Adsorption of Cu(II), Hg(II), and Ni(II) ions by modified natural wool chelating fibers

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ARTICLE INFO

ABSTRACT

The graft copolymerization of ethyl acrylate (EA) onto natural wool fibers initiated by potassium persulphate and Mohr's salt redox initiator system in limited aqueous medium was carried out in heterogeneous media. Ester groups of the grafted copolymers were partially converted into hydrazide function groups followed by hydrazone formation through reaction with isatin. Also the application of the modified fibers for metal ion uptake was studied using Cu(II), Hg(II) and Ni(II). The modified chelating fibers were characterized using FTIR spectroscopy, SEM and X-ray diffraction.

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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].

As well known, chelating adsorbents are effective to remove metal ions [7]. Many chelating resins have been reported, but show limited applicability because of their poor hydrophilicity, small surface area, low adsorption rate and poor adsorption capacity in low-concentration metal ion solutions [8,9]. Meanwhile, chelating fiber is a very promising adsorption material which possesses high adsorption rate and large adsorption capacity due to its low mass transfer resistance and large external surface area. It can make up these advantages to some extent by choosing suitable chelating group that possesses strong affinities toward certain metal ions.

In recent years the metal adsorption capacity of natural protein fibers has been investigated for the production of new types of adsorbents [10]; wool has been used as adsorbent to remove heavy metal pollutants from industrial effluents and to purify contaminated water supplies [10]. Moreover, there has been an increasing interest in incorporating metal ions into fibrous polymers, with the aim of conferring new textile performances on them, such as antistatic properties, electrical conductivity, and antimicrobial activity [11–13]. The metal uptake by protein fibers can be enhanced by chemically modifying the fibers with chelating agents able to coordinate metal ions [12,14,15]. In previous works, some of the authors investigated the absorption and binding of metal cations (Ag^+, Cu^{2+}, Co^{2+}) onto *Bombyx mori* (*B.m.*) and Tussah (*Antheraea pernyi*) silks and wool either by treatment with tannic acid (TA) or acylation with ethylenediaminetetraacetic (EDTA) dianhydride, as a function of fiber weight gain and pH of the metal solution [12,14,15].

In a previous paper [16], the results of an IR study on the Co^{2+} and Cu^{2+} binding mode of untreated, EDTA- and TA-modified *B.m.* and Tussah silk fibers were reported, at alkaline pH. This pH was chosen to obtain adsorption values as high as possible [12,15].

In the present work, the natural wool fibers were modified by graft copolymerization with ethylacrylate (EA) using potassium persulphate and Mohr's salt redox initiator system in limited aqueous medium. Ester groups of the grafted copolymers were partially converted into hydrazide function groups followed by hydrazone formation through reaction with isatin. Also the application of the modified copolymers for metal ion uptake was studied using Cu^{2+}, Hg^{2+} and Ni^{2+}. The structures of the modified wool

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fibers were confirmed using FTIR spectroscopy, SEM and X-ray diffraction.

2. Materials and methods

2.1. Materials

Wool fibers were collected and purified by carbonizing in 1% sulphuric acid, then by scouring in 1% (w/w) sodium hydroxide solution at 50 °C, and finally with cold distilled water until it was alkali free then dried at 40 °C till constant weight. EA (BDH-England) was treated with 3% sodium hydroxide solution, washed with distilled water till neutralization, dried over calcium chloride followed by molecular sieves. Potassium persulphate (BDH-England), Mohr's salt (Adwic), hydrazine hydrate (Adwic) and isatin (BDH-England) were reagent grade. All other chemicals were analytical grade or above and used as received without further purifications.

2.2. Synthesis of wool-g-poly(isatin acrylic hydrazone) (wool-g-PIAH) chelating fibers

The synthetic reaction was carried out as following three steps.

2.2.1. Step 1
The graft copolymer of wool fibers and ethyl acrylate (EA) was prepared by free radical polymerization. Briefly, 1 g of wool fibers was soaked in 50 ml distilled water in Pyrex tube. Then, the combined redox initiator system which consists of 10 ml of 2 mmol potassium persulphate and 10 ml 2 mmol Mohr's salt was added and the mixture was vigorously shaken for 5 min. 0.12 mol of the monomer EA was added and the reaction was conducted for 1 h with stirring at room temperature. Adding 10 ml hydroquinone solution (3%) finally terminated the polymerization process. The products were filtered and washed with distilled water. The extraction of PEA homopolymer was achieved with benzene. The grafted copolymer was dried at 40 °C till constant weight.

Grafting percentage (GP) was calculated as in the following expression (Eq. (1)):

$$\text{Grafting Percentage (GP)} = \left(\frac{A - B}{B}\right) \times 100 \tag{1}$$

where A and B are the weight of grafted product, and wool fibers respectively.

These grafted wool fibers prepared with GP values 156% were named wool-g-PEA.

2.2.2. Step 2
1 g sample of the modified wool-g-PEA fibers was taken and to which 50 ml 5% alcoholic hydrazine hydrate solution was added. The mixture was stirred at 50 °C for 2 h. The modified wool grafted poly(acrylic hydrazide) (wool-g-PAH) fibers were then filtered and washed with absolute ethanol then dried at 40 °C.

