Characteristics of equilibrium, kinetics studies for adsorption of Hg(II), Cu(II), and Ni(II) ions by thiourea-modified magnetic chitosan microspheres

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ABSTRACT

Magnetic chitosan microspheres were prepared and chemically modified with thiourea (TMCS) for adsorption of metal ions. TMCS obtained were investigated by means of X-ray diffraction (XRD), IR, magnetic properties and thermogravimetric analysis (TGA). The adsorption properties of TMCS toward Hg^{2+}, Cu^{2+}, and Ni^{2+} ions were evaluated. Various factors affecting the uptake behavior such as contact time, temperature, pH and initial concentration of the metal ions were investigated. The kinetics was evaluated utilizing the pseudo-first-order, pseudo-second-order, and the intra-particle diffusion models. The equilibrium data were analyzed using the Langmuir, Freundlich, and Tempkin isotherm models. The adsorption kinetics followed the mechanism of the pseudo-second-order equation for all systems studied, evidencing chemical sorption as the rate-limiting step of adsorption mechanism and not involving a mass transfer in solution. The best interpretation for the equilibrium data was given by Langmuir isotherm, and the maximum adsorption capacities were 625.2, 66.7, and 15.3 mg/g for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions, respectively. TMCS displayed higher adsorption capacity for Hg^{2+} in all pH ranges studied. The adsorption capacity of the metal ions decreased with increasing temperature. The metal ion-loaded TMCS with were regenerated with an efficiency of greater than 88% using 0.01–0.1 M ethylendiamine tetraacetic acid (EDTA).

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1. Introduction

Contamination of aquatic media by heavy metals is a serious environmental problem, mainly due to the discharge of industrial waste [1]. Heavy metals are highly toxic at low concentrations and can accumulate in living organisms, causing several disorders and diseases [2]. The main techniques that have been used on metal content reduction from industrial waste are chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis, solvent extraction, and adsorption [3–5]. However, these methods are limited by high operational cost and/or may also be inefficient in the removal of some toxic metal ions, mainly at trace level concentrations [1,6].

The application of magnetic adsorbent technology to solve environmental problems has received considerable attention in recent years. Magnetic adsorbents can be used to adsorb contaminants from aqueous or gaseous effluents. After the adsorption is carried out, the adsorbent can be separated from the medium by a simple magnetic process [7,8]. These adsorbents have a variety of surface functional groups which can be tailored for use in specific applications. Poly(2-hydroxyethyl methacrylate) [9], poly(oxy-2,6-dimethyl-1,4-phenylene) [10], polyvinyl-butyral [11], and chitosan [12] are typical adsorbents which are used in different applications.

The ability of a material to capture metals is controlled in part by the number of available functional groups used for binding metals. According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions will have a preference for complexing with ligands that have more or less electronegative donor atoms [13]. The sulfur group is known to form stable complexes with soft heavy metals of high polarizability such as Hg, Ag, Au, and to a lesser extent, Cd and Zn [14].

Chitosan is the second most abundant biopolymer in nature, obtained from the shells of shrimp, crabs, and lobsters, which are waste products of seafood processing industries [15]. Chitosan is a natural polysaccharide with many useful features such as hydrophilicity, biocompatibility, biodegradability, antibacterial properties, and remarkable affinity for many biomacromolecules. Chitosan and its derivatives have great potential application in the areas of biotechnology, biomedicine, food ingredients, and cosmetics. Chitosan is also capable of adsorbing a number of metal ions as

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its amino groups can serve as chelation sites. Due to their high nitrogen content and porosity, chitosan-based sorbents have exhibited relatively high sorption capacities and kinetics for most heavy metals [16–19]. However, lack of specificity toward several highly toxic heavy metals limits the use of chitosan as an effective sorbent.

In the present work, the thiourea-modified magnetic chitosan microspheres (TMCS) were prepared. The high content of amino groups makes possible chemical modification in magnetic chitosan with the purpose of improving its features as an adsorbent, such as selectivity and adsorption capacity. The adsorption equilibrium and the kinetics of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions in aqueous solutions with magnetic chitosan microspheres were also investigated. This adsorbent in our studies has magnetic properties and presents high adsorption capacity for metal ions, especially for Hg^{2+} ions.

Generally, biosorbed metal ions can be desorbed and concentrated by proper acid. Heavy metal ions can then be recovered selectively and efficiently through multi-stage precipitation by means of various solvents. However, acids such as HCl and HNO_3 may react with Fe_3O_4, which is the magnetic component of TMCS. Ethylenediamine tetraacetic acid (EDTA) is known as a very strong chelating agent for many heavy metals, and was proposed to replace the active groups on TMCS and preferentially complex with metal ions. Consequently, EDTA was chosen as the desorbent for metal ions.

2. Experimental

2.1. Materials

Chitosan with 40 mesh, 90% degree of deacetylation (DD) and molecular weight of 1.3×10^5 was purchased from Yuhuan Ocean Biology Company (Zhejiang, China). All the other reagents used in this work were of analytical grade. $HgCl_2$, $Cu(NO_3)_2 \cdot H_2O$, and $NiSO_4 \cdot 6H_2O$ were used as sources for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions, respectively. Stock solutions (1000 mg/L) of the studied metal ions were prepared in distilled water.

