



Preparation and characterization of chelating fibers based on natural wool for removal of Hg(II), Cu(II) and Co(II) metal ions from aqueous solutions

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ARTICLE INFO

Article history:

Received 25 February 2010

Received in revised form 29 July 2010

Accepted 6 August 2010

Available online 13 August 2010

Keywords:

Wool

Grafting

Acrylonitrile

Ethylcyanoacetate

ABSTRACT

The graft copolymerization of acrylonitrile (AN) onto natural wool fibers initiated by KMnO_4 and oxalic acid combined redox initiator system in limited aqueous medium was carried out in heterogeneous media. Moreover, modification of the grafted wool fibers was done by changing the nitrile group ($-\text{CN}$) into cyano-acetic acid α -amino-acrylic-hydrazide through the reaction with hydrazine hydrate followed by ethylcyanoacetate which eventually produce wool-grafted-poly(cyano-acetic acid α -amino-acrylic-hydrazide) (wool-g-PCAH) chelating fibers. The application of the modified fibers for metal ion uptake was studied using Hg^{2+} , Cu^{2+} and Co^{2+} . The modified chelating fibers were characterized using FTIR spectroscopy, SEM and X-ray diffraction.

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1. Introduction

The discharge of toxic heavy metal ions into the environment is a serious pollution problem affecting water quality. Major sources of water pollution with heavy metals are plating plants, mining, metal finishing, welding and alloys manufacturing [1]. Several methods have been applied during many years for the elimination of these metal ions present in the industrial wastewater. The traditional methods commonly used for removal of heavy metal ions from aqueous solution include ion-exchange [2], solvent extraction, chemical precipitation [3], nano-filtration [4], reverse osmosis [5] and adsorption [6–8].

Adsorption is an alternative technique for heavy metal removal. The activated carbon is the most widely used adsorbent material. In fact, the use of activated carbon is expensive for the regeneration required. Losses during the application processes could make it even more expensive. Many researchers have been investigating new adsorbent materials as alternative to activated carbon, such as seaweeds [9], marine algae [10], clays [11], activated sludge biomass [12,13], perlite [14] and maple sawdust [15] for the removal of heavy metal ions from wastewater.

In recent years, the metal adsorption capacity of natural protein fibers has been investigated for the production of new types of

adsorbents [16]. Wool has been used as an adsorbent to remove heavy metal pollutants from industrial effluents and to purify contaminated water supplies [16]. 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 [17–19]. The metal uptake by protein fibers can be enhanced chemically by modifying the fibers with chelating agents able to coordinate metal ions [18,20,21]. In previous work, some authors investigated the adsorption and binding of metal cations (Ag^+ , Cu^{2+} , Co^{2+}) onto *Bombyx mori* (*B.m.*) and Tussah (*Antheraea pernyi*) silk and wool either after the treatment of tannic acid (TA) or acylation with ethylenediaminetetraacetic (EDTA) dianhydride, as a function of fiber weight gain and pH of the metal solution. 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 [18,20–22].

In the present work, the natural wool fibers were modified by graft copolymerization with acrylonitrile (AN) using KMnO_4 and oxalic acid combined redox initiator system in limited aqueous medium. Cyano groups of the grafted copolymers were partially converted into hydrazidine functional groups which subsequently react with ethylcyanoacetate to produce the finally modified chelating fibers. Also, the application of the modified copolymers for metal ion uptake was studied using Hg^{2+} , Cu^{2+} and Co^{2+} . The structures of the modified wool fibers were confirmed using FTIR spectroscopy, SEM and X-ray diffraction.

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2. Materials and methods

2.1. Materials

Wool fibers were collected and purified by carbonization in 1% (v/v) sulfuric acid, then by scouring in 1% (w/w) sodium hydroxide solution at 50 °C, and finally with cold distilled water until they were alkali free then dried at 40 °C till constant weight. Acrylonitril (AN) (BDH-England) was treated with 3% (w/w) sodium hydroxide solution, washed with distilled water till neutralization and dried over calcium chloride followed by molecular sieves. KMnO₄ (BDH-England); oxalic acid (Adwic); hydrazine hydrate (Adwic); ethylcyanoacetate, HgCl₂, CuCl₂·2H₂O and CoCl₂·6H₂O were purchased from Sigma–Aldrich. All chemicals were used as received.

2.2. Synthesis of wool-grafted-poly(cyano-acetic acid α -amino-acrylic-hydrazide) (wool-g-PCAH) chelating fibers

The synthetic reaction was carried out as in the following three steps.

