

Preparation and Characterization of Selective Phenyl Thiosemicarbazide Modified Au(III) Ion-Imprinted Cellulosic Cotton Fibers

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ABSTRACT: In this study, a novel selective Au(III) chelating surface ion imprinted fibers based on phenyl thiosemicarbazide modified natural cotton (Au-C-PTS) has been synthesized, and applied for selective removal of Au(III) from aqueous solutions. Batch adsorption experiments were performed with various parameters, such as contact time, pH, initial Au(III) concentration, and temperature. The kinetic studies revealed that the adsorption process could be described by pseudo-second-order kinetic model, while the adsorption data correlated well with the Langmuir and Freundlich models. The maximum adsorption capacities calculated from the Langmuir equation are $140 \pm 1 \text{ mg g}^{-1}$ and $72 \pm 1 \text{ mg g}^{-1}$ at pH 5 for both Au-C-PTS and NI-C-PTS, respectively. The estimated thermodynamic parameters (Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy change (ΔS°)) indicated the spontaneity and exothermic nature of the adsorption process. Furthermore, the selectivity study revealed that the ion imprinted fibers was highly selective to Au(III) compared with Cu(II), Cd(II), Hg(II), and Fe(III). The adsorbent was successfully regenerated with a 0.1M HNO₃ solution. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40769.

KEYWORDS: adsorption; cellulose and other wood products; molecular recognition

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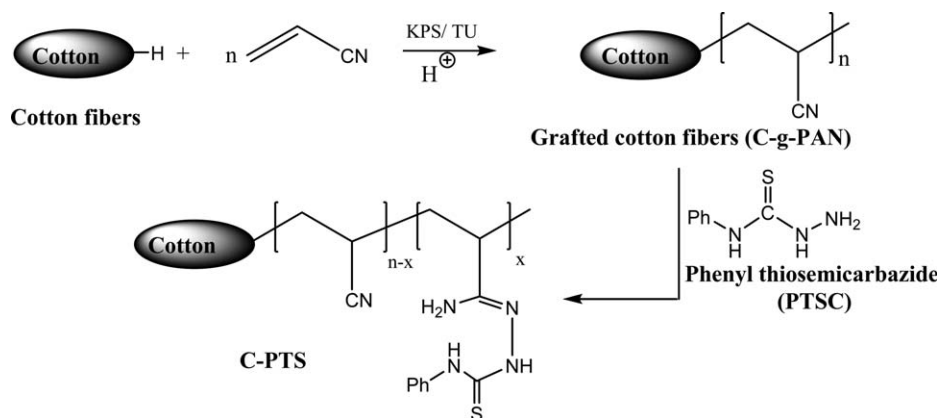
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INTRODUCTION

Recently, precious metals, particularly gold, have been extensively employed in various fields of applications. In addition to traditional jewelry materials, gold was utilized in some technologies and industries such as electronics, sensors, catalysis, and anticorrosion materials.^{1,2} Furthermore, recent studies were conducted to examine the utility of gold and precious metals in new applications such as renewable energy,³ pharmaceuticals,⁴ and environment.⁵ Gold exist in limited sources and usually other metals may coexist with it and subsequently, the conventional extraction technique using aqua regia will give a mixture of chlorocomplexes along with that of gold. In addition, the recovery of gold from electronic wastes may also face the same problem of the coexistence of other metals with gold.^{2,6,7} For these reasons, many efforts have been devoted for development of efficient techniques to selectively extract gold from its primary and secondary sources. These techniques include electro-deposition, solvent extraction and ion exchange process.⁸ Among these methods, adsorption onto active adsorbents considered one of the most common and preferred methods, especially from the economic point of view.⁹ Various adsorbents were developed for removal of gold such as chitosan derivatives² and chelating synthetic polymers.^{10,11} However, the main drawback of the previously mentioned methods is

the lack of selectivity, which increases the motivations to produce more efficient materials for selective removal and recovery of the targeted precious metal ions.

Molecular imprinting technique is a type of relatively new strategy for preparation of smart materials, which are able to selectively bind with particular specific target molecules or ion in presence of other interfering species.^{12–17} The conventional technique for synthesis of molecular imprinted polymers (MIPs) involve three main steps started with the interaction between the template target specie and polymerizable monomer, polymerization of the template-monomer complex in presence of suitable cross-linker and finally, elimination of the imprint species from the polymeric network leaving active recognition cavities match the geometry, shape, and size of the template specie.¹⁸ Numbers of MIPs have been synthesized for selective extraction and separation of various species such as amino acids,^{19,20} biologically active substances,^{21,22} and heavy metal ions.^{23–26} However, molecular imprinting technique according to the above conventional strategy may create some drawbacks such as entrapment of the template molecules or ions in the bulk of the cross-linked network, which will subsequently retard the rebinding abilities and irregular distribution of the recognition sites on the polymeric material.²⁷



Scheme 1. Synthesis of C-PTS chelating fibers.

Surface imprinting is another similar technique, which has been recently developed to avoid the disadvantages observed in the conventional molecular imprinting methods. In surface imprinting, the specific recognition cavities are created on the surface of a support material such as silicates, graphene or polymeric materials in form of beads or fibers.^{23,26,28–31} In this technique, the finally produced molecularly imprinted material maintains the original shape of the support material.

As a result of the well known high stability of the Au(III) complexes with thiosemicarbazide derivatives,^{32,33} active phenyl thiosemicarbazide moieties were chosen to functionalize the natural cellulosic cotton fibers in order to produce a novel Au(III) ion-imprinted chelating fibers (Au-C-PTS). The obtained fibers were fully characterized using various instrumental techniques such as SEM, FT-IR, XRD, and XPS spectra. The potential of the obtained fibers were then evaluated for selective removal of Au(III) ions from aqueous solution in presence of other interfering metal ions. In addition, the essential uptake parameters such as pH, temperature, contact time, and adsorption isotherms were also investigated.

