



Preparation of cross-linked magnetic chitosan-phenylthiourea resin for adsorption of Hg(II), Cd(II) and Zn(II) ions from aqueous solutions

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ABSTRACT

In this study, cross-linked magnetic chitosan-phenylthiourea (CSTU) resin were prepared and characterized by means of FTIR, ^1H NMR, SEM high-angle X-ray diffraction (XRD), magnetic properties and thermogravimetric analysis (TGA). The prepared resin were used to investigate the adsorption properties of Hg(II), Cd(II) and Zn(II) metal ions in an aqueous solution. The extent of adsorption was investigated as a function of pH and the metal ion removal reached maximum at pH 5.0. Also, the kinetic and thermodynamic parameters of the adsorption process were estimated. These data indicated that the adsorption process is exothermic and followed the pseudo-second-order kinetics. Equilibrium studies showed that the data of Hg(II), Cd(II) and Zn(II) adsorption followed the Langmuir model. The maximum adsorption capacities for Hg(II), Cd(II) and Zn(II) were estimated to be 135 ± 3 , 120 ± 1 and 52 ± 1 mg/g, which demonstrated the high adsorption efficiency of CSTU toward the studied metal ions.

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1. Introduction

Metal ions are among the most commonly encountered and difficult to treat environmental pollutants. Heavy metals have been continuously released into the environment due to rapid industrialization and have created a major global concern. Many toxic metals are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries [1,2]. A series of the most hazardous metals includes antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc. In general, an excess of heavy metals can drastically interfere in many beneficial uses of water due to their toxicity and to the biomagnification effects on ecology. Thus, the concentration of the toxic metals in usual water sources frequently needs a remediation operation [3–5]. There are many techniques for metal ions removal, such as chemical precipitation, ion exchange, membrane filtration, electrolytic methods and reverse osmosis [6–11]. However, these methods are limited

for high operational cost and inefficient in the removal of some heavy metal ions [12,13]. In contrast, the adsorption as an efficient method of metal ions removal has attracted a lot of interest for water treatment [14].

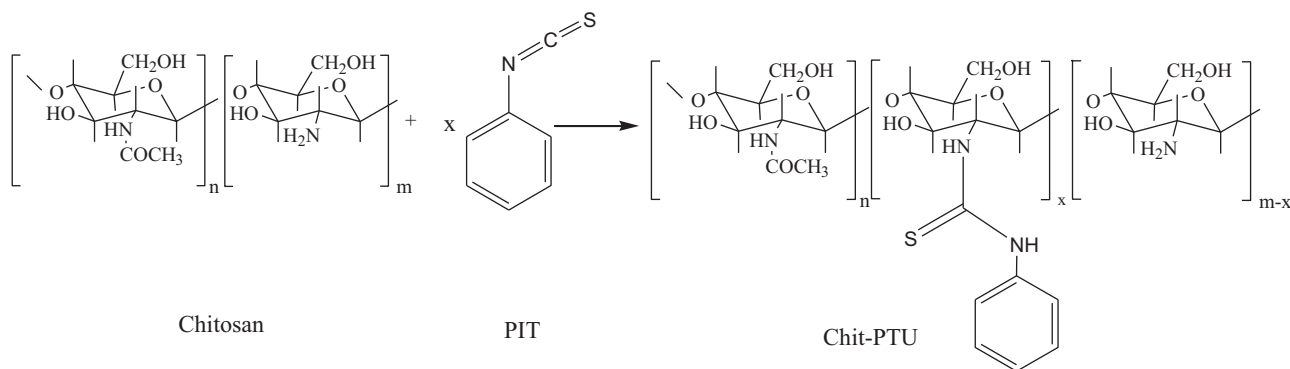
Chitosan has been reported to have high potential for adsorption of metal ions [15–19]. To improve its adsorption capacity and enhance the separation rate [20–24], the design and exploration of novel adsorbents are still necessary [25–27]. Recent research has been focused on the modification of chitosan for enhanced adsorption performance based on introducing chemical groups, like thiourea, isatin and diacetylmonoxime [28–31], which can offer more functional groups.

Chelating magnetic resins represent also an important category of promising adsorbents. They are highly selective, efficient and easily regenerable relative to other types of adsorbent [32], we reported on the use of chelating magnetic resins for the removal of some metal ions from aqueous solutions [30,31]. These magnetic resins is easily collected from aqueous media using an external magnetic field and displayed higher uptake capacity compared to the magnetic particles-free resin.

In this study cross-linked magnetic chitosan-phenylthiourea resin was prepared for the removal of Hg(II), Cd(II) and Zn(II) metal ions from aqueous solutions. The factors affecting the removal behavior were studied. Thermodynamic as well as kinetic properties of the removal process were also clarified.

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Scheme 1. Synthesis of chit-PTU.

2. Materials and methods

2.1. Materials

Chitosan (M.W. 1.79×10^6 amu) and degree of deacetylation 85% was prepared according to our previous study [33]. Phenylisothiocyanate (PIT), formaldehyde, HgCl_2 , CdCl_2 and ZnCl_2 were purchased from Sigma–Aldrich. All chemicals were used as received.

2.2. Preparation of chitosan beads

Chitosan (5 g) was dissolved in 1.0% aqueous acetic acid (250 mL). The chitosan solution was dropped through a syringe needle (1 mm in diameter) into a dilute aqueous NaOH solution, where the chitosan precipitated immediately to form gelatinous beads [31]. The chitosan particles were thoroughly washed with distilled water then with methanol.

2.3. Preparation of chitosan-phenylthiourea (chit-PTU)

The modification of chitosan with PIT was carried out via thioamide bond formation between the amino group in chitosan and the active isothiocyanate group of PIT as presented in Scheme 1. The methanol wet beads prepared in the previous step were suspended in 50 mL methanol, and 50 mL of PIT solution in methanol (100 g/L) was added. The reaction mixture was refluxed for 12 h. Then the product was isolated by filtration and thoroughly washed with methanol and distilled water. The quantitative determination of degree of substitution (DS) of the final modified chitosan was calculated using ^1H NMR spectra.

2.4. Preparation of cross-linked magnetic chitosan-phenylthiourea (CSTU) resin

Fe_3O_4 particles were prepared according to our previous work [31].

The preparation of cross-linked magnetic CSTU was carried out according to the following procedures; 5 g of the previously prepared chit-PTU was dissolved in 100 mL 1% acetic acid. 5 g of magnetite were suspended in 10 mL formaldehyde cross-linker which cross-links chitosan through the amino groups (Scheme 2). The latter suspension was gradually added to the chit-PTU solution. The contents were mechanically stirred with a mechanical stirrer at about 1000 rpm at room temperature. Ten minutes later, additional 5 mL formaldehyde was added. The gelatinous precipitate obtained was collected, dried in an oven at 60°C for 24 h and then washed thoroughly with hot water, 0.1 M NaOH solution, cold water, ethanol, acetone and then 0.1 M HCl.

Non-functionalized cross-linked magnetic chitosan (NCS) was prepared by the same procedure in the absence of PIT and treated in the same manner.

2.5. Characterization of samples

The surface morphologies of cross-linked CSTU resin samples were visualized using a FEI Quanta-200 scanning electron microscope (FEI Company, The Netherlands), operating at a typical accelerating voltage of 20 kV. The samples were sputter-coated with gold for 40 s at 15 mA prior to the observation.