2.2.1. Step 1

The graft copolymerization of wool fibers by poly-acrylonitrile (PAN) was carried out using free radical polymerization. Briefly, 1 g of wool was soaked in 50 ml distilled water in a conical flask. Then, the combined redox initiator system (10 ml of 2 mmol KMnO₄ and 10 ml 4 mmol oxalic acid) was added and the mixture was vigorously shaken for 5 min. The monomer AN (0.12 mol) was added and the reaction was conducted for 1 h with stirring at room temperature. Finally, hydroquinone solution (10 ml, 3% (w/w)) was added to terminate the polymerization process. The products were filtered and washed with distilled water. The extraction of PAN homopolymer was achieved with DMF. The grafted copolymer was dried at 40 °C till constant weight.

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

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

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

These grafted wool fibers prepared with GP values 160% were named as wool-g-PAN.

2.2.2. Step 2

1 g sample of the modified wool-g-PAN was taken and to which alcoholic hydrazine hydrate solution (50 ml, 10% (v/v)) was added. The mixture was refluxed at about 80 °C for 4 h. The modified wool-grafted-poly(acrylic hydrazidine) (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(cyano-acetic acid α -amino-acrylic-hydrazide) (wool-g-PCAH) chelating fibers were prepared by the action of the above wool-g-PAH fibers with 50 ml, 20% (v/v) alcoholic ethylcyanoacetate solution. The mixture was stirred at 50 °C for 2 h. Then, the wool-g-PCAH 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-PAN, wool-g-PAH and wool-g-PCAH were examined by IR-spectroscopy [PerkinElmer 1430] using KBr to prepare its discs.

2.4. SEM analysis

Scanning electron microscopy (SEM) analyses were 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 was dispersed onto a stub and placed within the chamber of analytical X-ray powder diffractometer (Japanese Dmax-rA, wavelength = 1.54 Å, Cu K α radiation). Generator intensity was 40 kV, generator current was 50 mA. The sample was then scanned from $2\theta = 5\text{--}70^\circ$, 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 copper and cobalt hollow cathode lamps was used. The instrument was set at 242.5 nm for cobalt and 324.7 nm for copper. For 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 30 °C by shaking 0.02 g of dry wool-g-PCAH 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); and Na₂HPO₄/KH₂PO₄ (pH 6).

2.6.3. Effect of the temperature

Uptake experiments were performed by placing 0.02 g of dry wool-g-PCAH 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

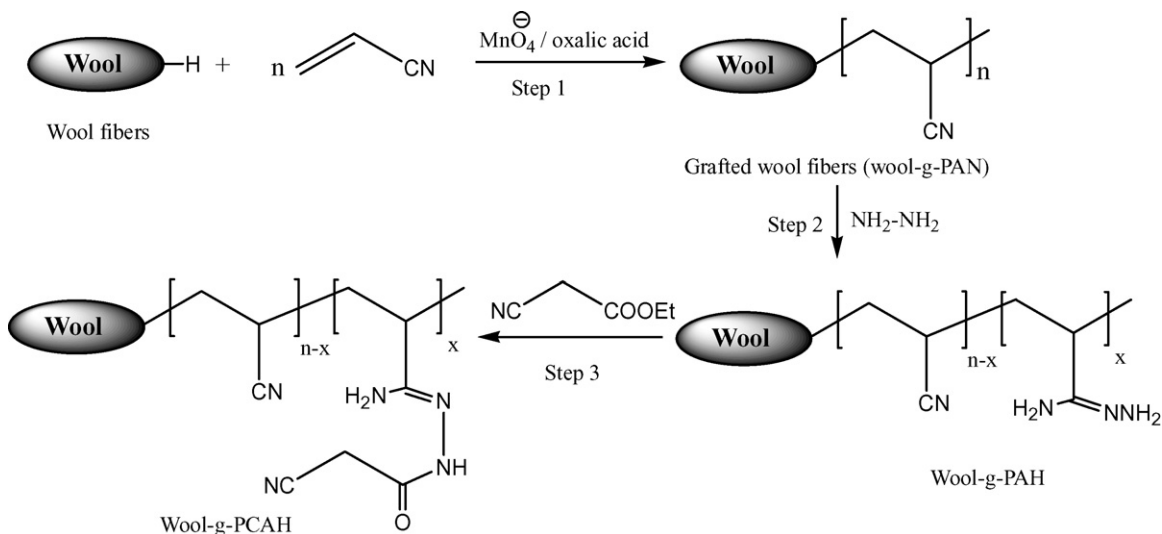
Measurements of metal ion uptake using a batch method were conducted by placing 0.2 g of dry wool-g-PCAH fibers in a flask containing 200 ml (100 mg/l) metal ion solution at pH 5.0. The contents of the flask were agitated on a shaker at 150 rpm and 30 °C. Samples were taken at time intervals for the 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 the modified wool-g-PCAH chelating fibers was evaluated by placing 0.02 g of dry wool-g-PCAH 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 30 °C for 3 h. After adsorption, the residual concentration of the metal ions was determined.