EXPERIMENTAL

Materials

Cotton fibers were collected from the farm of the Manoura high agriculture school and treated by scouring in 1% (w/v) NaOH solution, desizing in 1% (v/v) H₂SO₄ solution and finally washed by distilled water and ethanol then dried in oven at 40°C for 24 h. Acrylonitrile (AN) (Sigma-Aldrich) were treated by 3% (w/v) NaOH to remove the stabilizer and then washed with double distilled water till alkali free. Potassium persulfate (KPS) (Sigma-Aldrich), Thiourea (TU) (BDH-England); phenyl thiosemicarbazide (PTSC), Glyoxal and AuCl₃ were purchased from Sigma Aldrich. All chemicals were used as received.

Synthesis of (Au-C-PTS) Ion-Imprinted Fibers

In the first synthetic step, cotton fibers were modified by free radical graft copolymerization of polyacrylonitrile (PAN) using KPS/TU combined redox initiator. Dry cotton fibers (0.1 g) was placed in 100 mL conical flask and to which 50 mL aqueous solution containing a mixture of 2 mmol KPS and 2 mmol TU

was added; 0.5 mL 1% (v/v) H₂SO₄ solution was then added and the reaction mixture was then strongly shaken for about 10 min. AN monomer (2 mL) were then injected to the reaction mixture and the stirring was continued for an additional 2 h at 80°C. After this period, the reaction was terminated by adding 10 mL 3% (w/v) Hydroquinone solution. The grafted fibers were then eliminated from the reaction mixture, washed with DMF at 80°C to extract the PAN homopolymer and finally, the grafted fibers were dried at 50°C for 24 h.

The following mathematical expression was employed to estimate the grafting percentage (GP).

$$\text{Grafting Percentage (GP)} = (A - B/B) \times 100 \quad (1)$$

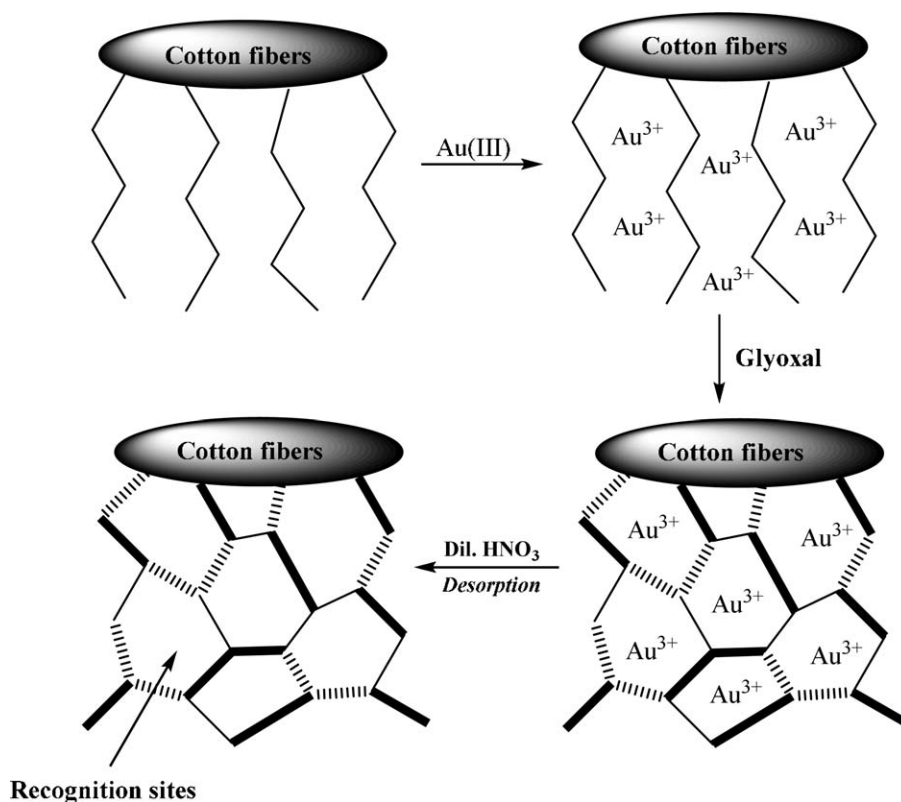
where *A* and *B* are the weight of grafted product and native cotton fibers, respectively.

The prepared grafted cotton fibers with GP values 135% were named as C-g-PAN.

The subsequent step involves the insertion of the active PTSC units onto the modified C-g-PAN fibers. The previously prepared dried grafted fibers were immersed in 100 mL 10% (w/v) alcoholic PTSC solution and the reaction flask was conducted to a reflux condenser and the temperature was raised to 80°C for 4 h. The modified chelating fibers (C-PTS) were then removed and washed with ethanol and dried at 40°C till constant weight. Scheme 1 presents the synthetic reactions involved in the preparation of C-PTS chelating fibers.

Loading of the C-PTS with Au(III) ions were performed by soaking the previously prepared C-PTS fibers into 50 mL 100 mg/L Au(III) solution at pH 5. The mixture was agitated on a shaker at 150 rpm for 3 h at 30°C. The Au-C-PTS fibers were then extracted from the mixture, washed with distilled water, and immersed in 50 mL glyoxal solution. The mixture was refluxed in water bath at 80°C for about 4 h.