2.2. Preparation of magnetic chitosan microspheres

Fe_3O_4 particles were prepared by coprecipitating Fe^{2+} and Fe^{3+} ions by ammonia solution and treating under hydrothermal conditions [12]. Ferric and ferrous chlorides (molar ratio 2:1) were dissolved in water at a concentration of 0.3 M iron ions. Chemical precipitation was achieved at 25 °C under vigorous stirring by addition of NH_4OH solution (29.6 wt.%). During the reaction process, the pH was maintained at about 10. The precipitates were heated at 80 °C for 30 min, washed several times with water and ethanol, and then finally dried in a vacuum oven at 70 °C.

The water/oil (W/O) emulsion cross-linking technique was used for the preparation of magnetic chitosan microspheres. In a typical procedure, 1.0 g of chitosan powder was dissolved in 100 mL of 2 wt.% aqueous acetic acid solution. Once dissolved, 1.0 g Fe_3O_4 particles was added and the mixture was sonicated for 30 min. The W/O emulsion was prepared by dropwising the acetic acid solution containing chitosan and Fe_3O_4 into the dispersion medium, which was composed of cyclohexane, n-hexanol (11:6, v/v) and an emulsifier (1.5 mL Triton X-100). The W/O ratio of the W/O emulsion was 4:17 (v/v). During this process, the dispersion medium was stirred with a mechanical stirrer at about 1000 rpm at room temperature. Ten minutes later, an additional 1 mL of glutaraldehyde was added to the dispersion medium. Similarly, 1 h later, another 1 mL of glutaraldehyde was added to the medium, which was then stirred for a further 2 h. At the end of this period, the magnetic chitosan microspheres were collected using a magnet and rinsed with ethanol and deionized water for three times. The microspheres were then dried in an oven at 60 °C for 24 h and kept in a vacuum dessicator for further analysis and use.

2.3. Modification of magnetic chitosan microspheres with thiourea

Grafting of sulfur groups using epichlorohydrin as a cross-linking agent was carried out according to the procedure described by Chassary et al. [20] with chitosan flakes. Four milliliters of epichlorohydrin was dissolved in 100 mL of acetone, the magnetic chitosan microspheres (2 g) were added, and the slurry was mixed at 35 °C for 24 h. Thiourea (2 g) was added, and stirring was continued for 6 h at 60 °C, followed by addition of further thiourea (4.6 g) with stirring at 60 °C. NaOH (1 M, 50 mL) was added, and the slurry was agitated (4 h, 60 °C). The solid product (thiourea derivative of magnetic chitosan, TMCS) was filtered and successively washed with acetone, demineralized water, and methanol, and dried in a vacuum oven at 60 °C.

2.4. Characterization of the samples

The geometry of the magnetic chitosan microspheres was observed by optical microscopy. X-ray diffraction (XRD) data were collected on a XRD-2000 X-ray diffractometer with Cu Kα radiation. FTIR spectra were measured on a Nicolet, Magna-550 spectrometer. The magnetic chitosan was mixed with KBr and pressed to a plate for measurement. Thermal gravimetric analysis of microspheres was conducted on Shimadzu TGA-50H with heating rate of 10 °C/min in the nitrogen flow. A vibrating-sample magnetometer (VSM) (EG & G Princeton Applied Research Vibrating Sample Magnetometer, Model 155, USA) was used at room temperature to characterize the magnetic properties of magnetic chitosan microspheres. The sulfur content of TMCS was determined by a Thermo Finnigam 1112 Elemental Analyzer. The specific surface area was measured by N_2 adsorption isotherm using an ASAP 2010 Micromeritics instrument and by Brunauer–Emmett–Teller (BET) method, using the software of Micromeritics. Pore diameter greater than 20 Å were determined by mercury porosimeter up to 2000 kg/cm^2 using a Carlo Erba model 200. The zeta potential of TMCS was measured on a Zeta Potential Analyzer (Brookhaven, USA). For zeta potential measurements, the samples were diluted with 0.1 mmol/L NaCl solution at pH 2.5–10.5 (adjusted by NaOH or HCl) and measured in the automatic mode.

2.5. Metal ion uptake experiments using batch method

2.5.1. Effect of pH
Uptake experiments were performed at controlled pH and 28 °C by shaking 0.03 g of dry TMCS with 20 mL (100 mg/L) metal ion solution for 8 h at 150 rpm. The buffer solutions used for adjusting the pH of the medium were KCl/HCl (pH 1, 2, and 3); acetic acid/sodium acetate (pH 4 and 5); and Na_2HPO_4/KH_2PO_4 (pH 6). Five milliliters of the solution were taken at the end of the experiment where the residual concentration of metal ion was determined using a GGX-9 atomic absorption spectrophotometer.