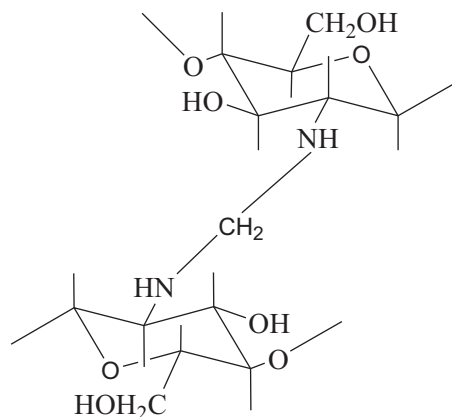
Infrared spectra (FTIR) were obtained with a Perkin-Elmer spectrometer. The chitosan and modified chitosan were dried overnight at 60°C under reduced pressure and pressurized with a glass slide on top of the quartz window of the ATR instrument.

^1H NMR spectra were recorded by an Oxford NMR instrument at 500 MHz at room temperature using 1% deuterated acetic acid in D_2O as a solvent.

Thermogravimetric analysis (TGA) was performed on chitosan and modified chitosan by using a DuPont-2000 instrument. Experiments were performed with 2–3 mg of the sample under a dynamic nitrogen atmosphere flowing at a rate of 50 mL/min and at a heating rate of $10^\circ\text{C}/\text{min}$.

High angle X-ray diffraction (XRD) patterns were recorded on X-ray diffractometer (D/Max2500VB2+/Pc, Rigaku, Japan) with $\text{Cu K}\alpha$ characteristic radiation (wavelength $\lambda = 0.154$ nm) at a voltage of 40 kV and a current of 50 mA. The scanning rate was $5^\circ/\text{min}$ and the scanning scope of 2θ was from 5° to 80° at room temperature.

A vibrating-sample magnetometer (VSM) (EG & G Princeton Applied Research Vibrating Sample Magnetometer, Model 155,



Scheme 2. Cross-linked chitosan by formaldehyde [34].

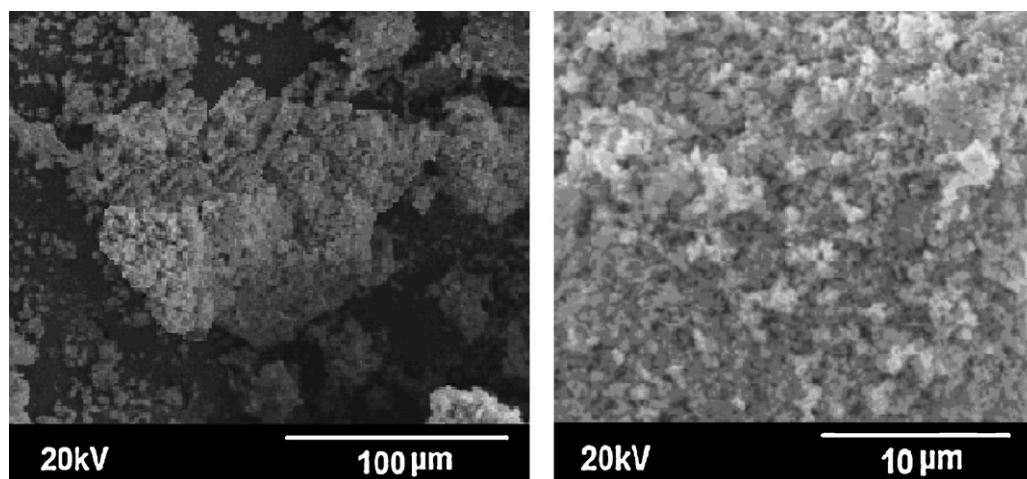


Fig. 1. The SEM photographs of CSTU resin.

USA) was used at room temperature to characterize the magnetic properties of cross-linked magnetic CSTU resin.

2.6. Metal ion uptake experiments using batch method

2.6.1. Instrumentation

A Perkin-Elmer Model 5000 atomic absorption spectrometer (Perkin-Elmer, Shelton, CT-USA) fitted with a Cadmium and Zinc hollow cathode lamps was used. The instrument was set at 228.8 nm for cadmium and 213.8 nm for zinc. For mercury, a Perkin-Elmer Model 4100ZL atomic absorption spectrometer was used equipped with a Perkin-Elmer FIAS-400 flow injection system and an AS-90 autosampler. A Perkin-Elmer mercury electrodeless discharge lamp was operated at 180 mA. The mercury absorbance was measured at 253.6 nm with a 0.7 nm spectral bandpass.

2.6.2. Effect of functionalization

Uptake experiments were performed by placing 0.03 g of dry CSTU and NCS resin in a series of flasks containing 30 mL (100 mg/L) of the metal ion solution at pH 5.0. The flasks were agitated on a shaker at 150 rpm for 3 h while keeping the temperature at 30 °C.

2.6.3. Effect of pH

Uptake experiments were performed at controlled pH and 30 °C by shaking 0.03 g of dry cross-linked magnetic CSTU with 30 mL (100 mg/L) metal ion solution for 3 h at 150 rpm. The buffer solutions used for adjusting the pH of the medium were KCl/HCl (pH 1, 2, and 3) and acetic acid/sodium acetate (pH 4 and 5).

2.6.4. Effect of the temperature

Uptake experiments were performed by placing 0.03 g of dry cross-linked magnetic CSTU in a series of flasks containing 30 mL (30 mg/L) of the metal ion solution at pH 5.0. The flasks were agitated on a shaker at 150 rpm for 3 h while keeping the temperature at 20, 30 or 40 °C. After adsorption, solution was filtered and the residual concentration of the metal ions was determined.

2.6.5. Effect of contact time

Measurements of metal ion uptake using a batch method were conducted by placing 0.3 g of dry cross-linked magnetic CSTU in a flask containing 300 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 30 °C. Samples were taken at time intervals for the analysis of residual metal concentration in solution.

2.6.6. Effect of the initial concentration of the metal ions

The effect of initial concentration of the metal ion on the uptake by CSTU obtained was carried out by placing 0.03 g of dry cross-linked magnetic CSTU in a series of flasks containing 30 mL of metal ions at definite concentrations (10–400 mg/L) and pH 5.0. The contents of the flasks were equilibrated on the shaker at 150 rpm and 30 °C for 8 h. After adsorption, the residual concentration of the metal ions was determined.

2.6.7. Adsorption experiments for multiple-metal system

To determine the adsorption characteristics of CSTU resin adsorbents in binary and ternary metal mixture, the initial concentration of each metal ion in the mixture was 100 mg/L. All the experiments for the multiple-metal system were conducted at pH 5.0, temperature 30 °C, and adsorbent dose 1 g/L for 3 h.