The ion-imprinted Au-C-PTS were finally prepared by leaching the Au(III) from the cross-linked network. This was achieved by agitating the Au(III) loaded cross-linked fibers with 100 mL 0.1M HNO₃ solution for 3 h at 30°C. This process were repeated several times till no Au(III) detected in the filtrate. For comparison reason, nonimprinted fibers (NI-C-PTS) were



Scheme 2. Ion-imprinting of Au(III) ions onto C-PTS fibers.

prepared with the same procedure but in absence of Au(III) ions. The imprinting process was schematically illustrated in Scheme 2.

Samples Characterization

Perkin–Elmer 240 C Elemental Analytical Instrument (USA) was utilized for elemental analysis of native cotton fibers, C-g-PAN and C-PTS. Perkin–Elmer spectrophotometer supplied with ATR instrument was employed for FT-IR spectra of the dried modified samples. Scanning electron microscope (SEM) (FEI Quanta-200 Company, The Netherlands) were used for visualizing the surface morphology of both native and modified fibers. ASAP 2010 Micromeritics instrument with Micromeritics software was used to measure the specific surface area through the BET method.

X-ray powder diffractometer (Japanese Dmax-rA, wavelength = 1.54 Å, Cu-K α radiation) was performed to determine the crystallinity of native and modified cotton samples. A continuous scan mode was applied to collect $2\theta = 5\text{--}60^\circ$. X-ray photoelectron spectrometry (XPS) of the modified and nonmodified fibers were performed in FAT mode with the X-ray gun of Mg target (1486.6 eV) at the power of 12 kV \times 15 mA, and the analytical background vacuum of 2×10^{-7} Pa, the channel energy of 100 eV and the step length of 0.1 eV/s, using a Kratos XSAM-800 multifunctional spectrometric apparatus (VG Science Instrument Co. Ltd., Britain). The surface of samples were sputtered with the Ar $^+$ ion to eliminate interference from contaminated substances and subsequently preserved in high vacuum.

Adsorption and Desorption Experiments

Effect of pH. The selective removal of Au(III) using Au-C-PTS and NI-C-PTS was carried out by placing 0.03 g of the fibers under study in 30 mL 100 mg/L aqueous Au(III) solution. The mixture was agitated on a shaker at 150 rpm for 3 h at 30°C. The adsorption was performed in pH range 1 to 5 using KCl/HCl for pH 1, 2, and 3; CH₃COOH/CH₃COONa for pH 4 and 5. The residual Au(III) content was then estimated using Perkin–Elmer Model 5000 atomic absorption spectrometer (Perkin–Elmer, Shelton, CT). The instrument was set at 242.795 nm.

Effect of the Temperature. Studied fibers (0.03 g) was agitated on a shaker at 150 rpm with 30 mL 30 mg/L Au(III) solution in a series of flasks at pH 5 and 30°C for 3 h. The experiments were performed under temperature range 20 to 40°C. The residual Au(III) concentration were then estimated.

Effect of Contact Time. For kinetic studies, 0.3 g of the studied fibers were equilibrated with 300 mL 100 mg/L aqueous Au(III) solution on a shaker at 150 rpm at pH 5 and 30°C. Each 10 min an aliquot of about 0.5 mL was taken to estimate the residual Au(III) content.

Adsorption Isotherm Studies

The adsorption isotherm studies for both Au-C-PTS and NI-C-PTS were carried out by equilibrating 0.03 g of the studied fibers with 30 mL Au(III) in a series of flasks with concentration range 10 to 400 mg/L at pH 5, 30°C for 3h. The residual Au(III) content was then determined.

Table I. Elemental Analysis of Cotton, C-g-PAN, and C-PTS

Fibers	C(%)	H(%)	O(%)	N(%)	S(%)
Cotton	42.3	5.99	50.98	0	0
C-g-PAN	57.1	5.9	21.8	15.39	0
C-PTS	53.01	5.48	7.61	21.8	12.7

The following series of equations were utilized to estimate the adsorption values:

$$q_e = (C_i - C_e)V/W \quad (2)$$

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

$$\text{Percent removal (\%)} = (C_i - C_e) \times 100 / C_i \quad (3)$$

Selective Adsorption

The competitive extraction of Au(III) ions was examined in a batch containing multi-component solution containing Cu(II), Cd(II), Hg(II), Fe(III) in addition to Au(III) each metal ion with initial concentration 20 mg/L. Studied fibers (Au-C-PTS or NI-C-PTS) (0.3 g) was agitated with 300 mL of the previously mentioned multicomponent solution on a shaker at 150 rpm at pH 5 and 30°C for 3 h. The residual content of each metal was determined using atomic absorption. The selectivity coefficient is defined as:^{34,35}

$$\beta_{\text{Au}^{3+}/M^{n+}} = D_{\text{Au}^{3+}} / D_M^{n+} \quad (4)$$

where $D_{\text{Au}^{3+}}$ and D_M^{n+} are the distribution ratios of the Au(III) ions and other coexistent cations, respectively. The distribution ratio (D) was calculated by using the following expression:

$$D = [(C_i - C_e) / C_e] V / W \quad (5)$$

Selectivity coefficient β_r was determined to evaluate the effect of the imprinting effect on the selectivity.³⁶

$$\beta_r = \beta_{\text{imprint}} / \beta_{\text{nonimprint}} \quad (6)$$

where β_{imprint} and $\beta_{\text{nonimprint}}$ are the selectivity coefficients of Au-C-PTS and NI-C-PTS fibers, respectively.