2.5.2. Effect of the temperature
Uptake experiments were performed by placing 0.03 g of dry TMCS in a series of flasks containing 20 mL (100 mg/L) of the metal ion solution at pH 5.0. The flasks were agitated on a shaker at 150 rpm for 8 h while keeping the temperature at 15, 20, 25, 28, 30, or 35 °C. After adsorption, solution was filtered and the residual concentration of the metal ions was determined.
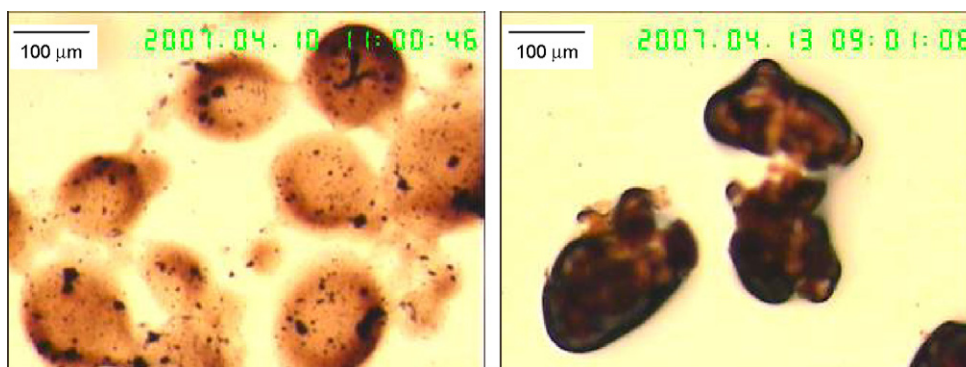
Fig. 1. Optical micrograph of magnetic chitosan microspheres before (left) and after (right) modification with thiourea.

2.5.3. Effect of contact time

Measurements of metal ion uptake using a batch method were conducted by placing 0.3 g of dry TMCS in a flask containing 200 mL (100 mg/L) metal ion solution at pH 5.0. The contents of the flask were agitated on a shaker at 150 rpm and 28 °C. Samples were taken at time intervals for the analysis of residual metal concentration in solution.

2.5.4. Effect of the initial concentration of the metal ions

The effect of initial concentration of the metal ion on the uptake by TMCS obtained was carried out by placing 0.03 g of dry TMCS in a series of flasks containing 20 mL of metal ions at definite concentrations (Hg^{2+}: 50–1500 mg/L; Cu^{2+}: 25–350 mg/L; Ni^{2+}: 25–250 mg/L) and pH 5.0. The contents of the flasks were equilibrated on the shaker at 150 rpm and 28 °C for 8 h. After adsorption, the residual concentration of the metal ions was determined.

2.5.5. Desorption experiments

For desorption studies, 0.15 g of TMCS was loaded with metal ions (Hg^{2+}, Cu^{2+}, and Ni^{2+}) using 100 mL (100 mg/L) metal ion solution at 28 °C, pH 5.0 and contact time of 8 h. The agitation rate was fixed as 150 rpm. Metal ion-loaded TMCS were collected, and gently washed with distilled water to remove any unabsorbed metal ions. The beads were then agitated with 100 mL of EDTA. The final concentration of metal ions in the aqueous phase was determined by means of an atomic absorption spectrophotometer. The desorption ratio of metal ions from TMCS was calculated from the amount of metal ions adsorbed on TMCS and the final concentration of metal ions in the desorption medium. To test the reusability of the beads, this adsorption–desorption cycle was repeated five times by using the same affinity adsorbent.

3. Results and discussion

3.1. Characterizations of the magnetic chitosan microspheres

Fig. 1 shows an optical micrograph of magnetic chitosan microspheres, and it can clearly be seen that the unmodified magnetic chitosan microspheres are well shaped spheres and have smooth surfaces. However, the shapes of the microspheres became irregular after modification with thiourea because of the grafting reaction of thiourea. The chitosan layer was formed around the small aggregates of several Fe_3O_4 particles. The chitosan magnetic microspheres have the diameter size range of 80–250 μm.

Elemental analysis of sulfur indicated that the magnetic chitosan modification with thiourea resulted in a product with a sulfur content of 2.12 mmol/g. According to mercury porosimetry data, the average pore size of the magnetic beads was 891 nm.

The BET surface area for TMCS was 62.3 m^2/g. As shown in FTIR spectra of TMCS, the carbonyl bands at around 1700 cm^{-1} showed that glutaraldehyde cross-linking in the case of the magnetic chitosan microspheres occurred. Because epichlorohydrin tends to bond to magnetic chitosan using their hydroxyl groups, the TMCS structure did not present different groups from the unmodified magnetic chitosan, except for the decrease in intensity of the peak at 1599 cm^{-1} (δ(N–H)) characteristic of magnetic chitosan. These results indicated a partial involvement of the amino groups in the cross-linking reaction. The peak due to sulfur group vibration was not detected, probably due to the weak signal. The peaks at 560–660 cm^{-1} were assigned to Fe–O bond vibration of Fe_3O_4.