2.6.6. Desorption experiments

For desorption studies, wool-g-PCAH fibers (0.2 g) were loaded with metal ions (Hg²⁺, Cu²⁺ and Co²⁺) using 200 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 wool-g-PCAH



Scheme 1. Schematic presentation for the preparation of wool-g-PCAH.

fibers were collected, and gently washed with distilled water to remove any unadsorbed 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-PCAH fibers was calculated from the amount of metal ions adsorbed on wool-g-PCAH 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-PCAH chelating fibers

The synthetic reactions of wool-g-PCAH chelating fibers were carried out in three steps. The first step involved the graft copolymerization of PAN onto wool fibers using KMnO_4 /oxalic acid as a combined redox initiator. The formed free radicals of the type $\cdot\text{COO}^-$ [23] abstract hydrogen atom from certain functional groups such as $-\text{OH}$, $-\text{SH}$, $-\text{COOH}$, $-\text{NH}_2$ and $-\text{NH}-$ to form active sites on wool backbone to start the grafting reaction.

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

3.2. FTIR characterization of the fibers

The IR spectra of pure wool and graft copolymer; wool-g-PAN with GP values 160%, wool-g-PAH and wool-g-PCAH 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 $3150\text{--}3500\text{ cm}^{-1}$ which may be related to the $-\text{NH}-$ stretching and $-\text{SH}$ bonds, as well as strong peaks at 1630 , 1535 , and 1230 cm^{-1} belonging to $-\text{CONH}-$ (amide I, amide II and C–N stretching of amide III, respectively) [17]. However, the IR spectrum of the graft copolymer (Fig. 1b) shows partial disappearance of the broad peak of $-\text{NH}-$, $-\text{SH}$ that has been found in pure wool spectrum (Fig. 1a). Additionally, a new peak is also observed at 2350 cm^{-1} that is related to cyano groups of PAN 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

3150 cm^{-1} which may be related to the two $-\text{NH}_2$ groups of the resulted hydrazidine, in addition to the clear disappearance of the cyano group peak from 2350 cm^{-1} and appearance of new peak at 1639 cm^{-1} which may be due to the $\text{C}=\text{N}$ groups. On the other

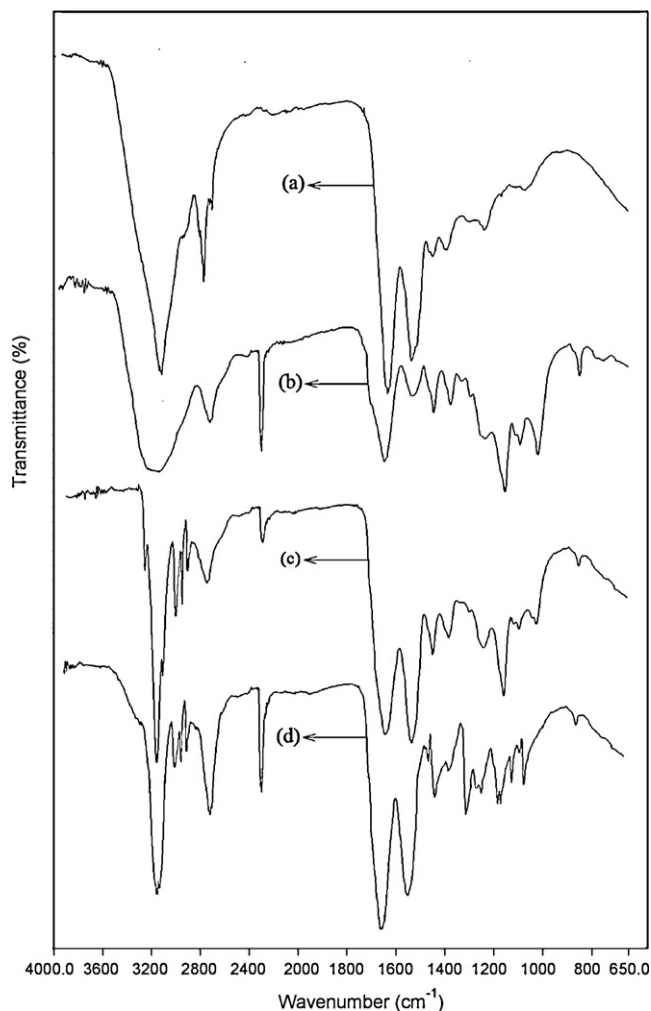


Fig. 1. FTIR spectra of (a) native wool, (b) wool-g-PAN, (c) wool-g-PAH and (d) wool-g-PCAH.