Desorption and Reuse After Desorption

Desorption and regeneration of the ion-imprinted Au-C-PTS was performed using 0.1M HNO₃ solution. The Au(III) ions loaded fibers was immersed in 100 mL nitric acid solution at 30°C. The mixture was agitated for 4 h on a shaker at 150 rpm. The desorbed Au(III) ions concentration was estimated and the fibers was removed, washed several times with deionized water, and reused again in the removal process. The adsorption-desorption cycle was repeated for five times.

RESULTS AND DISCUSSION

We have previously described modifications of cotton fibers through acrylonitrile grafting followed by ligand modification (see Scheme 1). For the purpose of gold recovery, the ligand

selected was a phenyl thiosemicarbazide (PTSC)^{32,33} similar to that of Marwani et al.³⁷

Characterization of the Polymeric Samples

Table I collects the elemental analysis data of both native and modified cotton fibers, the presence of nitrogen in C-g-PAN may give an evidence for the grafting of the PAN chains onto the cellulose backbone. Furthermore, the further modification upon treatment with PTSC was confirmed by the increase of sulfur and nitrogen content in case of C-PTS. The results indicated that the inserted PTSC units were estimated to be 3.97 mmol g⁻¹.

The morphological structure of native cotton fibers, NI-C-PTS and Au-C-PTS were examined using SEM and the obtained photos were presented in Figure 1. The obvious increase in size observed in case of NI-C-PTS and Au-C-PTS compared with the native cotton fibers, gives a clear evidence for the insertion of the PAN chains and subsequent modification using PTSC. In addition, the rough porous surface exhibited by Au-C-PTS, could be explained as a result of template Au(III) ions leaching from the cross-linked polymeric network created on the surface of the cellulosic cotton fibers.

The surface area measurements utilizing BET method indicated that the surface area of native cotton, NI-C-PTS and Au-C-PTS were 2.432, 3.345, and 7.454 m²/g. The observer higher surface area exhibited by Au-C-PTS could be due to the porous structure observed in Figure 1(c). Also, the relatively low surface area of the chelating fibers, confirms the adsorption of the precious Au(III) ions through the coordination with the inserted functional groups.

The successive modification steps of the cotton fibers were detected using FT-IR spectra and the results presented in Figure 2. The native cotton fibers [Figure 2(a)] showed the diagnostic peaks correspond to the cellulose backbone at 1070–1150 cm⁻¹, 1260–1410 cm⁻¹, 3600–3100 cm⁻¹, which are due to C–O stretching, O–H bending and stretching, respectively.³⁸ Also, the grafting of the PAN was obviously confirmed by the appearance of the characteristic –CN peak at approximately 2350 cm⁻¹ [Figure 2(b)]. Furthermore, the insertion of the PTSC moieties was revealed by the clear partial disappearance of the –CN peak and appearance of new signals at diagnostic C=S peaks at 1300 cm⁻¹ and 870 cm⁻¹, in addition to the peaks at 1580 cm⁻¹ and 770 cm⁻¹, which are related to the C=C and C–H of the inserted aromatic moieties.

As a result of the thioamide function group (NH–C=S), thiosemicarbazide derivatives may exist in thion-thiol tautomeric forms.³⁹ The chelating fibers C-PTS did not exhibit the thiol

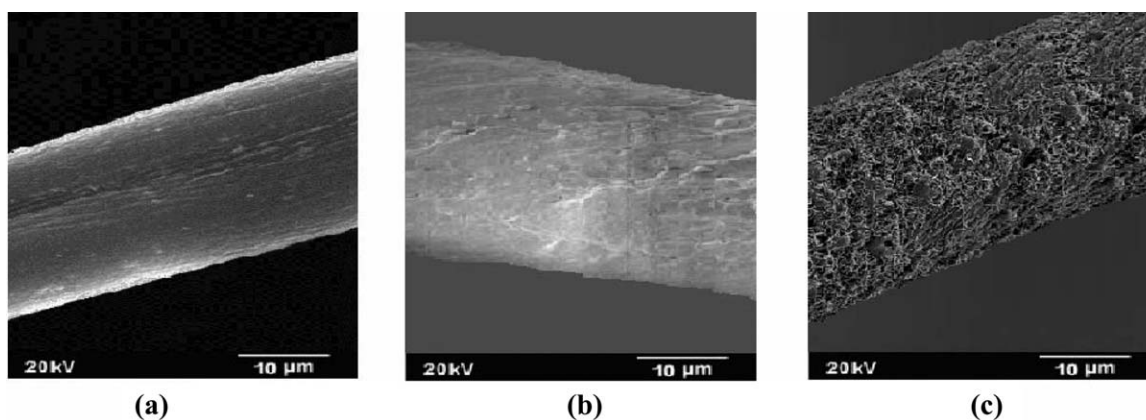


Figure 1. SEM photos of modified and unmodified cotton fibers. (a) Native unmodified cotton fibers, (b) NI-C-PTS, and (c) Au-C-PTS.

(S—H) and C—S peaks at 2300 cm^{-1} and 1200 cm^{-1} , respectively. In addition, the presence of the sharp C=S peaks at 1330 cm^{-1} and 870 cm^{-1} indicated the presence of the PTSC units in thion form.

Geometry optimization of PTSC units inserted onto the modified cotton fibers was performed using MM+ forcefield in HyperChem software version 8.03 implemented on a Dell core i5 personal computer and the molecularly modeled structure was presented in Structure 1. The estimated total energy of thion and thiol forms were 3.4886 and 10.3727 kcal/mol, indicating the theoretical stability of thion compared with thiol

form, which in agreement with the experimental results obtained from the IR spectra.