The thermogravimetric analysis (TGA) results showed that the principle chains of chitosan began to degrade at about 250 °C and the final temperature of decomposition was approximately 650 °C. The average mass content of Fe_3O_4 on TMCS by TGA was about 32%. The magnetic susceptibility measurements of TMCS had a value of 17.6 emu/g. These magnetic properties indicated the possibility of using this resin in wastewater treatment.

The XRD results of pure Fe_3O_4 and TMCS are shown in Fig. 2, which confirmed the components of the iron oxide particles. The XRD results of the magnetic chitosan particles and pure Fe_3O_4 particles were mostly coincident. Six characteristic peaks for Fe_3O_4 ($2\theta = 30.1°$, $35.5°$, $43.3°$, $53.4°$, $57.2°$, and $62.5°$), marked by their indices ((2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0)), were observed in both samples. These results indicated that the magnetic substance of TMCS was validated as Fe_3O_4.
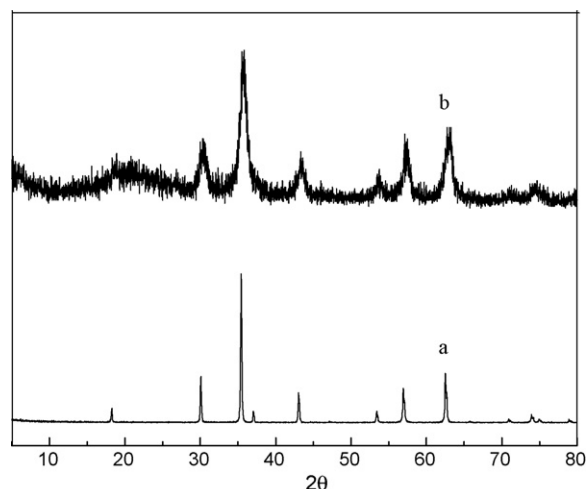

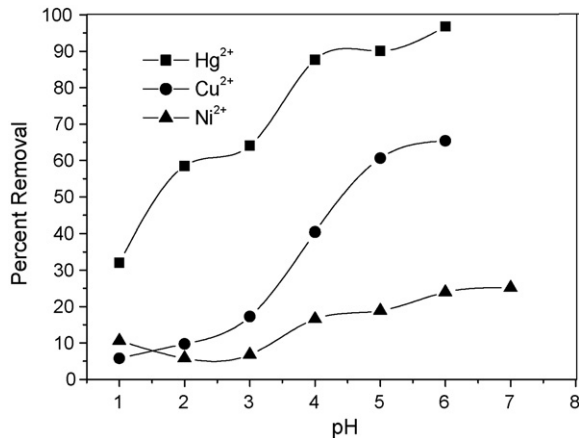**Fig. 2.** XRD patterns of pure Fe_3O_4 (a) and TMCS (b).

Fig. 3. Effect of pH on the uptake of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions by TMCS (initial concentration 100 mg/L; TMCS 1.5 g/L; contact time 8 h; shaking rate 150 rpm, 28 °C).

3.2. Effect of pH on metal ion adsorption and the zeta potential

The pH values selected in the experiments were prior to the precipitation limit of each metal ion (pH 6, 6, and 7 for Hg^{2+}, Cu^{2+}, and Ni^{2+}, respectively). As shown in Fig. 3, the higher uptake capacity was achieved at higher pH values. The observed lower uptake in an acidic medium may be attributed to the partial protonation of the active groups and the competition of H$^+$ with metal ions for adsorption sites on the TMCS. At pH < 2, no appreciable uptake was detected for Cu^{2+} and Ni^{2+} ions. The results indicate that the adsorption percent of Hg^{2+} is higher than Cu^{2+} and Ni^{2+} ions in all pH ranges studied, suggesting possible selectivity for this metal.

After adsorption of the metal ions for 8 h at low pH (pH 1–3), 0.8–1.5 wt.% of Fe$_3$O$_4$ particles on TMCS were dissolved in the acid solution. The results of thermogravimetric tests showed that the average mass content of Fe$_3$O$_4$ on TMCS decreased from 32.0% before adsorption to 31.2–30.5% (pH 1–3) after adsorption. TMCS is almost insoluble in acidic and alkaline mediums. No obvious leakage of resin materials and change of TMCS was observed in the experimental process. TMCS becomes more resistant to lower pH compared to their parent chitosan due to the cross-linking reaction in the preparation process.

The effect of pH values on the zeta potential of TMCS microspheres was plotted in Fig. 4. As shown in Fig. 4, the zeta potential of TMCS microspheres decreased as the pH
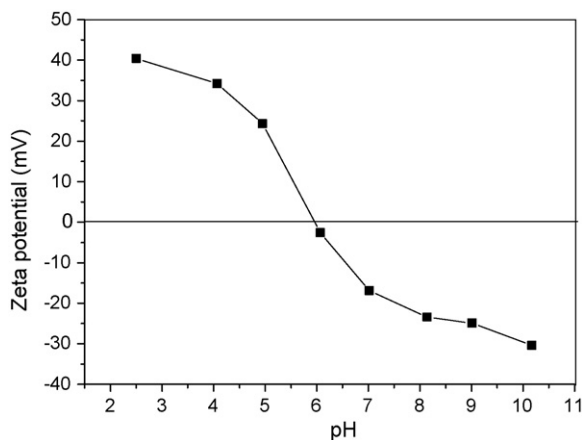
value increased. The isoelectric point (pI) of the TMCS was approximately 5.92. This revealed that the TMCS microspheres were positively charged at pH < 5.92 and negatively charged at pH > 5.92.