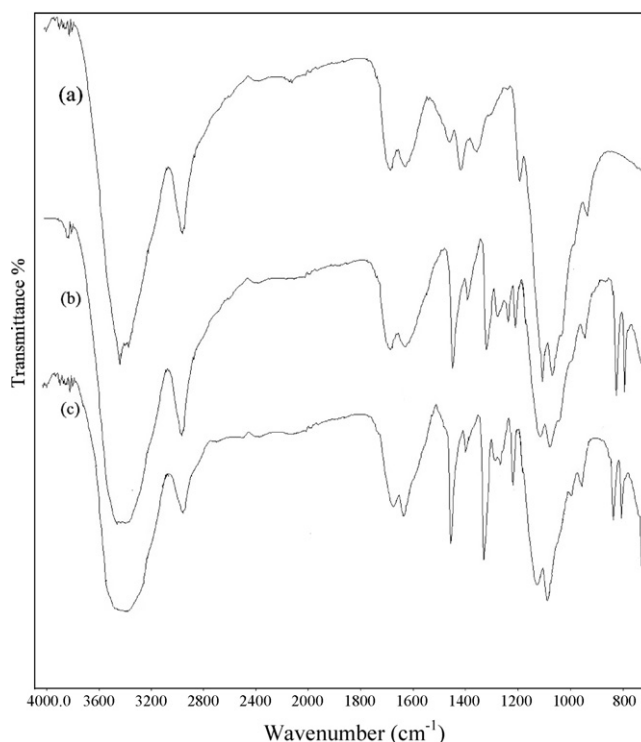


Fig. 2. FTIR spectra of: (a) chitosan, (b) chit-PTU, and (c) cross-linked CSTU.

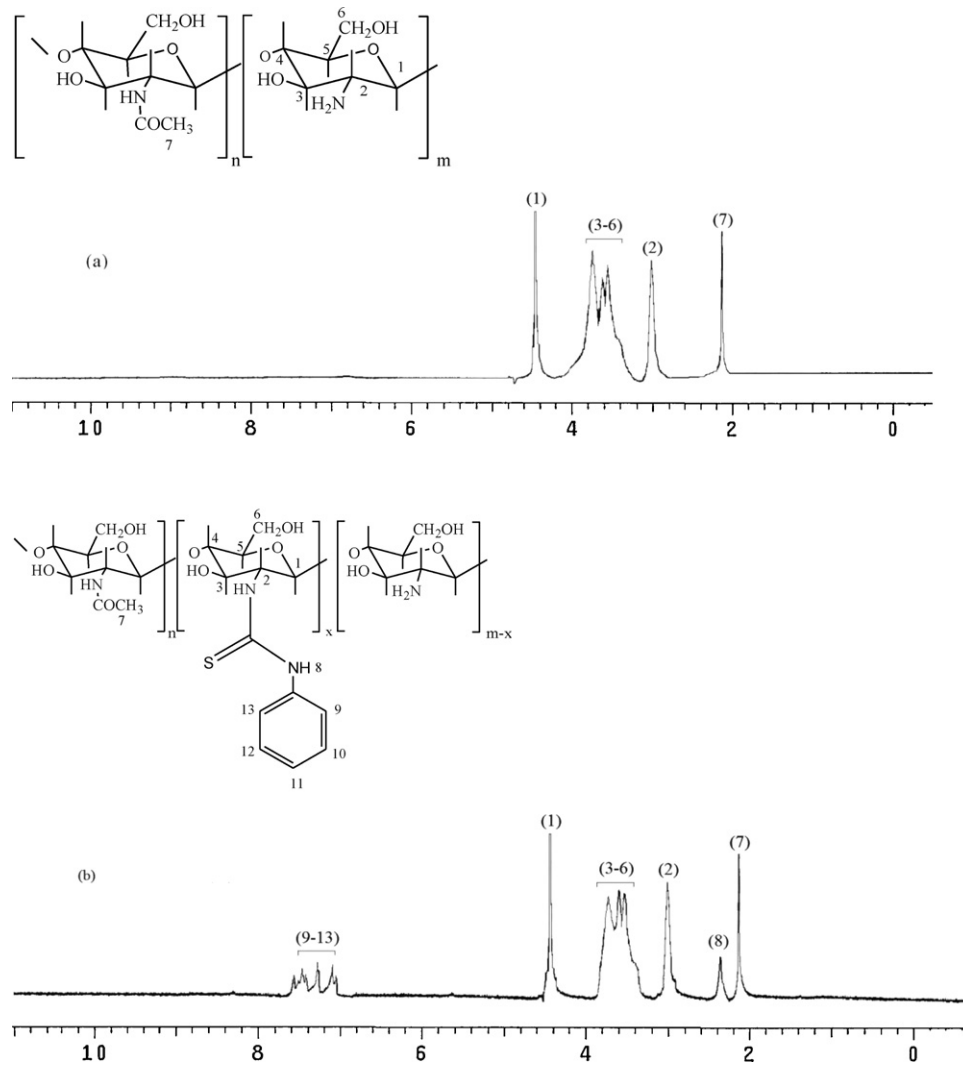


Fig. 3. ^1H NMR spectra of: (a) chitosan and (b) modified chit-PTU with $\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ as solvent.

In all of the above experiments, the adsorption values were calculated from the change in solution concentration using the following equation:

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

where q_e (mg/g) is the adsorption capacity; C_i (mg/L) and C_e (mg/L) are the initial and equilibrated metal ion concentrations, respectively, V (L) is the volume of added solution and W (g) is the mass of the adsorbent (dry).

$$\text{Percent removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

2.6.8. Desorption experiments

For desorption studies, 0.1 g of cross-linked magnetic CSTU was loaded with metal ions (Hg^{2+} , Cd^{2+} and Zn^{2+}) using 100 mL (100 mg/L) metal ion solution at 30°C , pH 5.0 and contact time of 3 h. The agitation rate was fixed as 150 rpm. Metal ion-loaded CSTU were collected, and gently washed with distilled water to remove any unabsorbed metal ions. The resin was then agitated with 100 mL of EDTA or 100 mL HCl. 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 CSTU was calculated from the amount of metal ions adsorbed on CSTU and the final concentration of metal ions

in the desorption medium. To test the reusability of the resin, this adsorption–desorption cycle was repeated five times by using the same affinity adsorbent. The desorption percentage ($D\%$) was calculated as Eq. (3).

$$D\% = \left(\frac{C_{\text{EDTA}}}{C_{\text{ad}}} \right) \times 100 \quad (3)$$

where C_{EDTA} is the metal ion desorbed to the EDTA solution (mg/L) and C_{ad} is the metal ion adsorbed onto the resin (mg/L).

3. Results and discussion

3.1. Characterization of the polymer

The SEM images of the CSTU are shown in Fig. 1. From Fig. 1 irregular image and porous surface could be observed. On the basis of this fact, it can be concluded that the adsorbent present an adequate morphology for the metal ion adsorption. The particle size was evaluated using optical micrographs. The related results show that the mean diameter of the particles was $130 \mu\text{m}$.

The FTIR spectra of chitosan, chit-PTU and cross-linked CSTU resin are shown in (Fig. 2a–c).

The main bands observed in the IR spectra of the chitosan, Fig. 2a, were in accordance with previous report [31,32]. The IR spectra of the chit-PTU biopolymer, Fig. 2b, presented a strong absorption

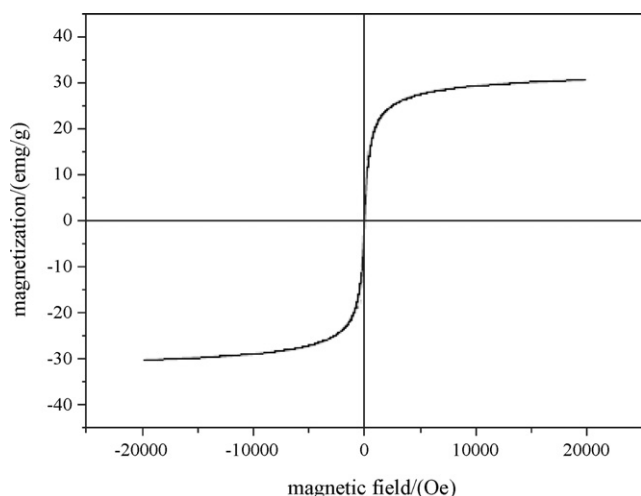


Fig. 4. VSM magnetization curves of cross-linked magnetic CSTU.

bands at 1377, 1577, 1264 and 760 cm^{-1} which are attributed to the C–N, C=C, C=S, and C–H of the inserted aromatic moieties, respectively [32].