XRD spectra was employed to hit upon the functionalization steps implemented in modification of cotton fibers, Figure 1(a) presents the crystalline pattern of native cotton fibers. As previously reported,⁴⁰ the main cellulosic crystalline peaks are observed at about 15° , 16° in addition to a sharp intense peak at about 23° . Moreover, C-g-PAN exhibited a sharp characteristic PAN peak at about 17° ⁴¹ [Figure 1(b)], revealing the growth of the PAN chains and formation of well organized crystalline pattern. In addition, observed slight lowering of the crystalline peaks of C-PTS [Figure 1(c)] could be related to the conversion of the —CN into $\text{H}_2\text{N}-\text{C}=\text{N}-\text{NH}-\text{CS}-\text{NH}-\text{Ph}$ after treatment with PTSC. Upon glyoxal cross-linking, the crystalline pattern presents an obvious strong decrease, which could be explained as a result of the hydrogen bond breaking and formation of amorphous structure.

The grafting and subsequent chemical modifications of the cotton fibers were also examined using X-ray photoelectron spectroscopy (XPS) which is extensively utilized in surface elemental analysis. The spectrum of the native unmodified cotton fibers [Figure 2(a)] exhibited only two peaks with bonding 286.5 eV and 531.6 eV related to C and O, respectively. However, upon PAN grafting, the spectrum of the grafted C-g-PAN fibers [Figure 2(b)] presents the main C1s peak at 284.9 eV, which could be attributed to the predominant C—C in the grafted cotton fiber surface compared with the predominant C—O in the native fibers. In addition, a new characteristic nitrogen peak was clearly observed at 402.3 eV. Moreover, the insertion of the phenyl thiosemicarbazide moieties was confirmed by the appearance of the S2p peak at 168.8 eV in the spectrum of the modified C-PTS chelating fibers [Figure 2(c)].

Au(III) Extraction Experiments

Effect of pH on Adsorption. Initial pH considered one of the vital parameters influencing the metal ion uptake.⁴² In the current work, the percent removal of Au(III) by Au-C-PTS and NI-C-PTS fibers has been investigated as a function of the initial pH. As can be seen in Figure 3, in both Au-imprinted and non-imprinted fibers, the Au(III) ions exhibit an obvious low values

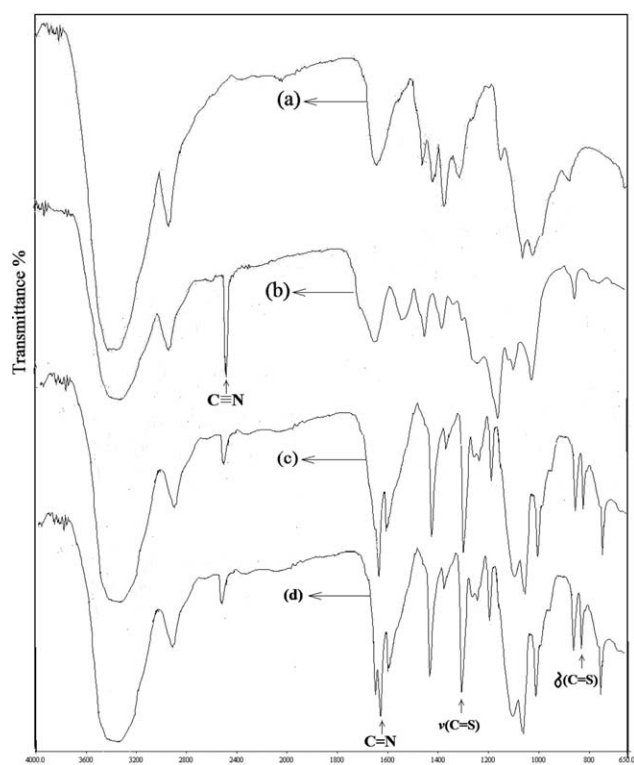
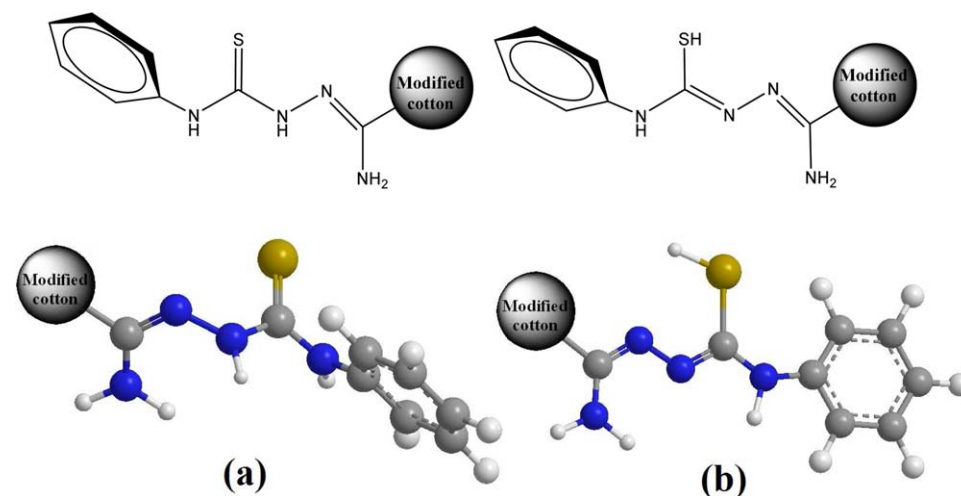


Figure 2. FT-IR spectra of (a) native cotton fibers, (b) C-g-PAN, (c) C-PTS, and (d) cross-linked C-PTS.



