SBA-15-APTS[b]	Pb^{2+}	1.1	[46]
Silica gel/nanometer titanium dioxide	Pb^{2+}	3.16	[47]
Amberlite XAD-7/xylenol orange	Pb^{2+}	3.14	[48]
Activated carbon/4,6-dihydroxy-2-mercaptopyrimidine	Cu^{2+} Pb^{2+}	0.63 0.45	[49]
Chestnut shell	Cu^{2+} Pb^{2+}	5.5 8.5	[50]
Nano-TiO_2-MBT[c]	Cu^{2+} Pb^{2+}	3.95 3.17	[51]
Nano-sized G/Co_3O_4 composite[d]	Cu^{2+} Pb^{2+}	77 58	[52]
MNPs-EDTA	Cu^{2+}	46.27	[53]
Nano-sized Fe_3O_4	Cu^{2+} Pb^{2+}	37.04 166.67	[54]
MS1	Cu^{2+} Pb^{2+}	4.7 2.27	Present work
MS2	Cu^{2+}	4.93	Present work
MS3	Cu^{2+} Pb^{2+}	6.04 3.33	Present work

[a] Sodium dodecyl sulfate-coated poly(vinyl)chloride modified with bis(2-hydroxyacetophenone)-1,4-butanediimine.
[b] γ-aminopropyl triethoxysilane (APTS).
[c] Nano-TiO_2 modified with 2-mercaptobenzothiazole.
[d] Nano-sized graphene/Co_3O_4 composite.

can describe the process. The results obtained based on the Langmuir and D–R isotherms (Table 4) showed an acceptable agreement between the calculated and experimental values for $q_{\max}$ ($q_{\max,\exp}$ and $q_{\max,\mathrm{cal}}$). The R_L values calculated by Langmuir isotherm revealed the processes are favorable. The n values derived from the Freundlich isotherm allow considering a favorable process for all the adsorption process. As presented in Table 4, the values of $1/n$ derived from the Freundlich model were between 0.089 and 0.188. This indicates that the metal ions were favorably adsorbed by modified adsorbents. Based on this parameter, the interaction between the adsorbed ion and the adsorbents varies as Pb/MS3 < Cu/MS3 < Cu/MS1 < Pb/MS1 < Cu/MS2.

In Langmuir isotherm model, the monolayer coverage of the sorbent surface is suggested. This model assumes also that the adsorbent surface is homogeneous and the surface sites are energetically identical [36]. The Freundlich isotherm considers multilayer adsorption of the sorbate on heterogeneous surface [37]. A linear decrease in the adsorption heat with coverage is considered in Temkin isotherm. In contrast, this relation is logarithmic in Freundlich equation [31]. The Dubinin–Radushkevich (D–R) isotherm does not assume a homogeneous or constant adsorption potential of the surface [38].

3.9. Kinetics

Kinetics of the processes were evaluated by applying pseudo-first-order and pseudo-second-order models [39,40]. The pseudo-first-order kinetics model is based on the assumption that adsorption is controlled by diffusion step, and the rate of adsorption is proportion to the difference value of equilibrium adsorption capacity at equilibrium and at any time t (q_e, and q_t, respectively, in mg/g). The corresponding equation is shown by:

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,\mathrm{ads}}}{2.303} t \tag{14}$$

where $k_{1,\mathrm{ads}}$ is the pseudo-first-order rate constant.

The pseudo-second-order model describes the relation between mass of the adsorbate per unit mass of the adsorbent and time:

$$\frac{t}{q_t} = \frac{1}{k_{2,\mathrm{ads}} q_e^2} + \frac{t}{q_e} \tag{15}$$

where $k_{2,\mathrm{ads}}$ denotes the pseudo-second-order rate constant. In this model, the initial rate of adsorption can be evaluated as q_t/t approaches to zero. It means:

$$h_0 = k_{2,\mathrm{ads}} q_e^2 \tag{16}$$

Here h_0 is the initial rate of adsorption (mg/g min).

Considering the values of correlation coefficients (Table 5), the pseudo-second-order kinetic model provided an impressive and comparable correlation for the adsorption of ions. It is noted that although R^2, obtained using pseudo-first-order model for some of the metal adsorption, was close to that found by the pseudo-second-order kinetic model, the values of q_e evaluated by the former was too far from that was found experimentally. A comparison of the evaluated adsorption capacity considering the pseudo-second-order equation (q_e) and that found experimentally ($q_{\exp}$) reconfirmed also the validity of the proposed model. It suggested that the rate-determining step of the adsorption might be chemical adsorption and the adsorption process involves the valence forces through sharing electrons between the metal ions and adsorbents [41–43]. The adsorbents MS1, MS2, and MS3, which have chelating functional groups on their surfaces, most probably behave as a chelating exchanger. Therefore, the complexation reaction was expected for the adsorption processes [44].

4. Conclusions

Silica particles modified by Schiff base ligands 3-methoxy salicylaldimine propyle triethoxysilane (MS1), 5-bromo salicylaldimine propyl triethoxysilane (MS2), and 3-hydroxy salicylaldimine propyl triethoxysilane (MS3) are potential adsorbents for selective removal of copper and lead ions from aqueous solutions. The excellent selectivity toward copper ions was demonstrated by MS2. Although in this report the efficiency of MS2 toward Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} ions is shown, a more investigation needs for optimization of the experimental conditions for a quantitative removal of these ions from aqueous solutions. The adsorption capacity values achieved with presented adsorbents were comparable with those achieved with a variety of adsorbents given in the literature (Table 6). However, although the adsorption capacity of the bulk MS1, MS2, and MS3 adsorbents was higher than that of the nanoadsorbent TiO_2-MBT, generally the nano-sized adsorbents G/Co_3O_4 composite, MNPs-EDTA and Fe_3O_4 showed higher adsorption capacity with respect to the studied adsorbents. Adsorption/desorption of the metal ions onto the adsorbents allows their multiple use for removal of copper and lead ions from aqueous solutions. Thermodynamic parameters showed that the adsorption processes are endothermic and are controlled by entropy changes. The isotherms describing the experimental results of the adsorption processes depend on the metal ions as well as the type of the adsorbent. The kinetics of processes follow the pseudo-second-order reaction kinetics, showing chemisorption is the rate-limiting mechanism.

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