2.2.3. Step 3
The finally modified wool grafted poly(isatin acrylic hydrazone) chelating fibers expressed as (wool-g-PIAH), were prepared by the action of the above wool-g-PAH fibers with 50 ml 5% alcoholic isatin solution. The mixture was stirred at 50 °C for 2 h. Then, the wool-g-PIAH fibers were filtered and washed with absolute ethanol then dried at 40 °C.

2.3. IR-spectroscopic analysis

The chemical structures of the native wool, wool-g-PEA, wool-g-PAH and wool-g-PIAH were examined by IR-spectroscopy [PerkinElmer 1430] using KBr to prepare its discs.

2.4. SEM analysis

Scanning electron microscopy (SEM) analysis was carried out with a X-650 microscope, at 10 kV acceleration voltage, after gold coating.

2.5. X-ray diffraction analysis

To determine the crystallinity of the treated samples under different conditions, the sample (powder) was dispersed onto a stub and placed within the chamber of analytical X-ray powder diffractometer (Japanese Dmax-rA, wavelength = 1.54 A°, CuKα radiation). Generator intensity was 40 kV, generator current was 50 mA. The sample was then scanned from $2\theta = 5$ to 70°, in step of 0.02°. The resultant graphs were printed out on the Origin graph plotting package.

2.6. Metal ion uptake experiments using batch method

2.6.1. Instrumentation
A PerkinElmer Model 5000 atomic absorption spectrometer (PerkinElmer, Shelton, CT-USA) fitted with a nickel and copper hollow cathode lamps was used. The instrument was set at 232.0 nm for nickel and 324.7 nm for copper. For measurements of mercury, a PerkinElmer Model 4100ZL atomic absorption spectrometer was used equipped with a PerkinElmer FIAS-400 flow injection system and an AS-90 autosampler. A PerkinElmer 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 pH
Uptake experiments were performed at controlled pH and 28 °C by shaking 0.02 g of dry wool-g-PIAH fibers with 20 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); acetic acid/sodium acetate (pH 4 and 5); Na_2HPO_4/KH_2PO_4 (pH 6 and 7).

2.6.3. Effect of the temperature
Uptake experiments were performed by placing 0.02 g of dry wool-g-PIAH fibers 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 3 h while keeping the temperature at 15, 20, 25, 28, 30 and 35 °C. After adsorption, solution was filtered and the residual concentration of the metal ions was determined.

2.6.4. Effect of contact time
Measurements of metal ion uptake using a batch method were conducted by placing 0.2 g of dry wool-g-PIAH fibers 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.

2.6.5. Effect of the initial concentration of the metal ions
The effect of initial concentration of the metal ion on the uptake by wool-g-PIAH fibers obtained was carried out by placing 0.02 g of dry wool-g-PIAH fibers in a series of flasks containing 20 ml of metal ions at definite concentrations (50–400 mg/l) and pH 5.0. The contents of the flasks were equilibrated on the shaker at 150 rpm and 28 °C for 3 h. After adsorption, the residual concentration of the metal ions was determined.

2.6.6. Desorption experiments
For desorption studies, 0.2 g of wool-g-PIAH fibers was loaded with metal ions (Cu^{2+}, Hg^{2+}, and Ni^{2+}) using 200 ml (100 mg/l)
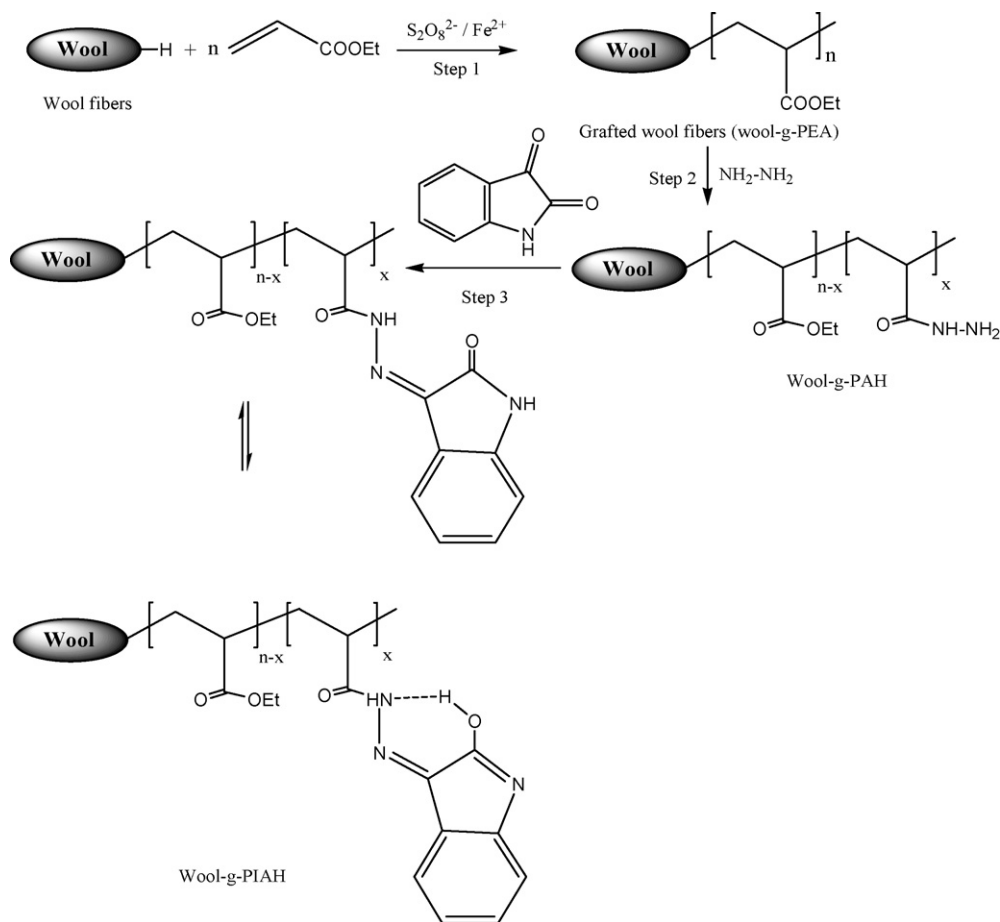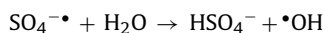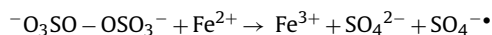
Scheme 1. Schematic presentation for the preparation of wool-g-PIAH.