Structure 1. Molecular modeling of the chelating fibers active center (a) thion form (b) thiol form. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in strong acidic medium. By rising the pH, the percent removal increases till reaches about 99% and 62% in case of Au-C-PTS and NI-C-PTS, respectively. The low adsorption in acidic medium could be attributed to the high H^+ concentration, which subsequently will compete with the Au(III) ions in coordination with the active functional groups inserted on the modified chelating fibers.

The mechanism through which the C-PTS could coordinate to the Au(III) ions can be evaluated by examining the FTIR spectra of the Au(III) loaded C-PTS fibers and compare it with the Au(III) free fibers. Table II lists the changes of the characteristic

C-PTS peaks, which are expected to be implemented in the Au(III) coordination. The absence of $\nu(S-H)$, $\nu(C=S)$, appearance of $\nu(C-S)$ and $\nu(C=N)^b$, in addition to the lower shift of the $\nu(C=N)^a$ stretching vibration of the complexes, suggested the coordination through the deprotonated thiol and azomethine nitrogen atom and formation of five membered ring as shown in the molecularly modeled Structure 2. This suggestion supported by the marked pH lowering after the Au(III) adsorption from 5 to about 3.

Thermodynamics of Adsorption

The fundamental thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy change (ΔS°) have been evaluated by examining the Au(III) removal by both Au-C-PTS and NI-C-PTS as a function of temperature. The removal experiments were studied by equilibrating 0.03 g of the studied fibers in 30 mL 30 mg/L Au(III) aqueous solution on a shaker at 150 rpm at pH 5 for 3 h in at 20, 30, and 40°C. The following equations were employed for evaluation of the aforementioned thermodynamic parameters.²³

$$K_C = C_{ad} / C_e \quad (7)$$

where K_C is the equilibrium constant, C_{ad} is the concentration of Au(III) ions adsorbed on the fibers at equilibrium (mg/g), and C_e is the equilibrium concentration of Au(III) ions in the solution (mg/L).

ΔG°_{ads} was evaluated as in the following:

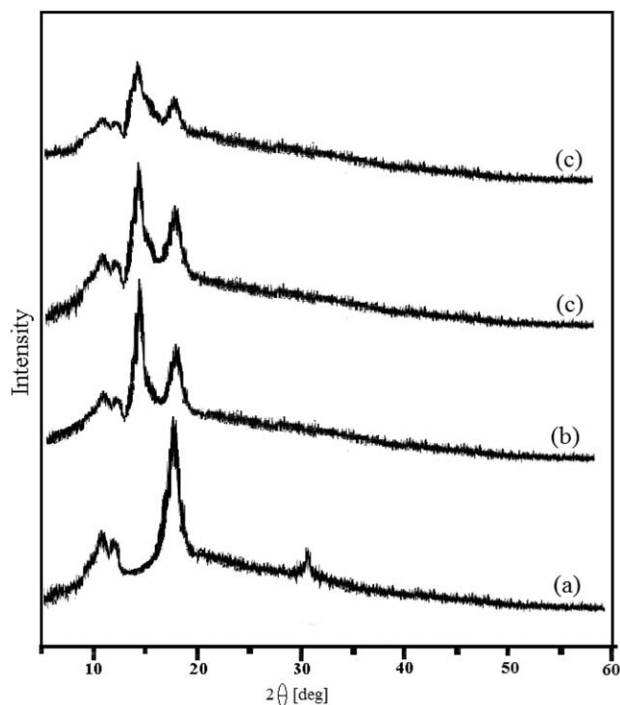


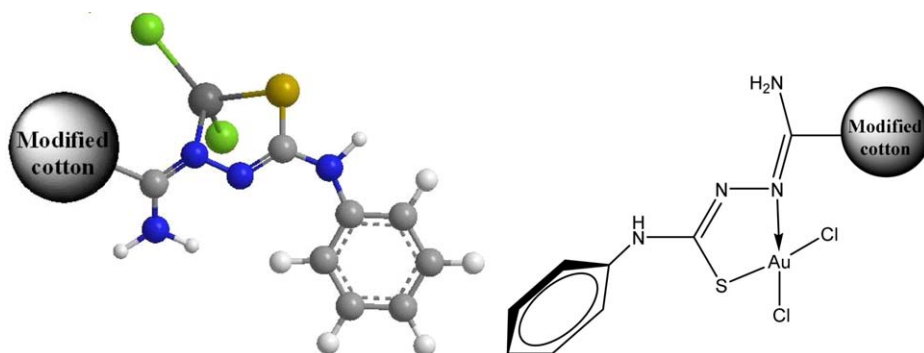
Figure 3. X-ray diffraction pattern of (a) Native cotton, (b) C-g-PAN, (c) C-PTS, and (d) cross-linked C-PTS.

Table II. Assignments of Characteristic IR Spectral Peaks (cm^{-1}) of C-PTS and Au-C-PTS

Fibers	$\nu(C=N)^a$	$\nu(C=N)^b$	$\nu/\delta(C=S)$	$\nu/\delta(C-S)$	$\nu(N-N)$
C-PTS	1660	-	1300, 870	-	1030
Au-C-PTS	1610	1630	-	1150, 650	1095

^a Azomethine.

^b New.