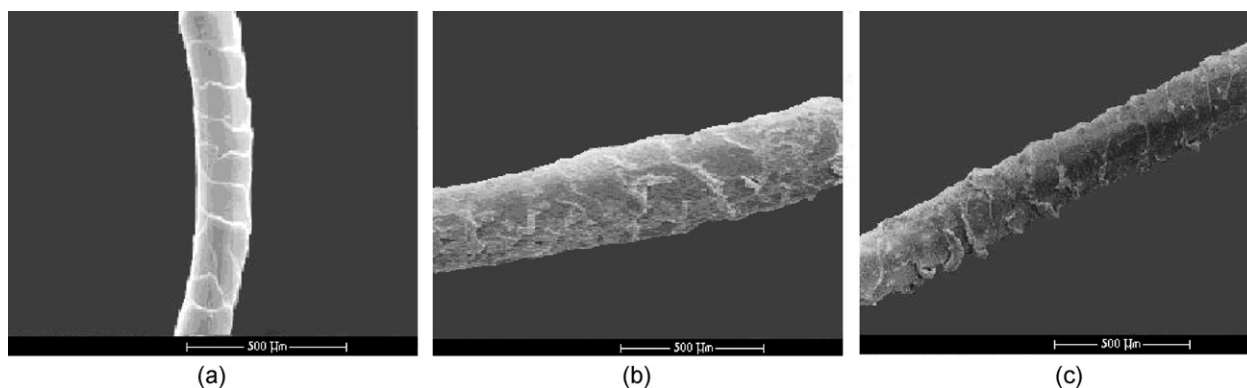


Fig. 2. SEM photos of modified and unmodified wool fibers. (a) Native unmodified wool fibers, (b) Wool-g-PAN, and (c) Wool-g-PCAH.

hand, the IR spectrum of wool-g-PCAH chelating fibers (Fig. 1d) presents an increase in the intensity of the sharp peak at 1639 cm^{-1} which may be attributed to the resulted hydrazide carbonyl groups ($-\text{CO}-\text{NH}-$) of the formed poly(cyano-acetic acid α -amino-acrylic-hydrazide). Also, the observed reappearance of the cyano sharp peak at 2350 cm^{-1} may confirm the insertion of the ethylcyanoacetate units.

3.3. Characterization of the fiber surface

Some scanning electron microscopy (SEM) images of the modified and unmodified wool fibers are shown in Fig. 2. The typical unmodified wool fibers with distinct overlapped tile-like edges are microscopically demonstrated in Fig. 2a. Also, the grafted wool fibers show an observed increase in roughness (Fig. 2b) which may be due to the insertion of the PAN chains onto the fiber surface. On the other hand, the roughness of the surface of the modified wool-g-PCAH chelating fibers (Fig. 2c) increase greatly which may confirm the partial conversion of PAN into PCAH grafted chains.

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 \AA , respectively [17], while the more intensive peaks of wool-g-PAN and wool-g-PCAH at around $2\theta = 17^\circ$ (Fig. 3b and c) were due to the overlapped diffraction peaks from the PAN's crystal planes of

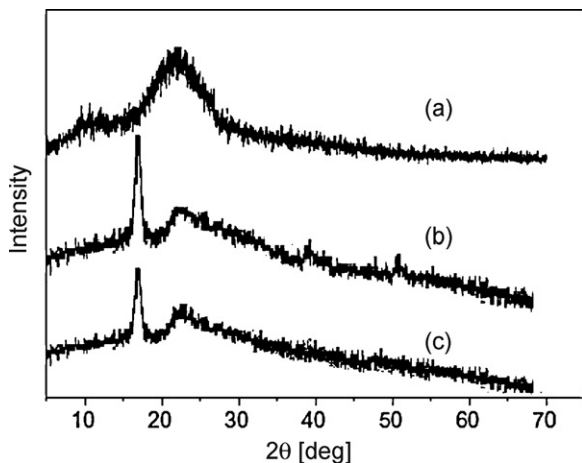


Fig. 3. X-ray diffraction pattern of (a) native unmodified wool fibers, (b) wool-g-PAN, and (c) wool-g-PCAH.