metal ion solution at 28 °C, pH 5.0 and contact time of 3 h. The agitation rate was fixed as 150 rpm. Metal ion-loaded wool-g-PIAH fibers were collected, and gently washed with distilled water to remove any unabsorbed metal ions. The fibers 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 wool-g-PIAH fibers was calculated from the amount of metal ions adsorbed on wool-g-PIAH fibers and the final concentration of metal ions in the desorption medium. To test the reusability of the fibers, this adsorption–desorption cycle was repeated five times by using the same affinity adsorbent.

3. Results and discussion

3.1. Synthesis of wool-g-PIAH chelating fibers

The synthetic reaction of wool-g-PIAH chelating fibers was carried out in three steps. The first step which involves the graft copolymerization of EA onto wool fibers was attempted by potassium persulphate and Mohr's salt as combined redox initiator under visible light irradiation. The formation of different free radicals may be explained on the bases of the following suggested mechanism [17]:

$$^-O_3SO - OSO_3{}^- + Fe^{2+} \rightarrow Fe^{3+} + SO_4{}^{2-} + SO_4{}^{-\bullet}$$

$$SO_4{}^{-\bullet} + H_2O \rightarrow HSO_4{}^- + {}^\bullet OH$$

The produced free radicals $SO_4{}^{-\bullet}$, or ${}^\bullet OH$ abstract hydrogen atom from certain functional groups such as –OH, –SH, –COOH, –NH$_2$ and –NH– to form active sites on wool backbone to start the grafting reaction.

In the second step the majority of the grafted polyethyl acrylate chains were converted into poly (acrylic hydrazide) by the reaction with hydrazine hydrate, followed by treatment with isatin in the third step to produce finally wool-g-PIAH chelating fibers as shown in Scheme 1.

3.2. Polymer characterization

The IR spectra of pure wool and graft copolymer of wool-g-PEA with GP values 156%, wool-g-PAH and wool-g-PIAH are shown in (Fig. 1a–d).