Structure 2. Molecular modeling of Au-C-PTS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln K_C \quad (8)$$

$\Delta H_{\text{ads}}^{\circ}$ and $\Delta S_{\text{ads}}^{\circ}$ have been evaluated using eq. (9) by plotting $\ln K_C$ versus $1/T$ (Figure 4).

$$\ln K_C = \Delta S_{\text{ads}}^{\circ} / R - \Delta H_{\text{ads}}^{\circ} / RT \quad (9)$$

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

Table III summarizes the thermodynamic functions estimated from the above equations. The spontaneous and exothermic nature of the extraction process at all studied temperatures was clearly confirmed by the negative $\Delta G_{\text{ads}}^{\circ}$ and $\Delta H_{\text{ads}}^{\circ}$ values. Furthermore, the estimated negative $\Delta S_{\text{ads}}^{\circ}$ values, indicated that the adsorption process is accompanied by lowering in entropy, which could be explained as a result of coordination and subsequently aggregation of the Au(III) ions onto the active sites on the fibers surface.

Adsorption Kinetics

The kinetic experiments are vital in order to anticipate the interaction mechanism between the Au(III) ions and the prepared chelating fibers. The kinetic studies were conducted by examining the effect of contact time on the Au(III) removal using both ion-imprinted Au-C-PTS and non-imprinted NI-C-PTS. As can be noticed in Figure 5, the adsorption exhibited an obvious rapid initial rate 3.45 and 1.65 mg/g min⁻¹ in case of Au-C-PTS and NI-C-PTS, respectively. The obtained kinetic

data were then fitted with the well known pseudo-first-order and pseudo-second-order kinetic models in order to evaluate the mechanism of the uptake process. Both models are mathematically expressed according to the following equations:²³

$$1/q_t = k_1/q_e t + 1/q_e \quad (10)$$

where k_1 is the pseudo-first-order rate constant (min⁻¹), q_e and q_t (mg/g) are the Au(III) adsorbed at equilibrium and time t (min), respectively. Plotting $1/q_t$ versus $1/t$ permits the estimation of the first order parameters.

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \quad (11)$$

where k_2 is the pseudo-second-order rate constant (g/(mg min)). Similarly, by plotting t/q_t versus t we can estimate the second order parameters.

The estimated first and second order parameters were collected in Table IV. Using the correlation coefficient (R^2) and standard deviation (SD) values we can anticipate the best model that fit with the obtained experimental kinetic data. As can be seen, the pseudo-second-order model showed the highest R^2 and lower SD values, revealing that this model is the best for describing the Au(III) removal process using both Au-C-PTS and NI-C-PTS. Accordingly, the chemical adsorption through the coordination with Au(III) could be identified as the rate limiting step.⁴³

The obtained results from the above kinetic studies are in agreement with that obtained by Lama et al.,¹ where Au(III) ions was removed using mesoporous adsorbents, by Ahamed et al.,² in which Au(III) ions were removed using ethylenediamine *N*-(2-(1-imidazolyl)ethyl) chitosan ion-imprinted polymer, by Sanchez et al.⁷ where Au(III) ions adsorbed using phosphine sulfide-type chelating polymers and Arrascue et al.,⁶ where Au(III) were adsorbed chitosan derivatives.

Adsorption Isotherm Studies

It's essential to perform the adsorption isotherm experiments for designing the adsorption system. In this work, a range of Au(III) ion concentration 10 to 400 mg/L was utilized for the performance of the isotherms in case of both Au-C-PTS and NI-C-PTS. Upon agitation of the studied adsorbent with the Au(III) adsorbate, the equilibrium concentration was plotted against the amount of Au(III) ions adsorbed onto both ion-imprinted and non-imprinted fibers and the isotherms were

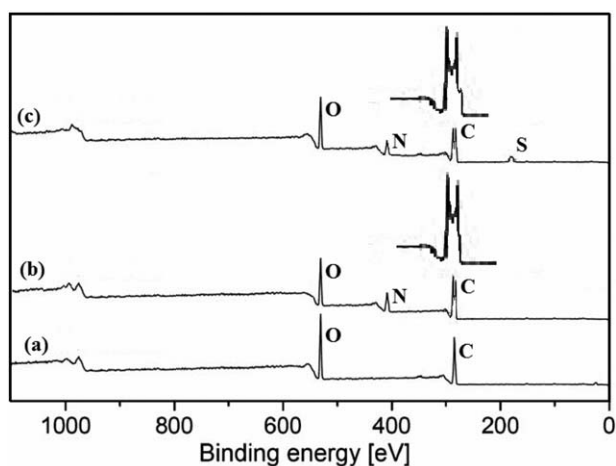


Figure 4. XPS spectra of: (a) cotton fiber; (b) C-g-PAN, and (c) C-PTS.

Table III. Thermodynamic Parameters for the Adsorption of Au(III) on Au-C-PTS and NI-C-PTS Fibers

System	K_c			$-\Delta G^\circ_{\text{ads}}$ (kJ/mol)			$\Delta H^\circ_{\text{ads}}$ (kJ/mol)	$\Delta S^\circ_{\text{ads}}$ (J/mol K)
	293 K	303 K	313 K	293 K	303 K	313 K		
Au-C-PTS	5999	2306.7	1499	21.19	19.49	19.03	-53.12	-109.62
NI-C-PTS	92.68	74.02	65.7	11.03	10.83	10.60	-13.39	-8.17

shown in Figure 6. Both Freundlich and Langmuir models, which were mathematically presented in eqs. (12) and (13), were utilized to understand the interaction between the adsorbent Au(III) ions and the adsorbent fibers.²³

$$\ln q_e = \ln K_F + 1/n(\ln C_e) \quad (12)$$

$$C_e/q_e = (1/K_L q_m) + (C_e/q_m) \quad (13)$$

where, K_F and n were Freundlich constants affecting the adsorption parameters such as adsorption capacity and intensity, respectively. Freundlich isotherm parameters were estimated by plotting $\ln q_e$ versus $\ln C_e$. q_m (mg g^{-1}) and K_L were Langmuir parameters corresponding to monolayer adsorption capacity and energy of adsorption, respectively.