3.3. Effect of the temperature on the uptake

As shown in Fig. 5(a), the adsorption capacity of the metal ions decreased with increasing temperature. The might be due to the fact that the interaction between the metal ions and the active groups of TMCS was lower at higher temperatures. The magnitude of the heat of adsorption can provide useful information concerning the nature of the surface and the adsorbed phase. The heat of adsorption determined at constant amounts of sorbate adsorbed is known as the isosteric heat of adsorption (ΔH_x) and is calculated using Clausius–Clapeyron equation [21]:

$$\Delta H_x = R \left[\frac{d(\ln C_e)}{d(1/T)} \right] \tag{1}$$

where R is molar gas constant (8.314 J/mol K). For this purpose, the equilibrium concentration (C_e) at constant amount of the adsorbed metal ions is obtained from the adsorption data at different temperatures. ΔH_x is calculated from the slope of the $\ln C_e$ versus $1/T$, as shown in Fig. 5(b). The calculated enthalpy changes are −46.19, −12.67, and −2.45 kJ/mol for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions, respectively, indicating that the adsorption process was exothermic in nature.

Fig. 4. Effect of pH values on the zeta potential of TMCS microspheres.
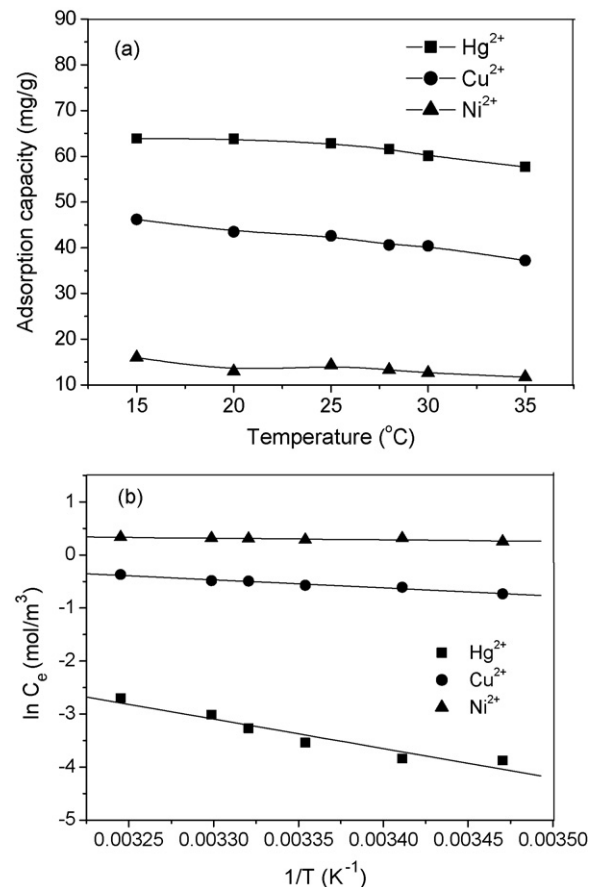
Fig. 5. (a) Effect of temperature on the uptake of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions by TMCS (initial concentration 100 mg/L, TMCS 1.5 g/L, pH 5.0, contact time 8 h, shaking rate 150 rpm, 15–35 °C) and (b) the plot of $\ln C_e$ against $1/T$.

3.4. Adsorption kinetics

Fig. 6 shows the kinetics of the adsorption of metal ions Hg^{2+}, Cu^{2+}, and Ni^{2+} by TMCS. Inspection of the uptake–time curves, it shows that the maximum uptake follows the order $Hg^{2+} > Cu^{2+} > Ni^{2+}$ at all time intervals. The kinetic curve for Hg^{2+} ions showed that the adsorption was initially rapid, and reached equilibrium after approximately 180 min. Cu^{2+} ions adsorption reached equilibrium in 250 min, and remained constant until the end of the experiment. Ni^{2+} ions adsorption showed the slowest kinetic profile of all, reaching equilibrium at approximately 350 min.

In order to evaluate the kinetic mechanism that controls the adsorption process, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models shown as Eqs. (2)–(5) were employed to interpret the experimental data [22–23]. A good correlation of the kinetic data explains the adsorption mechanism of the metal ions on the solid phase [24].

The pseudo-first-order equation was represented by

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \tag{2}$$

where k_1 (min^{-1}) is the pseudo-first-order adsorption rate constant, q_t is the amount adsorbed at time t (min), and q_e denotes the amount adsorbed at equilibrium, both in mg/g.

The pseudo-second-order equation can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where k_2 (g/(mg min)) is the adsorption rate constant of pseudo-second-order.