(110) and (200) [24]. Consequently, PAN had grown into enough long chain to form the regular crystalline region during the graft copolymerization. On the other hand, in the spectrum of wool-g-PAN, it is observed that diffraction intensity of the peak at around 22° was obviously weakened indicating that the crystallinity of the wool α -keratins decreased after modification.

3.5. Effect of pH on metal ion adsorption

The pH values selected in the experiments were prior to the precipitation limit of the metal ions (pH 6) as reported in previous reports [25,26]. 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-PCAH. At $\text{pH} < 2$, no appreciable uptake was detected for Co^{2+} ions. The results indicate that the adsorption percent of Hg^{2+} is higher than that of Cu^{2+} and Co^{2+} ions in all pH ranges studied, suggesting possible selectivity for this metal.

Wool-g-PCAH is almost insoluble in acidic and alkaline mediums. Neither obvious leakage of the fiber material nor changes of wool-g-PCAH was observed in the experimental process. Wool-g-PCAH becomes more resistant to lower and higher pH values compared to their parent wool fibers due to the insertion of hydrophobic grafted chains.

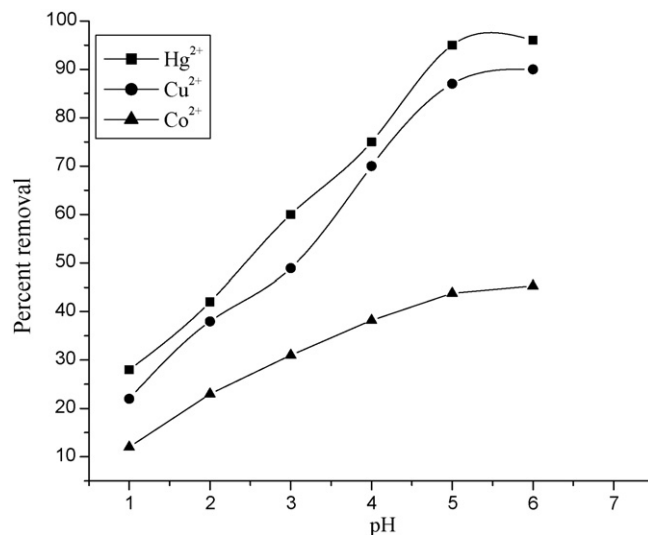


Fig. 4. Effect of pH on the uptake of Hg^{2+} , Cu^{2+} , and Co^{2+} ions by wool-g-PCAH (initial concentration 100 mg/l ; wool-g-PCAH 1 g/l ; contact time 3 h ; shaking rate 150 rpm ; 30°C).

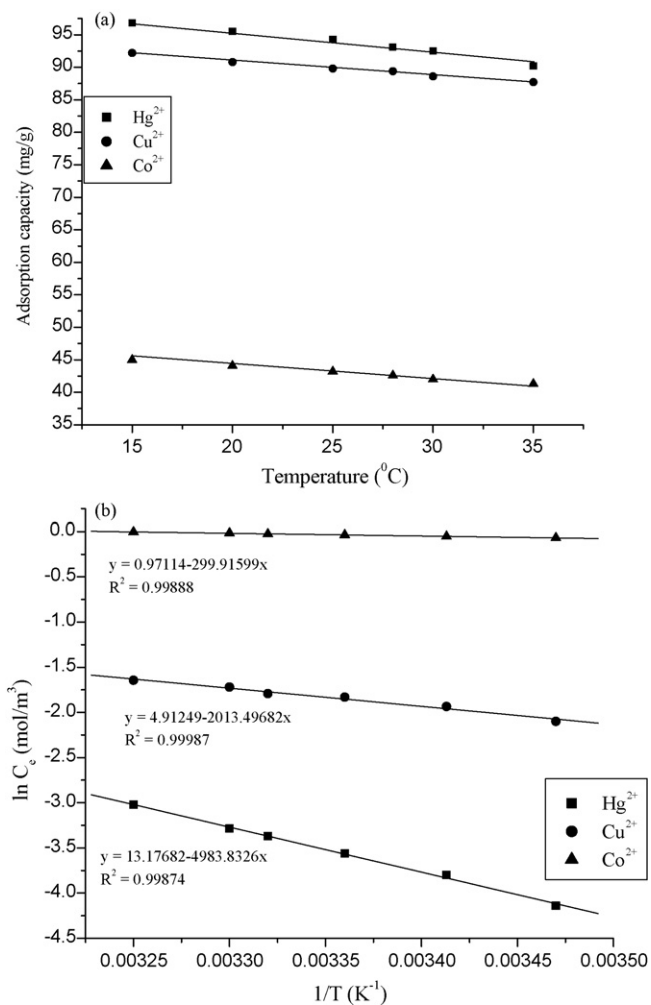


Fig. 5. (a) Effect of temperature on the uptake of Hg²⁺, Cu²⁺, and Co²⁺ ions by wool-g-PCAH (initial concentration 100 mg/l; wool-g-PCAH 1 g/l; pH 5.0; contact time 3 h; shaking rate 150 rpm; 15–35 °C) and (b) the plot of ln C_e against 1/T.