In addition, the IR spectra of the cross-linked CSTU resin (Fig. 2c) did not show a significant change from that of chit-PTU, just an increase in the intensity of the sharp peak at 1377 cm^{-1} which may be due to the stretching of C–N bond formed between the remained free amino groups of chitosan and formaldehyde cross-linker. Similar observations were reported [34].

The ^1H NMR spectra of chitosan and chit-PTU in D_3C COOD/ D_2O were shown in Fig. 3. The spectrum of chitosan (Fig. 3a) shows a small signal at about δ 2.03 ppm assigned to the presence of $-\text{CH}_3$ of the *N*-acetylated glucosamine residue. The signal at δ 3.08 ppm was assigned to H^2 of glucosamine and *N*-acetylated glucosamine, and the multiplet signal from δ 3.6 to 3.9 ppm were attributed to H^3 , H^4 , H^5 , and H^6 of glucosamine and *N*-acetylated glucosamine. There existed a signal at about δ 4.78 ppm because of the presence of H^1 of glucosamine and *N*-acetylated glucosamine [35].

The ^1H NMR spectra of chit-PTU is presented (Fig. 3b). The spectrum confirms incorporation of the phenylthiourea units by the presence of amidic proton peaks at δ 2.30 ppm, aromatic proton peaks at about δ 7.58 ppm which are characteristic for monosubstituted benzene derivatives. The DS determined by comparing the integrated intensity of the aromatic or amidic peaks of the inserted phenylthiourea units to the integral intensity of the H^2 of glucosamine and *N*-acetylated glucosamine was estimated to be 58%.

According to mercury porosimetry data, the average pore size of the magnetic resin was 860 nm. The BET surface area for cross-linked CSTU was 64.5 m^2/g .

The thermogravimetric analysis (TGA) results showed that the principle chains of cross-linked CSTU began to degrade at about 230 $^\circ\text{C}$ and the final temperature of decomposition was approximately 670 $^\circ\text{C}$. The average mass content of Fe_3O_4 on cross-linked magnetic CSTU was estimated to be about 35%.

The magnetization measurement performed with VSM (Fig. 4) indicated that the saturation magnetization of the magnetic particles was 30.5 emu/g. As mentioned in a previous report, this magnetic susceptibility value is sufficient for this adsorbent to be used in wastewater treatment [32].

XRD patterns of pure Fe_3O_4 , CSTU and magnetic CSTU are shown in Fig. 5, indicating the existence of iron oxide particles (Fe_3O_4), which has magnetic properties and can be used for the magnetic separation. The XRD analysis results of pure Fe_3O_4 and cross-linked magnetic CSTU were mostly coincident. Six characteristic peaks for

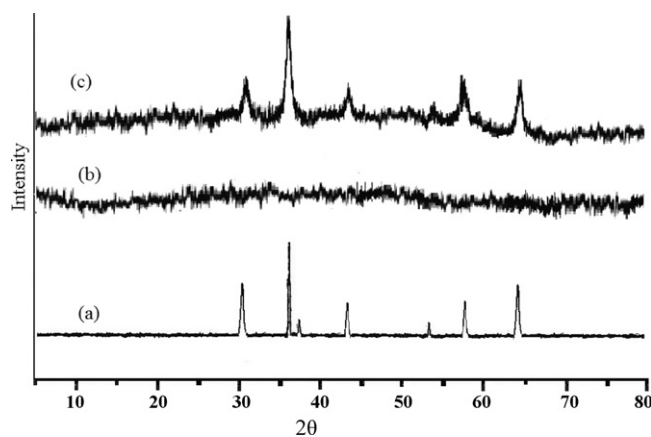


Fig. 5. XRD patterns of: (a) pure Fe_3O_4 , (b) cross-linked chit-PTU, and (c) cross-linked magnetic CSTU (2).

Fe_3O_4 ($2\theta = 30.1^\circ$, 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 three samples.

3.2. Metal ions uptake studies

3.2.1. Effect of functionalization

The potential of the modified (CSTU) and unmodified (NCS) chelating magnetic resins for removal of Hg^{2+} , Cd^{2+} and Zn^{2+} ions was evaluated and the results were presented in Table 1. As can be seen, the percent removal of the three metal ions Hg^{2+} , Cd^{2+} and Zn^{2+} showed an obvious increase in case of functionalized CSTU resin this of course could be attributed to the higher availability of the active groups of the inserted phenylthiourea moieties which are able to chelate the metal cations. These results confirmed that the modification of the cross-linked chitosan resin by incorporation of PTU moieties greatly improves the metal uptake properties of chitosan.

3.2.2. Effect of pH

The pH of the metal ion solution plays an important role in the whole adsorption process and particularly on the adsorption capacity by the modification of the level of ionization of chitosan derivatives [20]. Fig. 6 showed the effect of solution pH on the percent removal of CSTU magnetic resin for Hg^{2+} , Cd^{2+} and Zn^{2+} .

It can be seen from Fig. 6 that the amount of M^{2+} adsorbed by CSTU magnetic resin significantly increased when pH of M^{2+} solution increased from 1 to 5, the optimum adsorption pH being located at 5. At low pH, most of the functional groups such as $-\text{NH}-$, $-\text{OH}$ and $\text{C}=\text{S}$ in the resin were protonated and presented in the positively charged form, electrostatic repulsion between M^{2+} and the positively charged groups may prevent the adsorption of M^{2+} ions onto the resin. According to our control experiment, at $\text{pH} > 5$ the M^{2+} retention decreased because small amount of M^{2+} started to deposit as $\text{M}(\text{OH})_2$. This also supports the chelation of M^{2+} on the CSTU magnetic resin. Considering the formation of $\text{M}(\text{OH})_2$ when the pH value of M^{2+} solution exceeds 5, the pH of 5 was selected

Table 1

Effect of the degree of functionalization on the percent removal of Hg^{2+} , Cd^{2+} and Zn^{2+} .

Resin	Percent removal (%)		
	Hg^{2+}	Cd^{2+}	Zn^{2+}
NCS	33	24	11
CSTU	83	78	52

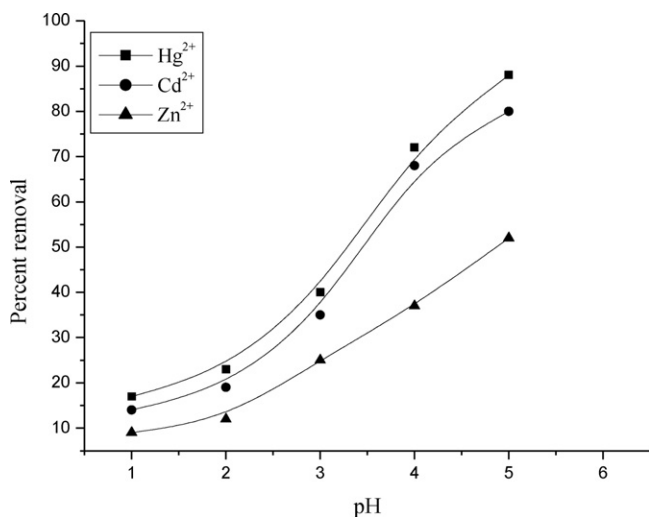


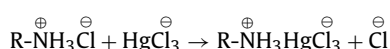
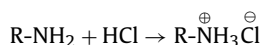
Fig. 6. Effect of pH on the uptake of Hg²⁺, Cd²⁺, and Zn²⁺ ions by cross-linked magnetic CSTU (initial concentration 100 mg/L; cross-linked magnetic CSTU 1 g/L; contact time 3 h; shaking rate 150 rpm, 30 °C).

as the initial pH value of M²⁺ solution for the following adsorption experiments.