The linear form of the intra-particle diffusion equation is given by

$$\ln q_e = \ln k_p + \left(\frac{1}{2}\right) \ln t \tag{4}$$

where k_p (mg/(g min$^{1/2}$)) is the intra-particle diffusion rate constant.

The initial adsorption rate (h) can be determined from k_2 and q_e values [22] using

$$h = k_2 q_e^2 \tag{5}$$

The kinetic parameters for adsorption of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions by TMCS are given in Table 1. The experimental q_e values are in agreement with the calculated values using pseudo-first-order
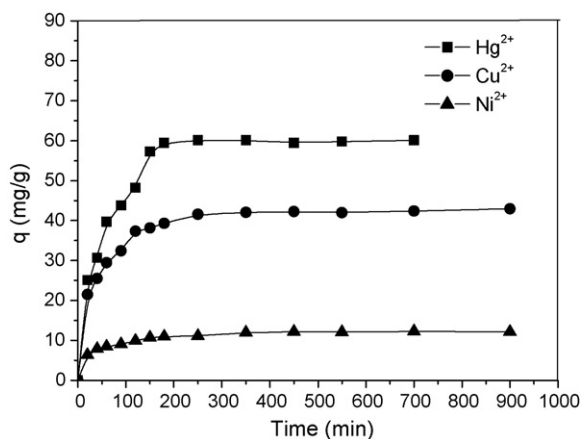

Fig. 6. Effect of contact time on the uptake of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions by TMCS (initial concentration 100 mg/L; TMCS 1.5 g/L; pH 5.0; shaking rate 150 rpm, 28 °C).

Table 1
Kinetic parameters for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions adsorption by TMCS

Metals	First-order model		
	k_1 (min^{-1})	q_1 (mg/g)	R^2
Hg^{2+}	33.75	64.10	0.9539
Cu^{2+}	22.35	43.29	0.9580
Ni^{2+}	19.55	12.05	0.9504

Metals	Second-order model			
	k_2 (g/(mg min))	q_2 (mg/g)	h (mg/(g min))	R^2
Hg^{2+}	5.55×10^{-4}	62.50	2.17	0.9975
Cu^{2+}	1.08×10^{-3}	43.67	2.06	0.9996
Ni^{2+}	2.93×10^{-3}	12.64	0.47	0.9994

Metals	Inter-particle model	
	k_p (mg/(g min$^{1/2}$))	R^2
Hg^{2+}	13.61	0.8469
Cu^{2+}	15.17	0.8356
Ni^{2+}	4.19	0.9227

and pseudo-second-order kinetics, which does not happen with the intra-particle diffusion kinetic equation. This indicates that an intra-particle diffusion is not the rate-controlling step. Based on the obtained correlation coefficients, the pseudo-second-order equation was the model that furthered the best fit for the experimental kinetic data, suggesting chemical sorption as the rate-limiting step of the adsorption mechanism and no involvement of a mass transfer in solution [22–24]. The adsorption of the investigated metal ions onto TMCS may be considered to consist of two processes with initial adsorption rate of 2.17, 2.06, and 0.47 mg/(g min) for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions, respectively.

TMCS is characterized by its high percentage of nitrogen and sulfur, present in the form of amine and sulfur groups that are responsible for metal ion binding through chelation mechanisms. Amine and sulfur sites are the main reactive groups for metal ions though hydroxyl groups, especially in the C-3 position, and they may contribute to adsorption [15,25]. However, TMCS is positively charged with a pI of 5.92. Therefore, in acidic solutions it is protonated and possesses electrostatic properties. Thus, it is also possible to adsorb metal ions through anion exchange mechanisms [26]. Physical adsorption plays little role in the interaction between TMCS and the metal ions because TMCS microspheres have a small surface area (62.3 m^2/g). Polysaccharides are, in general, nonporous and their derivatives possess a low surface area. Chitosan has a very low specific area ranging between 2 and 30 m^2/g. However, most commercial activated carbons have a specific area of the order of 800–1500 m^2/g [27].

The rate constant for Hg^{2+} ions was higher than the values found for Cu^{2+} and Ni^{2+} ions, which is seen on the kinetic curve. The pseudo-second-order kinetic model also provided the best correlation of the experimental data in the studies carried out by Atia et al. [28] on adsorption of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions onto Co_3O_4-containing resin, by Sag and Aktay [29] on adsorption of Cr^{6+} and Cu^{2+} ions onto chitosan, and by Wu et al. [24] on adsorption of Cu^{2+} ions onto chitosan in the presence of complexing agents. The adsorption of Cd^{2+} and Ni^{2+} ions by activated carbons developed from a biosource in the study carried out by Basso et al. [3] also was best described by the pseudo-second-order model, in agreement with the kinetic results found in our study with TMCS for these metals.

3.5. Adsorption isotherms

Fig. 7 shows the adsorption equilibrium isotherms obtained for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions by TMCS. A relationship was observed between the amount of metal ion adsorbed on the adsorbent surface and the remaining metal ion concentration in the aqueous phase at equilibrium. It was shown that the adsorption capacity increased with the equilibrium concentration of the metal ion in solution, progressively saturating the adsorbent. For interpretation of the adsorption data, the Langmuir [30], Freundlich [31], and Tempkin and Pyzhev [32] isotherm models were used.