The IR spectrum of pure wool fibers (Fig. 1a) has various distinctive absorption peaks: a broad one in the range of 3150–3500 cm^{-1} which may be related to the –NH– stretching and –SH bonds, as well as strong peaks at 1630, 1535, and 1230 cm^{-1} belonging to –CONH– (amide I), amide II and C–N stretching of amide III respectively [11]. However, the IR spectrum of the graft copolymer (Fig. 1b) shows partial disappearance of the broad peak of –NH–, –SH that has been found in pure wool spectrum (Fig. 1a). Additionally a new peak is also observed at 1740 cm^{-1} that related to ester groups of ethyl acrylate grafted chains onto wool fibers. Also, the IR spectrum of wool-g-PAH fibers (Fig. 1c) shows an appearance of a sharp duplet peak at 3130 cm^{-1} which may be related to the –NH$_2$ of the hydrazide, in addition to the clear displacement of the carbonyl ester peak from 1740 to 1712 cm^{-1} and appearance of new
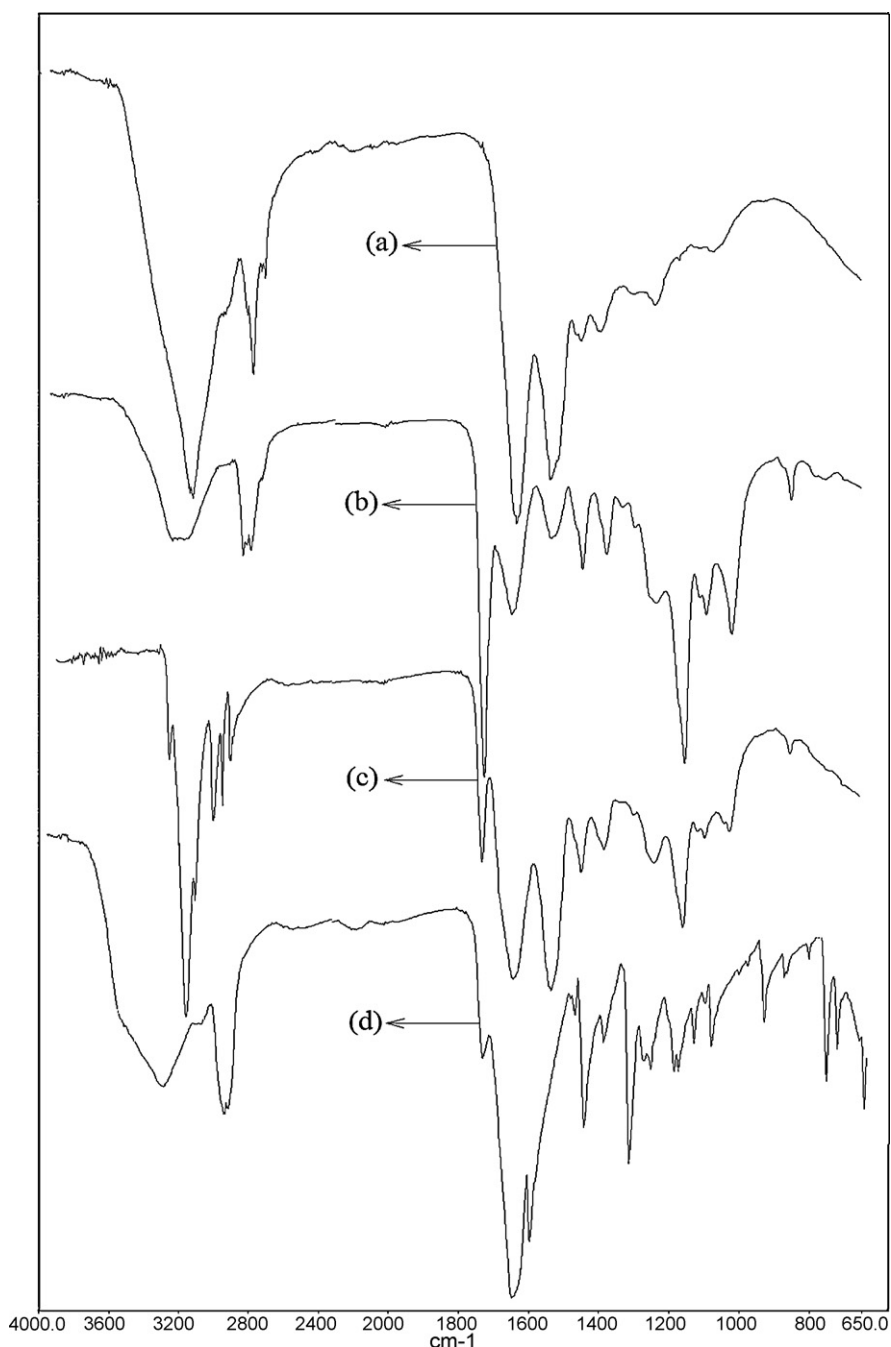
Fig. 1. FTIR spectra of (a) pure wool, (b) wool-g-PEA, (c) wool-g-PAH and (d) wool-g-PIAH.

peak at 1639 cm^{-1} which may be due to the conversion of the ester (–COOEt) to hydrazide (–CO–NH–NH$_2$) group. On the other hand, the IR spectrum of wool-g-PIAH chelating fibers (Fig. 1d) present an increase in the intensities of the sharp peaks at 1639 and 2890 cm^{-1} which could be attributed to the C=N of the formed isatin acrylic hydrazone and the isatin aromatic C–H bonds respectively. Also, a shift and broading of the sharp peak at 3130 cm^{-1} corresponding to –NH$_2$ to 3200 cm^{-1} which may be due to the enolic –OH group of the stable enol form of isatin acrylic hydrazone due to hydrogen bonding as presented in Scheme 1. The bands at 1581.5, 1278.7, and 752.2 cm^{-1}, are attributed to the C=C, C–O, and C–H stretching in the aromatic ring of the isatine.

3.3. Characterization of fiber surface

Some scanning electron microscopy (SEM) images of the modified and unmodified wool fabrics are shown in Fig. 2. The typical unmodified wool fiber with distinct overlapped tilelike edges is microscopically demonstrated in Fig. 2a. Also, the grafted wool fibers show an observed increase in roughness (Fig. 2b) which may be due to the copolymer poly(ethylacrylate) chains onto the fiber surface. On the other hand, the roughness of the surface of the modified wool-g-PIAH chelating fibers (Fig. 2c) increases greatly which may confirm the partial conversion of PEA into PIAH grafted chains.
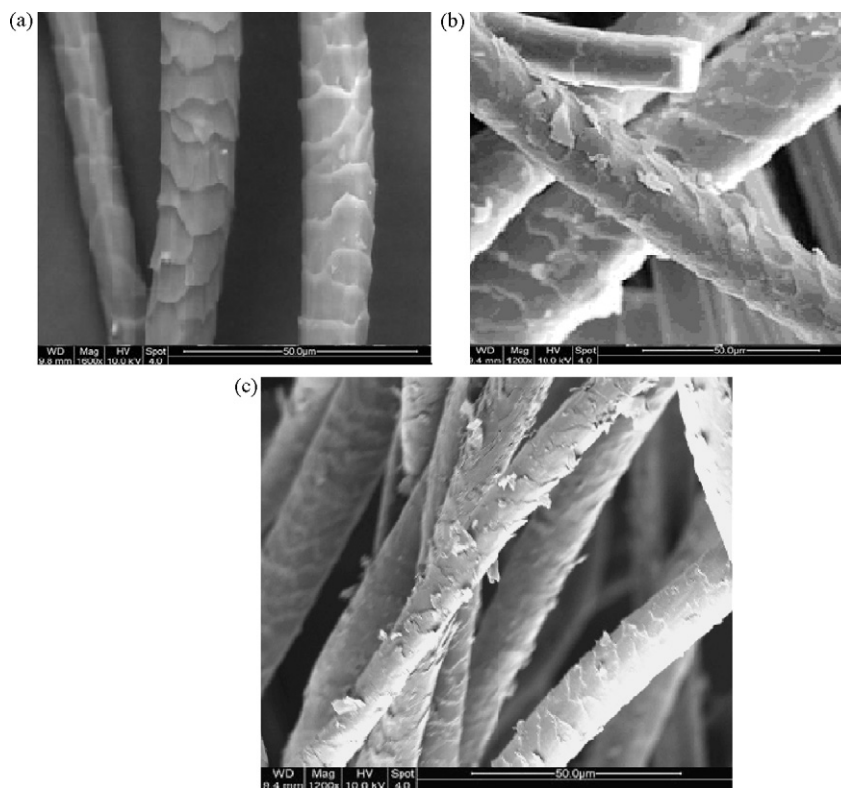
Fig. 2. SEM photos of modified and unmodified wool fibers (a) native unmodified wool fibers, (b) wool-g-PEA, and (c) wool-g PIAH.