After adsorption of the metal ions for 3 h at low pH (pH 1–3), 1.2–2 wt.% of Fe₃O₄ particles in cross-linked CSTU were dissolved in the acid solution. The results of thermogravimetric tests showed that the average mass content of Fe₃O₄ on cross-linked CSTU decreased from 35% before adsorption to 33.8–33% (pH 1–3) after adsorption. This could be attributed to the partial swelling of the surfaces of the resin particles under this low pH values as a result of the protonation of the functional groups of chitosan derived resin material which permit partial diffusion of the acidic solution and hence, some of the embedded Fe₃O₄ particles will react with the HCl which was used to adjust the pH and dissolve as FeCl₂ and FeCl₃. Similar observations were reported [32]. The resistance of the cross-linked CSTU was tested against acidic and basic medium and the results indicated that there was no obvious leakage of resin materials or changes of the cross-linked CSTU were observed in the experimental process. Cross-linked CSTU becomes more resistant to lower pH compared to their parent chitosan due to the cross-linking reaction in the preparation process.

The mechanism through which the metal ions adsorbed on the CSTU resin may be attributed to the complex formation between metal ion and deprotonated thiol form of the PTU units as shown in Scheme 3 and was previously reported by Donia et al. [25].

The released H⁺ was detected by the marked depression of the pH of the solution at the end of reaction to pH 3. The abundant of H⁺ in the medium may leads to another type of interaction (ion exchange mechanism) through the protonation of the unsubstituted amino groups, and the formation of the mercury anions (HgCl₃⁻). This mechanism can be represented as follows [25]:



As the adsorption greatly reduced at low pH values, we can conclude that the adsorption mainly due to the chemical adsorption through the complexation between the metal ions and the deprotonated thiol form of the PTU units rather than the ion exchange mechanism. This could be attributed to the consumption of the majority of the -NH₂ during the functionalization with PTU units and cross-linking with formaldehyde cross-linker.

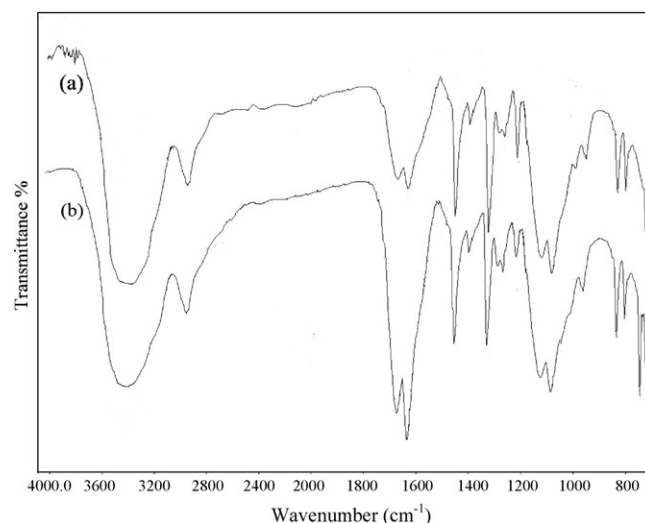


Fig. 7. FTIR spectra of cross-linked CSTU: (a) before Hg²⁺ adsorption and (b) after Hg²⁺ adsorption.

The FTIR spectra of the CSTU resin before and after adsorption of Hg²⁺ were presented in Fig. 7. The appearance of the strong peaks at about 1630 and 760 cm⁻¹ that correspond to C=N and C-S bonds respectively, confirm the adsorption through the complex formation mechanism.

3.2.3. Effect of temperature

To evaluate the thermodynamic parameters of the metal cation adsorption on the resin under study, the adsorption experiments were performed at three different temperatures (293, 303 and 313 K). 30 mL of the cation metal solution with a concentration of 30 mg/L was allowed to equilibrate with 0.03 g of resin. The equilibrium constant for the adsorption process, K_C , calculated with Eq. (4) [36,37], was evaluated at 293, 303 and 313 K for each metal cation (Table 2):

$$K_C = \frac{C_{ad}}{C_e} \quad (4)$$

where C_{ad} is the concentration of solute adsorbed on the resin at equilibrium (mg/L) and C_e is the equilibrium concentration of metal ion in the solution (mg/L).

To calculate the free energy of the adsorption (ΔG°_{ads}), the following equation was employed:

$$\Delta G^\circ_{ads} = -RT \ln K_C \quad (5)$$

Eq. (6), allows evaluating the standard enthalpy (ΔH°_{ads}) and entropy (ΔS°_{ads}) of the adsorption by plotting $\ln K_C$ vs. $1/T$.

$$\ln K_C = \frac{\Delta S^\circ_{ads}}{R} - \frac{\Delta H^\circ_{ads}}{RT} \quad (6)$$

where R (8.314 J mol⁻¹ K⁻¹) is the gas constant.

The values of the slope $-\Delta H^\circ_{ads}/R$ and the intercept $\Delta S^\circ_{ads}/R$ from Fig. 8 give ΔH°_{ads} and ΔS°_{ads} for the adsorption of Hg²⁺, Cd²⁺ and Zn²⁺ ions on the resin.

The values of the thermodynamic parameters (ΔG°_{ads} , ΔH°_{ads} , ΔS°_{ads}) were collected in Table 2.

As presented in Table 2, at all temperatures, the values of K_C arranged in the following order Hg²⁺ > Cd²⁺ > Zn²⁺ which indicate that the affinity of CSTU resin toward Hg²⁺ higher than that of Cd²⁺ and Zn²⁺. In addition, the negative values of ΔG°_{ads} for all ions under all conditions indicate the spontaneous nature of the adsorption. The negative ΔH°_{ads} and ΔS°_{ads} values means a chemical exothermic process accompanied by a lowering in the entropy due to the adsorption of the metal ions on the resin surface, which is

Table 3Kinetic parameters for Hg²⁺, Cd²⁺ and Zn²⁺ ions adsorption by cross-linked magnetic CSTU.

Metals	First-order model		
	k ₁ (min ⁻¹)	q _{e1} (mg/g)	R ²
Hg ²⁺	7.951	86 ± 4	0.9543
Cd ²⁺	7.543	81 ± 3	0.9254
Zn ²⁺	3.858	50 ± 2	0.9154
Metals	Second-order model		
	k ₂ (g/(mg min))	q _{e2} (mg/g)	R ²
Hg ²⁺	4.2 × 10 ⁻³	85 ± 3	0.9989
Cd ²⁺	3.6 × 10 ⁻³	78 ± 2	0.9987
Zn ²⁺	1.12 × 10 ⁻³	52 ± 1	0.9999

gradual adsorption stage where intraparticle diffusion controls the adsorption rate until finally the metal uptake reaches equilibrium.