The linear form of the Langmuir isotherm is given by

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{6}$$

where q_e and C_e are the amount adsorbed (mg/g) and the adsorbate concentration in solution (mg/L), both at equilibrium. K_L (L/g) is the Langmuir constant and q_m (g/mg) is the maximum adsorption capacity for monolayer formation on adsorbent.

The Freundlich equation is given by

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{7}$$

where both K_F and n are constants.

The Tempkin isotherm has been used in the following form [32]:

$$q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C_e \tag{8}$$

where

$$B = \frac{RT}{b} \tag{9}$$

A plot of q_e versus $\ln C_e$ enables the determination of the constants A and B. The constant B is related to the heat of adsorption.

The results obtained from adsorption isotherms for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions by TMCS are shown in Table 2. For the three studied systems, the Langmuir isotherm correlated better ($R^2 > 0.989$) than Freundlich and Tempkin isotherm with the experimental data from adsorption equilibrium of metal ions by TMCS, suggested a monolayer adsorption. The maximum adsorption values were 625.2, 66.7, and 15.3 mg/g for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions, respectively, which are in good accordance with experimentally obtained values.

The maximum adsorption capacity (q_m) obtained by Langmuir isotherm for Hg^{2+} was higher than the values found for Cu^{2+} and Ni^{2+}, showing the following capacity order: $Hg^{2+} > Cu^{2+} > Ni^{2+}$. Denizli et al. [33] reported the adsorption selectivity order of

Table 2
Parameters for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions adsorption by TMCS according to different equilibrium models

Metals	Langmuir isotherm constants		
	K_L (L/g)	q_m (mg/g)	R^2
Hg^{2+}	8.0×10^{-3}	625.2	0.9896
Cu^{2+}	2.7×10^{-2}	66.7	0.9893
Ni^{2+}	2.4×10^{-2}	15.3	0.9903
Metals	Freundlich isotherm constants		
	K_F	n	R^2
Hg^{2+}	12.39	1.60	0.9538
Cu^{2+}	1.38	2.31	0.9145
Ni^{2+}	6.11	2.33	0.9145
Metals	Tempkin isotherm constants		
	A	B	R^2
Hg^{2+}	1.01	110.94	0.9476
Cu^{2+}	1.08	12.34	0.9198
Ni^{2+}	1.33	3.52	0.9523

$Hg^{2+} > Cu^{2+} > Ni^{2+}$ using different chelating resins, which was in agreement with the order observed in this study. A high adsorption affinity for Hg^{2+} is expected, especially due to the involvement of the sulfur group. Mercury is characterized as a "soft" Lewis acid due to its high polarizability. It forms strong covalent bonds with "soft" Lewis bases, notably with reduced sulfur. The higher affinity for Cu^{2+} than that of Ni^{2+} may be attributed to Jahn–Teller effect which is predominant for copper complexes [33].

Atia et al. [28] reported maximum adsorption capacities (q_m) of 454, 143, and 76 mg/g for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions, respectively, using ehylenediamine-modified Co_3O_4-containing resin. Other authors have reported q_m values of 334, 27, and 20 mg/g for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions, respectively, using different synthetic chelating resins; and 234, 35, and 25 mg/g for Hg^{2+}, Cu^{2+}, and Ni^{2+} ions, respectively, using Dowex-50×-100 with –SO_3H functionality [33]. In terms of total capacity, our modified magnetic chitosan microspheres (TMCS) displayed magnetic properties along with higher efficiency in the removal of Hg^{2+}, due to the high affinity of the sulfur group and Hg^{2+} to form stable complexes. The q_m values of the unmodified magnetic chitosan microspheres for Hg^{2+}, Cu^{2+}, and Ni^{2+} are 412.1, 38.2, and 8.7 mg/g, respectively, which are lower than those of TMCS. These results indicated that chemical modification of magnetic chitosan with thiourea improved the adsorption capacity for the investigated metal ions, especially for Hg^{2+} and Cu^{2+} ions.

3.6. Desorption characteristics

As shown in Table 3, the desorption ratio of metal ions using 0.1 M EDTA was 94.5, 96.7, and 95.5% for Hg^{2+}, Cu^{2+}, and Ni^{2+}, respectively. The desorption ratio of metal ions increased as EDTA concentration increased. However, the desorption ratio of the
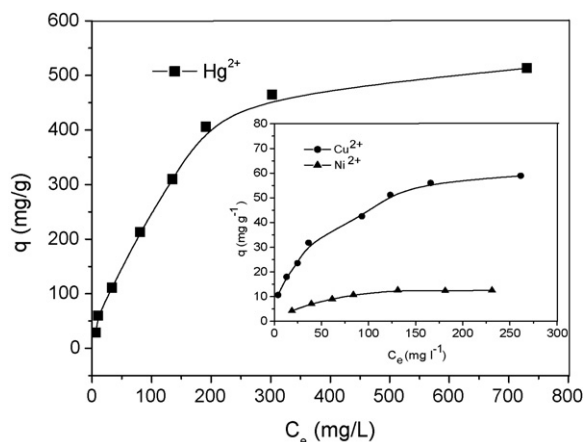

Fig. 7. Adsorption isotherms of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions by TMCS (initial concentration: Hg^{2+} 50–1500 mg/L; Cu^{2+} 25–350 mg/L; Ni^{2+} 25–250 mg/L; TMCS 1.5 g/L; pH 5.0; contact time 8 h; shaking rate 150 rpm, 28 °C).