3.4. X-ray analysis

Results of X-ray diffraction of the samples are shown in Fig. 3. Fig. 3a shows the typical diffraction pattern of native unmodified wool α-keratins with a prominent 2θ peak at 22°, and a minor peak at 10°, corresponding to the crystalline spacing of 4.39 and 9.82 A₂, respectively [11]. Modified wool fibers wool-g-PEA and wool-g-PIAH (Fig. 3b and c) exhibited a smaller characteristic peak of crystallinity than unmodified wool fibers, and. This lowering in crystallinity can be attributed to the insertion of the grafted chains onto the wool backbone may led to breaking the hydrogen bonding in the wool protein structure, resulting in an amorphous structure.

3.5. Effect of pH on metal ion adsorption

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. 4, the higher uptake capacity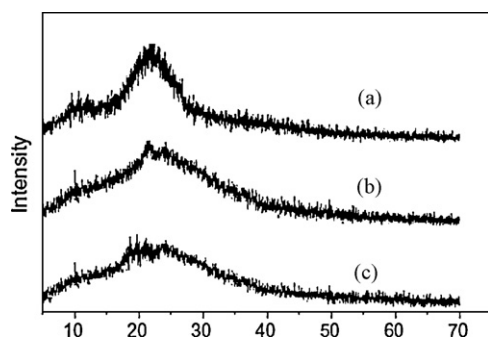 was achieved at higher pH values. The observed lower uptake in an acidic medium may be attributed to the partial protonation of the active groups and the competition of H^+ with metal ions for adsorption sites on the wool-g-PIAH. At pH < 2, no appreciable uptake was detected for Hg^{2+} and Ni^{2+} ions. The results indicate that the adsorption percent of Cu^{2+} is higher than Hg^{2+} and Ni^{2+} ions in all pH ranges studied, suggesting possible selectivity for this metal.

Wool-g-PIAH is almost insoluble in acidic and alkaline mediums. No obvious leakage of fiber materials and change of wool-g-PIAH were observed in the experimental process. Wool-g-PIAH becomes more resistant to lower and higher pH values compared to their parent wool fibers due to the insertion of hydrophobic grafted chains.

Fig. 3. X-ray diffraction pattern of (a) native unmodified wool fibers, (b) wool-g-PEA, and (c) wool-g-PIAH.
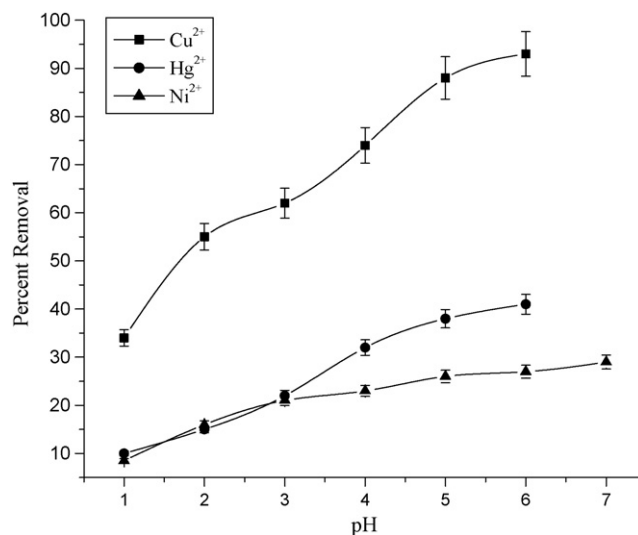