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-PCAH is weak 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 [27]:

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

where R is molar gas constant (8.314 J/molK). For this purpose, the equilibrium concentrations (C_e) at constant amount of the adsorbed metal ions are 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 -41 ± 1.2 , -16 ± 0.70 , and -2 ± 0.5 kJ/mol for Hg²⁺, Cu²⁺ and Co²⁺ ions, respectively. This indicated that the adsorption process was exothermic in nature. As the adsorption process is usually accompanied by a decrease in the entropy (ΔS is negative) so increasing the temperature will lead to a decrease in the negativity of ΔG value

and subsequently retard the interaction between the wool-g-PCAH and the metal ions.

3.7. Adsorption kinetics

Fig. 6 shows the kinetics of the adsorption of metal ions Hg²⁺, Cu²⁺ and Co²⁺ by wool-g-PCAH chelating fibers. Investigating the uptake–time curves show that the maximum uptake follows the order Hg²⁺ > Cu²⁺ » Co²⁺ at all time intervals. The kinetic curves for Hg²⁺ and Cu²⁺ ions showed that the adsorption was initially rapid, and reached equilibrium after approximately 60 min and remained constant until the end of the experiment. Co²⁺ ions adsorption showed the slowest kinetic profile of all, reaching equilibrium after approximately 90 min.

The uptake time data obtained were treated in the form of two simplified kinetic models including pseudo-first and pseudo-second-order. The pseudo-first-order model is expressed as shown in Eq. (2) [28]:

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \quad (2)$$

where k_1 (min⁻¹) is the pseudo-first-order rate constant 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 values of $1/q_t$ were calculated from the experimental results and plotted against $1/t$ (min⁻¹). On the other hand, the pseudo-second-order model is expressed as shown in Eq. (3) [29]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e} \right) t \quad (3)$$

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

The aforementioned two models are 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 [25,26]. Consequently, the adsorption rate may be controlled by intraparticle diffusion or interaction step. The kinetic parameters for adsorption of Hg²⁺, Cu²⁺ and Co²⁺ ions by wool-g-PCAH chelating fibers are given in Table 1. The experimental q_e values are in agreement with the calculated values using pseudo-first-order and pseudo-second-order kinetics. Based on the obtained correlation coefficients (R^2), the pseudo-second-

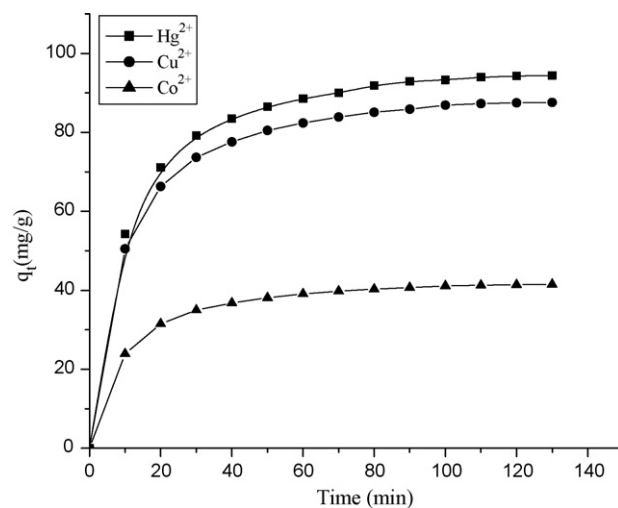


Fig. 6. Effect of contact time on the uptake of Hg²⁺, Cu²⁺, and Co²⁺ ions by wool-g-PCAH (initial concentration 100 mg/l; wool-g-PCAH 1 g/l; pH 5.0; shaking rate 150 rpm; 30 °C).

Table 1
Kinetic parameters for Hg²⁺, Cu²⁺, and Co²⁺ ions adsorption by wool-g-PCAH.