In many cases, the pseudo-second-order kinetic model provided better results on the adsorption of Cu²⁺ on chitosan derivatives [28], Cu²⁺, Co²⁺ and Ni²⁺ on chemically modified chitosan [30], Hg²⁺, Cu²⁺ and Ni²⁺ ions on modified chitosan magnetic microspheres [24].

3.2.5. Adsorption isotherms

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between the adsorbate and adsorbent, and is important in the design of adsorption systems. For the adsorption isotherm studies, the initial metal ion concentrations are in the range of 10–400 mg/L. The expression for the Langmuir isotherm is:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_m} \right) + \left(\frac{C_e}{q_m} \right) \quad (9)$$

where q_e and C_e are the adsorption capacity (mg/g) and the equilibrium concentration of the adsorbate (mg/L), respectively, while q_m represents the maximum adsorption capacity of adsorbents (mg/g) and K_L is the Langmuir constant (L/mg) related to the affinity of binding sites and is a measure of the energy of adsorption. Langmuir isotherm assumes that the adsorption occurs at specific homogeneous adsorption sites within the adsorbent. Furthermore, it assumes monolayer adsorption and maximum adsorption occurs when adsorbed molecules on the surface of the adsorbent form a saturated layer. All adsorption sites involved are energetically identical and the intermolecular force decreases as the distance from the adsorption surface increases.

Different from Langmuir isotherm model, the Freundlich isotherm expresses adsorption at multilayer and on energetically heterogeneous surface which can be expressed as Eq. (10).

$$\ln q_e = \ln K_F + \left(\frac{1}{n} \right) \ln C_e \quad (10)$$

where K_F (mg/g) and n are the empirical constants those indicate the relative sorption capacity and sorption intensity, respectively. Temkin isotherm, which considers the effects of the heat of adsorption that, decreases linearly with coverage of the adsorbate and adsorbent interactions [30]. Temkin isotherm has been used in the form as follows:

$$q_e = \left(\frac{RT}{b} \right) \ln A + \left(\frac{RT}{b} \right) \ln C_e \quad (11)$$

where $B = RT/b$, and b is the Temkin constant related to heat of sorption (J mol⁻¹). A is the Temkin isotherm constant (L/mg), R is the gas constant (8.3145 J mol⁻¹ K⁻¹) and T is the absolute temperature (K). Therefore, plotting q_e vs. $\ln C_e$ enables one to determine the constants, A and B . Fig. 10 shows the adsorption equilibrium isotherms

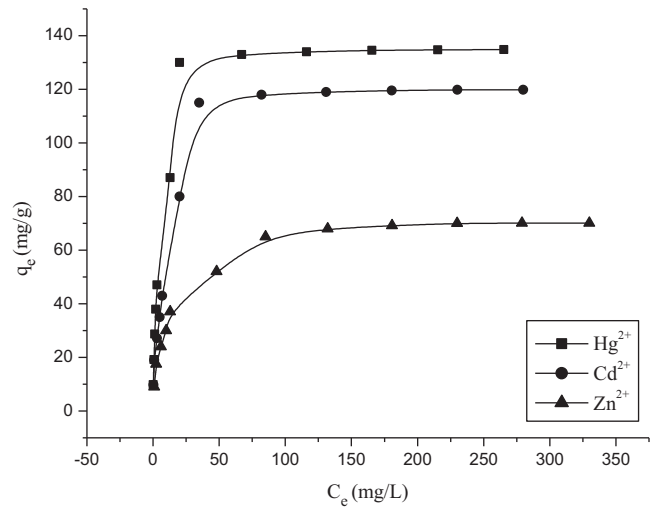


Fig. 10. Adsorption isotherms of Hg²⁺, Cd²⁺, and Zn²⁺ ions by cross-linked magnetic CSTU (initial concentration 10–400 mg/L, cross-linked magnetic CSTU 1 g/L, pH 5.0, shaking rate 150 rpm, 30 °C).

obtained for Hg²⁺, Cd²⁺, and Zn²⁺ ions by cross-linked magnetic CSTU.

The model parameters obtained by applying Langmuir, Freundlich and Temkin models to the experimental data are given in Table 4. From the better correlation coefficient and the fact that the equilibrium adsorption capacities (q_m) obtained from Langmuir model are close to the experimentally observed saturation capacities, it can be concluded that the monolayer Langmuir adsorption isotherm is more suitable to explain the adsorption of Hg²⁺, Cd²⁺ and Zn²⁺ onto CSTU magnetic resin.

The maximum adsorption capacity (q_m) obtained by Langmuir isotherm for Hg²⁺ was higher than the values found for Cd²⁺ and Zn²⁺, showing the following capacity order: Hg²⁺ > Cd²⁺ > Zn²⁺. Zhou et al. [24] and Denizli et al. [41] reported the adsorption selectivity order of Hg²⁺ > Cu²⁺ > Ni²⁺ using different chelating resins, which was in agreement with the order observed in this study. A high adsorption affinity for Hg²⁺ 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.

Table 4Parameters for Hg²⁺, Cd²⁺ and Zn²⁺ ions adsorption by cross-linked magnetic CSTU according to different equilibrium models.

Metals	Langmuir isotherm constants		
	K _L (L/mg)	q _m (mg/g)	R ²
Hg ²⁺	7.53 × 10 ⁻²	135 ± 3	0.9987
Cd ²⁺	7.04 × 10 ⁻²	120 ± 1	0.9989
Zn ²⁺	3.65 × 10 ⁻²	52 ± 1	0.9987
Metals	Freundlich isotherm constants		
	K _F (mg/g)	n	R ²
Hg ²⁺	21.831	6.451	0.8769
Cd ²⁺	17.875	5.874	0.9125
Zn ²⁺	8.654	2.345	0.8987
Metals	Temkin isotherm constant		
	ln A	b (J mol ⁻¹)	R ²
Hg ²⁺	0.235	152.1	0.9076
Cd ²⁺	2.011	287.3	0.8826
Zn ²⁺	1.873	252.2	0.8798

Table 5
Maximum adsorption capacities for the adsorption of Hg(II), Cd(II) and Zn(II) onto various bioadsorbents.

Adsorbent	Maximum adsorption capacity			Reference
	Hg ²⁺	Cd ²⁺	Zn ²⁺	
Rice straw	27.7	14.6	8.5	[2]
Ca-alginate	31.7	36.6	–	[3]
Modified wool chelating fibers	49.3	–	–	[4]
Chitosan-epichlorohydrin-triphosphate	–	83.7	–	[15]
Chitosan-ethylenediamine	341.2	–	–	[16]
Carboxymethyl-chitosan	280.8	–	130.8	[17]
Chitosan/polyvinyl alcohol	–	109.2	–	[18]
Modified magnetic chitosan	–	–	35.3	[19]
Present study	135.5	120.3	52.5	

Table 6
Competitive adsorption in binary and quaternary systems.

Metal system	Percent removal (%)		
	Hg ²⁺	Cd ²⁺	Zn ²⁺
Single	90.2	83.5	53.3
Hg ²⁺ + Cd ²⁺	81.4	63.1	–
Hg ²⁺ + Zn ²⁺	87.7	–	28.1
Cd ²⁺ + Zn ²⁺	–	80.3	22.6
Hg ²⁺ + Cd ²⁺ + Zn ²⁺	79.4	55.4	17.8

The maximum adsorption capacities (q_m) for Hg(II), Cd(II) and Zn(II) ion adsorption onto other modified bioadsorbents which were prepared under different conditions as reported in the literature, are compared in Table 5. It can be seen that the q_m value varies considerably for different adsorbents and that, by comparison, the CSTU system exhibits a good capacity to adsorb Hg(II), Cd(II) and Zn(II) ions from aqueous solutions.