Table 3
Desorption ratio of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions for various concentration of EDTA

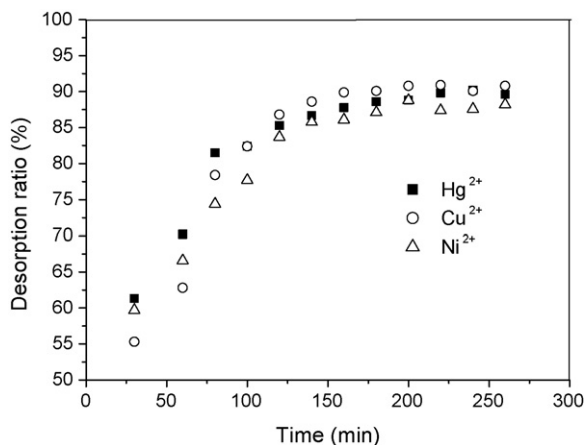| Concentration of EDTA (M)	Desorption ratio (%)		
	Hg^{2+}	Cu^{2+}	Ni^{2+}
0.1	94.5	96.7	95.5
0.05	91.8	93.6	92.5
0.01	89.6	90.8	88.2
0.005	74.8	78.4	81.1
0.001	52.2	48.8	60.1

Fig. 8. Desorption ratio of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions respect to time using 0.01 M EDTA.

investigated ions was more than 88% and was almost the same in the range over 0.01 M of EDTA concentration. Therefore, the best concentration of EDTA was determined to be 0.01 M for economical process. As shown in Fig. 8, desorption ratio of mercury ions increased over time. It was generally reported that most desorption processes finished within 180 min [18]. In the case of this study, it almost completed within 160 min, indicating a fast desorption process. The adsorption capacity of the TMCS could still be maintained at 90% level at the 5th cycle, as shown in Table 4. These results indicated that no appreciable loss in activity over at least five cycles.

3.7. Reactor configuration and magnetic particle separation

There have been several magnetic separation approaches performed under magnetic field [34,35]. The most well known technique is the liquid magnetically stabilized fluidized bed (MSFB). The MSFB combines of the best characteristics of both packed and fluidized bed. These include the efficient fluid–solid mass transfer, elimination of particle mixing, low pressure drop, high feed-stream solid tolerances, good fluid–solid contact, elimination of fouling and continuous countercurrent operation [9]. A schematic diagram of the liquid MSFB was described elsewhere [35]. Briefly, the bed center was positioned at the origin of the magnetic field. Liquid phase was supplied from the bottom inlet of the bed by a pump. Two permanent magnets were placed apart, and the field orientation was perpendicular to the flow. The intensity of the applied magnetic field could be adjusted by the distance between two permanent magnets. At a constant magnetic field intensity, the bed changed with increasing liquid velocity from the unfluidized bed to a stably fluidized bed. After adsorption, the adsorbent can be separated from the treated water by applying the magnetic field.

4. Conclusions

Magnetic chitosan microspheres modified with thiourea were obtained and characterized. Analysis indicated that the Fe_3O_4 particles were well dispersed in TMCS. The thiourea-modified chitosan magnetic microspheres showed greatly improved uptake properties of metal ions such as Hg^{2+}, Cu^{2+}, and Ni^{2+} ions compared to the unmodified ones, as well as previously reported synthetic ones. The higher affinity of Hg^{2+} and Cu^{2+} ions toward the resin was explained on the basis of soft acid nature of Hg^{2+} and Jahn–Teller effect for Cu^{2+} complexes, respectively. The adsorption kinetics followed the pseudo-second-order equation for all systems studied. The equilibrium data was well described by the Langmuir isotherm. Regeneration of TMCS obtained was achieved by using 0.01–0.1 M EDTA with efficiency of greater than 88%. Feasible improvements in the uptake properties along with the magnetic properties encourage efforts for TMCS obtained to be used in water and wastewater treatment.

Acknowledgements

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Table 4
Repeated adsorption of Hg^{2+}, Cu^{2+}, and Ni^{2+} ions by TMCS (adsorption conditions: initial concentration 100 mg/L, TMCS 1.5 g/L, pH 5.0, contact time 8 h, 150 rpm, 28 °C)

Cycle number	Adsorption capacity (mg/g)		
	Hg^{2+}	Cu^{2+}	Ni^{2+}
1	60.06	42.93	12.15
2	58.29	41.36	11.86
3	56.48	40.62	11.44
4	55.76	40.18	11.22
5	54.87	39.42	11.03

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