Fig. 4. Effect of pH on the uptake of Cu^{2+}, Hg^{2+}, and Ni^{2+} ions by wool-g-PIAH (initial concentration 100 mg/l; wool-g-PIAH. 1 g/l; contact time 3 h; shaking rate 150 rpm, 28 °C).
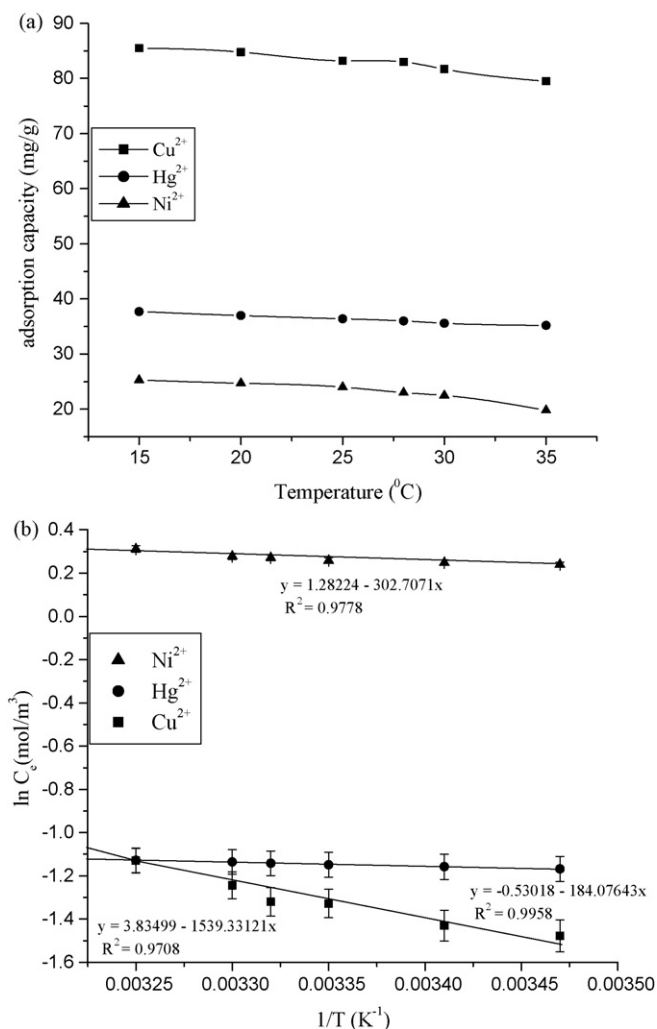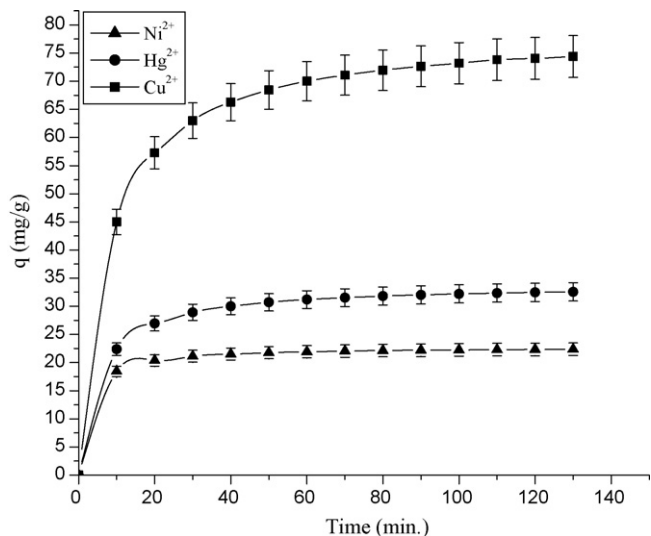
Fig. 6. Effect of contact time on the uptake of Cu^{2+}, Hg^{2+}, and Ni^{2+} ions by wool-g-PIAH (initial concentration 100 mg/l, wool-g-PIAH 1 g/l, pH 5.0, shaking rate 150 rpm, 28 °C).

3.7. Adsorption kinetics

Fig. 6 shows the kinetics of the adsorption of metal ions Cu^{2+}, Hg^{2+} and Ni^{2+} by wool-g-PIAH. Inspection of the uptake–time curves shows that the maximum uptake follows the order $Cu^{2+} > Hg^{2+} > Ni^{2+}$ at all time intervals. The kinetic curve for Cu^{2+} ions showed that the adsorption was initially rapid, and reached equilibrium after approximately 40 min. Hg^{2+} ions adsorption reached equilibrium in 50 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 60 min.

The uptake time data obtained was treated in the form of two simplified kinetic models including pseudo-first and pseudo-second-order. The pseudo-first-order model is expressed as Eq. (3) [19]:

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \qquad (3)$$

where k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption and q_e and q_t (mg/g) are the amounts of metal ion adsorbed at equilibrium and time t (min), respectively. The value of $1/q_t$ was calculated from the experimental results and plotted against $1/t$ (min^{-1}). On the other hand, the pseudo-second-order model is expressed as Eq. (4) [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (4)$$

where k_2 (g/(mg min)) is the pseudo-second-order rate constant of adsorption (g/(mg min)). The aforementioned two models basically considering external film diffusion, intraparticle diffusion and interaction step for adsorption process. The rate determining step of adsorption reaction may be one of the above three steps. The external film diffusion is eliminated by stirring. So, the adsorption rate may be controlled by intraparticle diffusion or interaction step. The kinetic parameters for pseudo-first and pseudo-second-order models are determined from the linear plots of $1/q_t$ versus $1/t$ (min^{-1}) or (t/q_t) versus t, respectively, Fig. 7. The validity of each model is checked by comparing the R^2 values. Accordingly as shown in Table 1, the adsorption of Cu^{2+}, Hg^{2+} and Ni^{2+} on the modified chelating fibers fit pseudo-second-order model rather than pseudo-first-order one. This behavior implies the dependence of the reaction rate on the textural properties of the chelating fibers.