Metals	k_1 (min ⁻¹)	q_{e1} (mg/g)	R^2
First-order model			
Hg ²⁺	8.68	101 ± 3	0.9576
Cu ²⁺	8.56	94 ± 2	0.9435
Co ²⁺	8.32	44 ± 3	0.9543
Metals	k_2 (g/(mg min))	q_{e2} (mg/g)	R^2
Second-order model			
Hg ²⁺	1.19×10^{-3}	101 ± 2	0.9997
Cu ²⁺	1.29×10^{-3}	94 ± 0.7	0.9989
Co ²⁺	2.77×10^{-2}	44 ± 1	0.9999

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 [30,31]. The adsorption of the investigated metal ions onto wool-g-PCAH may be considered to consist of two processes with initial adsorption rate of 5.52, 5.06, and 2.21 mg/(g min) for Hg²⁺, Cu²⁺ and Co²⁺ ions, respectively.

Wool-g-PCAH chelating fibers are characterized by its high percentage of nitrogen and sulfur contents in form of -NH₂, C=N, -CO-NH-, -CN of the grafted PAN chains and inserted cyano-acetic hydrazide units in addition to the sulfur containing amino acids which are essential component in the structure of the wool protein that are responsible for metal ion binding through chelation mechanisms.

The pseudo-second-order kinetic model also provided the best correlation of the experimental data in the studies carried out by Atia et al. [32] on adsorption of Hg²⁺, Cu²⁺, and Ni²⁺ ions onto Co₃O₄⁻ containing resin; by Sag and Aktay [33] on adsorption of Cr⁶⁺ and Cu²⁺ ions onto chitosan; by Zhou et al. [25] on adsorption of Hg²⁺, Cu²⁺ and Ni²⁺ ions; by modified chitosan magnetic resin and by Wu et al. [31] on adsorption of Cu²⁺ ions onto chitosan in the presence of complexing agents which are in agreement with the kinetic results found in our study.

3.8. Adsorption isotherms

Fig. 7 shows the adsorption equilibrium isotherms obtained for Hg²⁺, Cu²⁺, and Co²⁺ ions by wool-g-PCAH chelating fibers. For

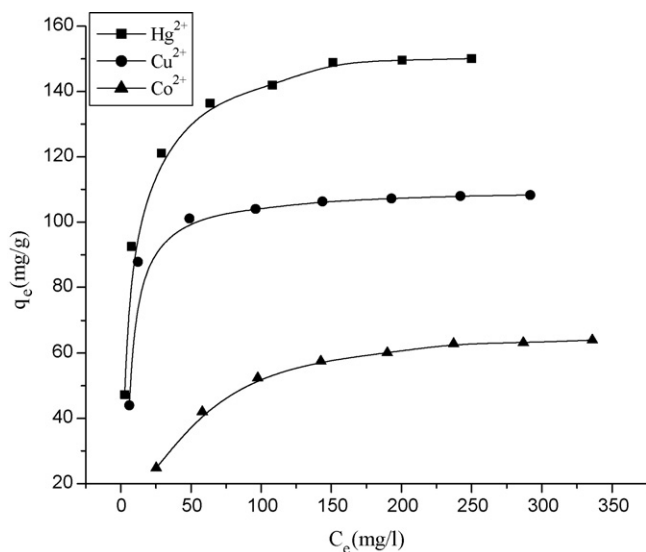


Fig. 7. Adsorption isotherms of Hg²⁺, Cu²⁺, and Co²⁺ ions by wool-g-PCAH (initial concentration 50–400 mg/l; wool-g-PCAH 1 g/l; pH 5.0; shaking rate 150 rpm; 30 °C).

Table 2
Parameters for Hg²⁺, Cu²⁺ and Co²⁺ ions adsorption by wool-g-PCAH according to different equilibrium models.

Metals	K_L (l/g)	q_m (mg/g)	R^2
Langmuir isotherm constants			
Hg ²⁺	14.43×10^{-2}	154.32	0.9998
Cu ²⁺	17.4×10^{-2}	110.49	0.9997
Co ²⁺	2.38×10^{-2}	72.88	0.9999
Metals	K_F	n	R^2
Freundlich isotherm constants			
Hg ²⁺	48.394	4.411	0.9445
Cu ²⁺	43.081	5.576	0.8789
Co ²⁺	9.274	2.581	0.9577
Metals	$\ln A$	B	R^2
Tempkin isotherm constant			
Hg ²⁺	1.823	21.64	0.9543
Cu ²⁺	2.864	13.44	0.8897
Co ²⁺	1.357	15.16	0.9456

interpretation of the adsorption data, the Langmuir [34], Freundlich [35], and Tempkin and Pyzhev [36] isotherm models were used (Eqs. (4)–(6)).