The degree of suitability of resin toward metal ions was estimated from the values of separation factor constant (R_L) which gives indication for the possibility of the adsorption process to proceed. $R_L > 1.0$ unsuitable; $R_L = 1$ linear; $0 < R_L < 1$ suitable; $R_L = 0$ irreversible [16]. The value of R_L could be calculated from the relation

$$R_L = \frac{1}{1 + C_i K_L} \quad (12)$$

where K_L (L/mg) is the Langmuir equilibrium constant and C_i is the initial concentration of Hg(II), Cd(II) and Zn(II). The values of R_L lie between 0.032 and 0.211 for Hg(II), 0.034 and 0.220 for Cd(II), 0.064 and 0.352 for Zn(II) indicating that the adsorption of Hg(II), Cd(II) and Zn(II) on CSTU is favorable and useful for the removal of these metal ions.

3.2.6. Adsorption from multiple-metal system

The competitive adsorption was carried out in the binary system (Hg²⁺ + Cd²⁺, Hg²⁺ + Zn²⁺ and Cd²⁺ + Zn²⁺) and ternary system (Hg²⁺ + Cd²⁺ + Zn²⁺). The initial concentration of each metal ion in the mixed solution was 100 mg/L. The results were shown in Table 6. In binary system, the presence of Cd²⁺ slightly decrease the adsorption of Hg²⁺. On the other hand, presence of Zn²⁺ had

no obvious effect on adsorption of both Hg²⁺ and Cd²⁺ by CSTU resin. In ternary system, the obtained results were similar to the results obtained in the binary system; the adsorption of Hg²⁺ was not greatly affected by the presence of Cd²⁺ and Zn²⁺. When the three metals were present, CSTU resin adsorbed the heavy metals in the following order: Hg²⁺ > Cd²⁺ > Zn²⁺ which was the same affinity order in the single metal adsorption studies.

3.2.7. Regeneration of CSTU

For potential practical application, it is important to examine the possibility of desorbing the metal ions adsorbed on CSTU and reusing them. Both EDTA and HCl solutions were examined in the study for CSTU. The effect of five adsorption–desorption consecutive cycles on the efficiency of the individual adsorption of Hg²⁺, Cd²⁺ and Zn²⁺ on CSTU was studied. Table 7 shows the corresponding desorption efficiencies obtained at EDTA and HCl solutions. For desorption conducted with EDTA solution, it was found that the Hg²⁺, Cd²⁺ and Zn²⁺ adsorbed on CSTU were easily desorbed. The desorption efficiency reached about 99% after the first cycle. The desorbed CSTU was highly effective for the re-adsorption of Hg²⁺, Cd²⁺ and Zn²⁺, and the adsorption ability of CSTU was kept constant after several repetitions of the adsorption–desorption cycles. For desorption conducted with the HCl solution, the desorption efficiency reached about 93% after the first cycle which is lower than the EDTA solution. This may be attributed to the different mechanisms of the two reagents. EDTA can form steady complex with metal ions. However, the desorption took place in the HCl solution mainly due to the ion exchange. It can be concluded that EDTA is a better desorption solution than the HCl solution.

Table 7
Desorption efficiencies of Hg²⁺, Cd²⁺ and Zn²⁺ on CSTU from five adsorption–desorption cycles.

Cycle number	EDTA solution desorption percentage (%)			HCl solution desorption percentage (%)		
	Hg ²⁺	Cd ²⁺	Zn ²⁺	Hg ²⁺	Cd ²⁺	Zn ²⁺
1	98.3	97.2	99.0	95.1	93.7	93.6
2	96.7	96.6	98.4	90.4	88.5	87.8
3	94.4	94.4	95.5	84.6	83.4	82.4
4	91.3	89.5	91.7	79.5	77.3	73.3
5	87.8	85.8	88.6	75.7	74.8	68.6

4. Conclusions

The present study focuses on adsorption of Hg^{2+} , Cd^{2+} and Zn^{2+} from aqueous solution using the cross-linked magnetic CSTU as an efficient adsorbent. Adsorption of Hg^{2+} , Cd^{2+} and Zn^{2+} is found to be effective in the higher pH range and at lower temperatures. In addition, the very fast adsorption and settling for the CSTU make this material suitable for continuous flow water treatment systems. Equilibrium isotherm data were fitted using different three-parameter models. Among these models, Langmuir model is in good agreement with the experimental data with high R^2 . Kinetic study showed that the pseudo-second order model is appropriate to describe the adsorption process. The adsorption of Hg^{2+} , Cd^{2+} and Zn^{2+} dependence on temperature was investigated and the thermodynamic parameters ΔG° , ΔH° and ΔS° were calculated. The results show a feasible, spontaneous and exothermic adsorption process. The mechanism of adsorption includes mainly ionic interactions (chemical interactions) between metal cations and CSTU. The adsorption–desorption cycle results demonstrated that the regeneration and subsequent use the CSTU would enhance the economics of practical applications for the removal of Hg^{2+} , Cd^{2+} and Zn^{2+} from water and wastewater.