Fig. 5. (a) Effect of temperature on the uptake of Cu^{2+}, Hg^{2+}, and Ni^{2+} ions by wool-g-PIAH (initial concentration 100 mg/l, wool-g-PIAH 1 g/l, pH 5.0, contact time 3 h, shaking rate 150 rpm, 15–35 °C) and (b) the plot of $\ln C_e$ against $1/T$.

3.6. Effect of the temperature on the uptake

As shown in Fig. 5a, the adsorption capacity of the metal ions decreased with increasing temperature. This might be due to the fact that the interaction between the metal ions and the active groups of wool-g-PIAH 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 [18] (Eq. (2)):

$$\Delta H_x = R\left[\frac{d(\ln C_e)}{d(1/T)}\right] \qquad (2)$$

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. 5b. The calculated enthalpy changes are -12.80 ± 1.2, -1.53 ± 0.20, and, -2.52 ± 0.12 kJ/mol for Cu^{2+}, Hg^{2+} and Ni^{2+} ions, respectively, indicating that the adsorption process was exothermic in nature.
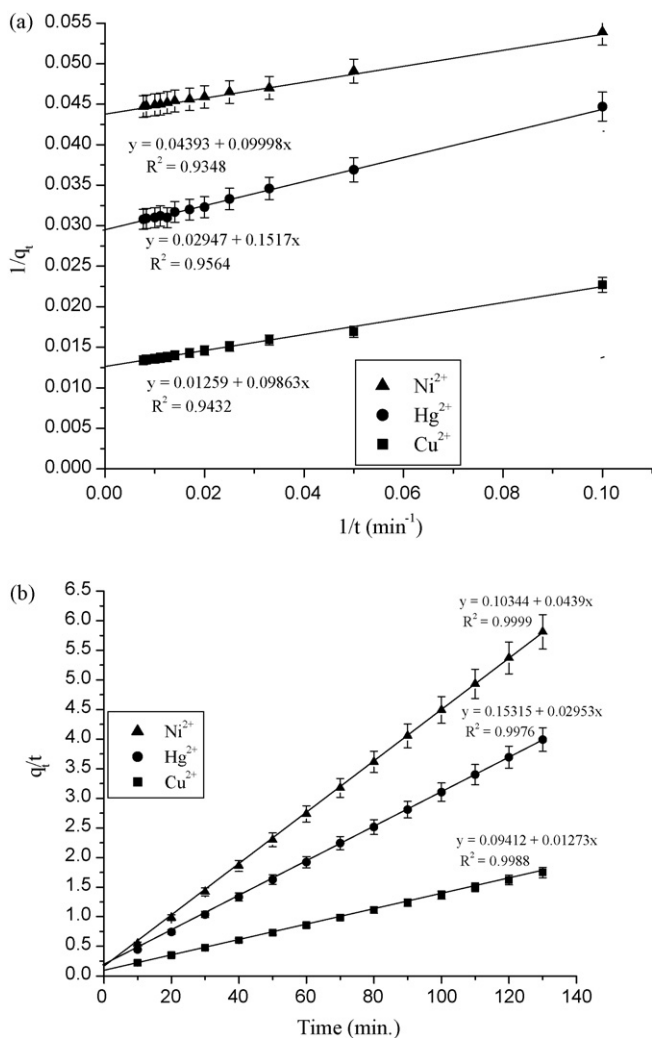
Fig. 7. (a) Pseudo-first and (b) pseudo-second kinetics of the uptake of Cu^{2+}, Hg^{2+}, and Ni^{2+} ions by wool-g-PIAH (initial concentration 100 mg/l, wool-g-PIAH 1 g/l, pH 5.0, shaking rate 150 rpm, 28 °C).

3.8. Adsorption isotherms

Fig. 8 shows the adsorption equilibrium isotherms obtained for Cu^{2+}, Hg^{2+}, and Ni^{2+} ions by wool-g-PIAH. 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 inter-

Table 1
Kinetic parameters for Cu^{2+}, Hg^{2+}, and Ni^{2+} ions adsorption by wool-g-PIAH.

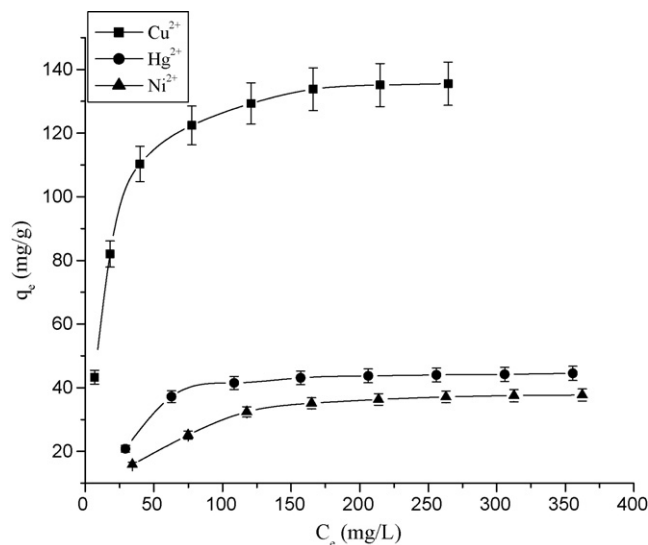| Metals	First-order model		
	k_1 (min^{-1})	q_{e1} (mg/g)	R^2
Cu^{2+}	7.468	79 ± 8	0.9432
Hg^{2+}	5.127	34 ± 5	0.9564
Ni^{2+}	2.351	23 ± 2	0.9348
Metals	Second-order model		
	k_2 (g/(mg min))	q_{e2} (mg/g)	R^2
Cu^{2+}	1.86×10^{-3}	78 ± 5	0.9988
Hg^{2+}	5.58×10^{-3}	34 ± 4	0.9976
Ni^{2+}	1.16×10^{-2}	23 ± 2	0.9999

Fig. 8. Adsorption isotherms of Cu^{2+}, Hg^{2+}, and Ni^{2+} ions by wool-g-PIAH (initial concentration 50–400 mg/l, wool-g-PIAH 1 g/l, pH 5.0, shaking rate 150 rpm, 28 °C).

pretation of the adsorption data, the Langmuir [21], Freundlich [22], and Tempkin and Pyzhev [23] isotherm models were used (Eqs. (5–7)).