The linear form of the Langmuir isotherm is given by

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_m} \right) + \left(\frac{C_e}{q_m} \right) \quad (4)$$

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

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \quad (5)$$

where both K_F and n are constants.

The Tempkin isotherm has been used in the following form [36]:

$$q_e = \left(\frac{RT}{b} \right) \ln A + \left(\frac{RT}{b} \right) \ln C_e \quad (6)$$

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 Hg²⁺, Cu²⁺, and Co²⁺ ions by wool-g-PCAH are shown in Table 2. For the three studied systems, the Langmuir isotherm showed more significant correlation ($R^2 > 0.997$) than in case of Freundlich and Tempkin isotherm with the experimental data from adsorption equilibrium of metal ions by wool-g-PCAH chelating fibers suggested a monolayer adsorption. The maximum adsorption values were 154.32, 110.49, and 72.88 mg/g for Hg²⁺, Cu²⁺, and Co²⁺ ions, respectively, which are in agreement with the experimentally obtained values. The maximum adsorption capacity (q_m) obtained by Langmuir isotherm for Hg²⁺ was higher than the values found for Cu²⁺ and Co²⁺, showing the following capacity order: Hg²⁺ > Cu²⁺ > Co²⁺. The higher affinity for Hg²⁺ than that for Cu²⁺ and Co²⁺ may be attributed to the involvement of the sulfur 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 sulfur [25,26]. The higher affinity toward Cu²⁺ than Co²⁺ is in agreement with the study carried out by Vold et al. [37], where chitosan adsorbed Cu²⁺ selectively in the presence of Ni²⁺, Zn²⁺, and Cd²⁺ ions, even though no selectivity was observed for the other ions in the absence of Cu²⁺.

Varma et al. [38] reported that polymeric derivatives containing nitrogen as heteroatom, presented the order of affinity for divalent

Table 3
Desorption ratio of Hg²⁺, Cu²⁺ and Co²⁺ ions for various concentration of EDTA.

Concentration of EDTA	Desorption ratio (%)		
	Hg ²⁺	Cu ²⁺	Co ²⁺
0.1	93.3	96.2	93.5
0.05	92.1	94.1	90.5
0.01	87.8	89.3	84.3
0.005	76.4	72.6	74.2
0.001	60.2	58.3	62.5

Table 4
Repeated adsorption of Hg²⁺, Cu²⁺, and Co²⁺ ions by wool-g-PCAH (initial concentration 100 mg/l, wool-g-PCAH 1 g/l, pH 5.0, contact time 3 h, shaking rate 150 rpm, 30 °C).

Cycle number	Adsorption capacity (%)		
	Cu ²⁺	Hg ²⁺	Ni ²⁺
1	100	100	100
2	99.5	99.2	98.4
3	97.9	98.5	97.6
4	95.8	96.3	95.8
5	92.4	91.6	90.7

metal ions Cu²⁺ > Cd²⁺ > Ni²⁺ which agrees with the one observed in this study. Also, The higher affinity for Cu²⁺ than that for Co²⁺ may be attributed to the high stability constants of Cu²⁺ with amine molecules having nitrogen atom as a ligand [30], or may also be due to Jahn–Teller effect which is predominant for copper complexes [25,39].

These results indicated that chemical modification of wool fibers with polycyano-acetic acid α -amino-acrylic-hydrazide improved the adsorption capacity for the investigated metal ions, especially for Hg²⁺ and Cu²⁺ ions.

3.9. Desorption characteristics

As shown in Table 3, the desorption ratios of metal ions using 0.1 M EDTA were 93.3, 96.2 and 93.5% for Hg²⁺, Cu²⁺, and Co²⁺, respectively. The desorption ratio of metal ions increased as EDTA concentration increased. However, the desorption ratios of the investigated ions were more than 84% and were 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-PCAH 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.

4. Conclusions

Chemically modified wool chelating fibers wool-g-PCAH were prepared and tested against the removal of Hg²⁺, Cu²⁺, and Co²⁺ from their aqueous solutions. Hg²⁺ showed higher adsorption affinity towards the studied fibers relative to Cu²⁺, and Co²⁺. The adsorption kinetics followed the pseudo-second-order equation for all systems have been studied. The equilibrium data were well described by the Langmuir isotherm. Regeneration of the fibers obtained was achieved by using 0.01–0.1 M EDTA with efficiency greater than 84%. Feasible improvements in the uptake properties encourage efforts for wool-g-PCAH obtained to be applied for water and wastewater treatment.

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