References

- [1] J.Z. Xie, H.L. Chang, J.J. Kilbane, Removal and recovery of metal ions from wastewater using biosorbents and chemically modified biosorbents, *Bioresour. Technol.* 57 (1996) 127–136.
- [2] C.G. Rocha, D.A.M. Zaia, R.V. da Silva Alfaya, A.A. da Silva Alfaya, Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents, *J. Hazard. Mater.* 166 (2009) 383–388.
- [3] Y. Kacar, C. Arpa, S. Tan, A. Denizli, O. Genc, M.Y. Arica, Biosorption of Hg(II) and Cd(II) from aqueous solutions: comparison of biosorptive capacity of alginate and immobilized live and heat inactivated *Phanerochaete chrysosporium*, *Process Biochem.* 37 (2002) 601–610.
- [4] M. Monier, D.M. Ayad, A.A. Sarhan, Adsorption of Cu(II), Hg(II), and Ni(II) ions by modified natural wool chelating fibers, *J. Hazard. Mater.* 176 (2010) 348–355.
- [5] A. Khan, S. Badshah, C. Airoidi, Biosorption of some toxic metal ions by chitosan modified with glycidylmethacrylate and diethylenetriamine, *Chem. Eng. J.* 171 (2011) 159–166.
- [6] K. Inoue, H. Paudyal, H. Nakagawa, H. Kawakita, K. Ohto, Selective adsorption of chromium(VI) from zinc(II) and other metal ions using persimmon waste gel, *Hydrometallurgy* 104 (2010) 123–128.
- [7] S. Koter, A. Warszawski, A new model for characterization of bipolar membrane electro dialysis of brine, *Desalination* 198 (2006) 111–123.
- [8] R. Vinodh, R. Padmavathi, D. Sangeetha, Separation of heavy metals from water samples using anion exchange polymers by adsorption process, *Desalination* 267 (2011) 267–276.
- [9] N. Geffen, R. Semiat, M.S. Eisen, Y. Balazs, I. Katz, C.G. Dosoretz, Boron removal from water by complexation to polyol compounds, *J. Membr. Sci.* 286 (2006) 45–51.
- [10] Y. Tanaka, A computer simulation of continuous ion exchange membrane electro dialysis for desalination of saline water, *Desalination* 249 (2009) 809–821.
- [11] G. Issabayeva, M.K. Aroua, N.M. Sulaiman, Electrodeposition of copper and lead on palm shell activated carbon in a flow-through electrolytic cell, *Desalination* 194 (2006) 192–201.
- [12] E. Salehi, S.S. Madaeni, Adsorption of humic acid onto ultrafiltration membranes in the presence of protein and metal ions, *Desalination* 263 (2010) 139–145.
- [13] J.W. Post, H.V.M. Hamelers, C.J.N. Buisman, Influence of multivalent ions on power production from mixing salt and fresh water with a reverse electro dialysis system, *J. Membr. Sci.* 330 (2009) 65–72.
- [14] H. Sepehrian, S.J. Ahmadi, S. Waqif-Husain, H. Faghian, H. Alighanbari, Adsorption studies of heavy metal ions on mesoporous aluminosilicate, novel cation exchanger, *J. Hazard. Mater.* 176 (2010) 252–256.
- [15] R. Laus, T.G. Costa, B. Szpoganicz, V.T. Favere, Adsorption and desorption of Cu(II), Cd(II) and Pb(II) ions using chitosan crosslinked with epichlorohydrin-triphosphate as the adsorbent, *J. Hazard. Mater.* 183 (2010) 233–241.
- [16] L. Zhou, Z. Liu, J. Liu, Q. Huang, Adsorption of Hg(II) from aqueous solution by ethylenediamine-modified magnetic crosslinking chitosan microspheres, *Desalination* 258 (2010) 41–47.
- [17] S. Sun, A. Wang, Adsorption properties and mechanism of cross-linked carboxymethyl-chitosan resin with Zn(II) as template ion, *React. Funct. Polym.* 66 (2006) 819–826.
- [18] M. Kumar, B.P. Tripathi, V.K. Shahi, Crosslinked chitosan/polyvinyl alcohol blend beads for removal and recovery of Cd(II) from wastewater, *J. Hazard. Mater.* 172 (2009) 1041–1048.
- [19] L. Fan, C. Luo, Z. Lv, F. Lu, H. Qiu, Preparation of magnetic modified chitosan and adsorption of Zn^{2+} from aqueous solutions, *Colloid Surf. B: Biointerfaces* 88 (2011) 574–581.
- [20] M.V. Dinu, E.S. Dragan, Evaluation of Cu^{2+} , Co^{2+} and Ni^{2+} ions removal from aqueous solution using a novel chitosan/clinoptilolite composite: kinetics and isotherms, *Chem. Eng. J.* 160 (2010) 157–163.
- [21] L.C.A. Oliveira, D.I. Petkowicz, A. Smaniotto, S.B.C. Pergner, Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water, *Water Res.* 38 (2004) 3699–3704.
- [22] J.F. Liu, Z.S. Zhao, G.B. Jiang, Coating Fe_3O_4 magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water, *Environ. Sci. Technol.* 42 (2008) 6949–6954.
- [23] M. Ozmen, K. Can, G. Arslan, A. Tor, Y. Cengeloglu, M. Ersoz, Adsorption of Cu(II) from aqueous solution by using modified Fe_3O_4 magnetic nanoparticles, *Desalination* 254 (2010) 162–169.
- [24] L. Zhou, Y. Wang, Z. Liu, Q. Huang, Characteristics of equilibrium, kinetics studies for adsorption of Hg(II), Cu(II), and Ni(II) ions by thiourea-modified magnetic chitosan microspheres, *J. Hazard. Mater.* 161 (2009) 995–1002.
- [25] A.M. Donia, A.A. Atia, A.M. Heniesh, Efficient removal of Hg(II) using magnetic chelating resin derived from copolymerization of bithiourea/thiourea/glutaraldehyde, *Sep. Purif. Technol.* 60 (2008) 46–53.
- [26] P. Chassary, T. Vincent, E. Guibal, Metal anion sorption on chitosan and derivative materials: a strategy for polymer modification and optimum use, *React. Funct. Polym.* 60 (2004) 137–149.
- [27] E. Guibal, N. Von Offenberg Sweeney, T. Vincent, J.M. Tobin, Sulfur derivatives of chitosan for palladium sorption, *React. Funct. Polym.* 50 (2002) 149–163.
- [28] A. Ramesh, H. Hasegawa, W. Sugimoto, T. Maki, K. Ueda, Adsorption of gold(III) platinum(IV) and palladium(II) onto glycine modified crosslinked chitosan resin, *Bioresour. Technol.* 99 (2008) 3801–3809.
- [29] A.P. Zhu, M.B. Chan-Park, S. Dai, L. Li, The aggregation behavior of o-carboxymethyl chitosan in dilute aqueous solution, *Colloids Surf. B: Biointerfaces* 43 (2005) 143–149.
- [30] M. Monier, D.M. Ayad, Y. Wei, A.A. Sarhan, Adsorption of Cu(II), Co(II), and Ni(II) ions by modified magnetic chitosan chelating resin, *J. Hazard. Mater.* 177 (2010) 962–970.
- [31] M. Monier, D.M. Ayad, Y. Wei, A.A. Sarhan, Preparation and characterization of magnetic chelating resin based on chitosan for adsorption of Cu(II), Co(II), and Ni(II) ions, *React. Funct. Polym.* 70 (2010) 257–266.
- [32] K.Z. Elwakel, A.A. Atia, A.M. Donia, Removal of Mo(VI) as oxoanions from aqueous solutions using chemically modified magnetic chitosan resins, *Hydrometallurgy* 97 (2009) 21–28.
- [33] A.A. Sarhan, D.M. Ayad, D.S. Badawy, M. Monier, Phase transfer catalyzed heterogeneous N-deacetylation of chitin in alkaline solution, *React. Funct. Polym.* 69 (2009) 358–363.
- [34] A. Singh, S.S. Narvi, P.K. Dutta, N.D. Pandey, External stimuli response on a novel chitosan hydrogel crosslinked with formaldehyde, *Bull. Mater. Sci.* 29 (2006) 233–238.
- [35] Q. Li, D. Yang, G. Ma, Q. Xu, X. Chen, F. Lu, J. Nie, Synthesis and characterization of chitosan-based hydrogels, *Int. J. Biol. Macromol.* 44 (2009) 121–127.
- [36] A. Baraka, P.J. Hall, M.J. Heslop, Preparation and characterization of melamine–formaldehyde–DTPA chelating resin and its use as an adsorbent for heavy metals removal from wastewater, *React. Funct. Polym.* 67 (2007) 585–600.
- [37] M.V. Dinu, E.S. Dragan, Heavy metals adsorption on some iminodiacetate chelating resins as a function of the adsorption parameters, *React. Funct. Polym.* 68 (2008) 1346–1354.
- [38] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.* 34 (2000) 735–742.
- [39] M. Yurdakoc, Y. Scki, S.K. Yuedakoc, Kinetic and thermodynamic studies of boron removal by Siral 5, Siral 40, and Siral 80, *J. Colloid Interface Sci.* 286 (2005) 440–446.
- [40] F.C. Wu, R.L. Tseng, R.S. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, *Water Res.* 35 (2001) 613–618.
- [41] A. Denizli, S. Senel, G. Alsancak, N. Tuzmen, R. Say, Mercury removal from synthetic solutions using poly(2-hydroxyethylmethacrylate) gel beads modified with poly(ethyleneimine), *React. Funct. Polym.* 55 (2003) 121–130.