The linear form of the Langmuir isotherm is given by

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L + q_m}\right) + \left(\frac{C_e}{q_m}\right) \tag{5}$$

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:

$$\ln q_e = \ln K_F + \frac{1}{n}(\ln C_e) \tag{6}$$

where both K_F and n are constants.

The Tempkin isotherm has been used in the following form [23]:

$$q_e = \frac{RT}{b}(\ln A) + \frac{RT}{b}(\ln C_e) \tag{7}$$

where $B = RT/b$.

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 Cu^{2+}, Hg^{2+}, and Ni^{2+} ions by wool-g-PIAH are shown in Table 2. For the three studied systems, the Langmuir isotherm correlated better ($R^2 > 0.989$) than Freundlich and Tempkin isotherms with the experimental data from adsorption equilibrium of metal ions by wool-g-PIAH, suggested a monolayer adsorption. The maximum adsorption values were 625.2, 66.7, and 15.3 mg/g for Cu^{2+}, Hg^{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 Cu^{2+} was higher than the values found for Hg^{2+} and Ni^{2+}, showing the following capacity order: $Cu^{2+} > Hg^{2+} > Ni^{2+}$.

A high adsorption affinity for Cu^{2+} is expected, especially due to the involvement of the hydrazone group, which shows copper (II) selectivity [24]. The higher affinity for Hg^{2+} than that of Ni^{2+} may be attributed to the involvement of the sulphur containing amino acids in the wool protein. 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 sulphur [25]. These results indicated that chemical modification of wool fibers with

Table 2
Parameters for Cu^{2+}, Hg^{2+} and Ni^{2+} ions adsorption by wool-g-PIAH according to different equilibrium models.

Metals	Langmuir isotherm constants		
	K_L(l/g)	q_m(mg/g)	R^2
Cu^{2+}	7.01×10^{-2}	142.5	0.9986
Hg^{2+}	1.01×10^{-2}	49.33	0.9957
Ni^{2+}	1.65×10^{-2}	46.7	0.9989
Metals	Freundlich isotherm constants		
	K_F	n	R^2
Cu^{2+}	29.96	2	0.9231
Hg^{2+}	19.11	3.091	0.9165
Ni^{2+}	21.76	4.327	0.8967
Metals	Tempkin isotherm constant		
	A	B	R^2
Cu^{2+}	9.984	22.61	0.9231
Hg^{2+}	6.7412	3.8	0.9142
Ni^{2+}	15.38	7.32	0.9113

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

Concentration of EDTA	Desorption ratio (%)		
	Cu^{2+}	Hg^{2+}	Ni^{2+}
0.1	92.5	94.3	91.7
0.05	91.1	93.2	89.8
0.01	88.6	90.4	85.4
0.005	78.2	74.7	79.3
0.001	61.3	59.9	63.8

Table 4
Repeated adsorption of Cu^{2+}, Hg^{2+}, and Ni^{2+} ions by wool-g-PIAH (initial concentration 100 mg/l, wool-g-PIAH 1 g/l, pH 5.0, contact time 3 h, shaking rate 150 rpm, 28 °C).

Cycle number	Adsorption capacity (%)		
	Cu^{2+}	Hg^{2+}	Ni^{2+}
1	100	100	100
2	99.3	98.6	99.5
3	98.8	98.1	98.2
4	96.6	95.8	95.3
5	93.1	93.3	92.7

polyisatinacrylic hydrazide improved the adsorption capacity for the investigated metal ions, especially for Cu^{2+} and Hg^{2+} ions.

3.9. Desorption characteristics

As shown in Table 3, the desorption ratio of metal ions using 0.1 M EDTA was 92.5, 94.3, and 91.7% for Cu^{2+}, Hg^{2+}, and Ni^{2+}, respectively. The desorption ratio of metal ions increased as EDTA concentration increased. However, the desorption ratio of the investigated ions was more than 85% 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. The adsorption capacity of the wool-g-PIAH could still be maintained at 92% level at the 5th cycle, as shown in Table 4. These results indicated no appreciable loss in activity over at least five cycles.

4. Conclusions

Chemically modified wool chelating fibers wool-g-PIAH were prepared and tested against the removal of Cu^{2+}, Hg^{2+}, and Ni^{2+} from their aqueous solutions. Cu^{2+} showed higher adsorption affinity toward the studied fibers relative to Hg^{2+}, and Ni^{2+}. 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 the fibers obtained was achieved by using 0.01–0.1 M EDTA with efficiency of greater than 85%. Feasible improvements in the uptake properties encourage efforts for wool-g-PIAH obtained to be used in water and wastewater treatment.

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