The calculated parameters based on the above models were collected in Table V. Also, R^2 values were taken as a measure for the suitability of the studied isotherm model with the obtained experimental results. As can be seen, Langmuir isotherm model exhibited the best fit with the obtained experimental results for both Au-C-PTS and NI-C-PTS fibers with approximate maximum adsorption capacity of 140 and 72 mg/g , respectively, which indicated the homogeneous monolayer adsorption of the Au(III) onto energetically equivalent active adsorption sites. Furthermore, the obvious high maximum adsorption capacity observed in case of Au-C-PTS compared with NI-C-PTS could be explained as a result of both the higher surface area due to the porous morphological structure and the imprinting process,

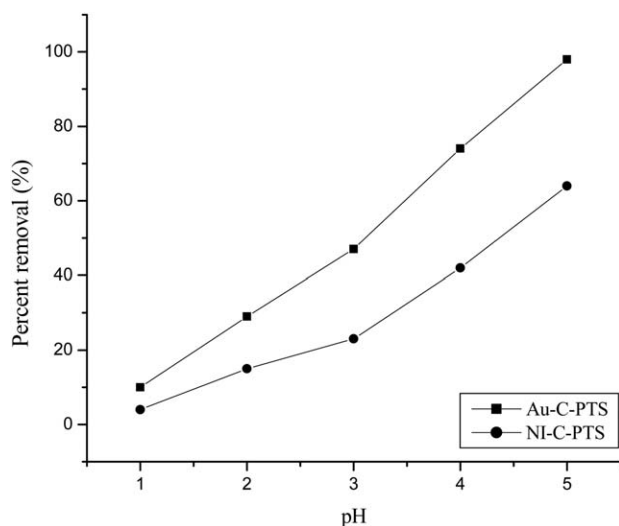


Figure 5. Effect of pH on the uptake of Au(III) ions by Au-C-PTS and NI-C-PTS (initial concentration 100 mg/L ; adsorbent, 1 g/L ; contact time 3 h; shaking rate 150 rpm, 30°C).

which creates Au(III) ion-selective adsorption sites. The obtained q_{max} value indicated that about 20% of the inserted PTS units sharing in coordination with Au(III). This could be attributed to the blocking of high percentage of the active units as a result of the cross-linking. Comparison of these previously mentioned values with similar reported in the literature (Table VI) shows that the q_{max} value obtained for the Au-C-PTS ion-imprinted fibers is remarkably higher, except for the sorbents reported by Arrascue et al.⁶ However, the adsorption time and adsorbent dosage used in this reported study was higher than that used in this study, indicating the adsorption process for extraction of Au(III) ions by the synthesized Au-C-PTS ion-imprinted fibers has more economic value than the cited materials.

The suitability of the adsorption process could be evaluated by calculating the separation factor constant (R_L): $R_L > 1.0$, unsuitable; $R_L = 1$, linear; $0 < R_L < 1$, suitable; $R_L = 0$, irreversible.³³ The R_L value can be estimated according to the following equation:

$$R_L = 1/(1 + C_0 K_L) \quad (14)$$

where K_L is the Langmuir equilibrium constant and C_0 (10–400 mg/L) is the initial concentration of the Au(III) ions. The values of R_L lie between 0.254 and 0.0085, indicating the suitability of the imprinted resin as adsorbents for Au(III) from aqueous solution.

These results are in agreement with that of Lama et al.,¹ where Au(III) ions were removed using mesoporous adsorbents, by Ahamed et al.,² in which Au(III) ions were removed using ethylenediamine *N*-(2-(1-imidazolyl)ethyl) chitosan ion-imprinted polymer, by Sanchez et al.⁷ where Au(III) ions adsorbed using phosphine sulfide-type chelating polymers and Arrascue et al.,⁶ where Au(III) were adsorbed chitosan derivatives.

Table IV. Kinetic Parameters for Au(III) Adsorption by Au-C-PTS and NI-C-PTS Fibers

Fibers			
First-order model	k_1 (min^{-1})	q_{e1} (mg/g)	R^2
Au-C-PTS	9.876	98 ± 4	0.8987
NI-C-PTS	8.785	59 ± 4	0.9112
Second-order model	k_2 ($\text{g}/(\text{mg min})$)	q_{e2} (mg/g)	R^2
Au-C-PTS	6.5×10^{-3}	98 ± 1	0.9999
NI-C-PTS	6.0×10^{-3}	61 ± 2	0.9989

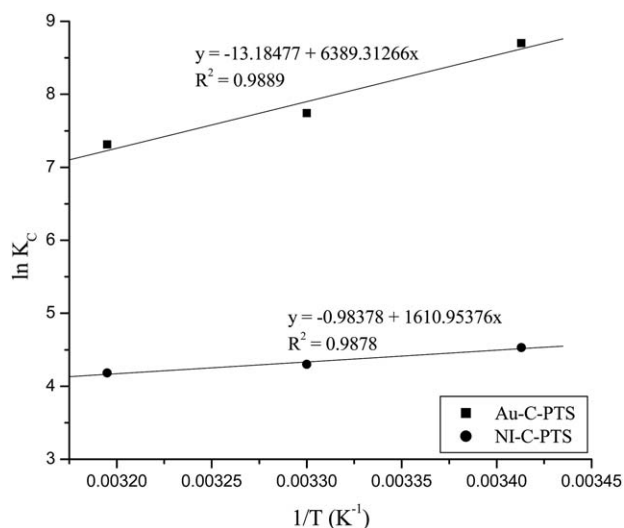


Figure 6. Plot of $\ln K_C$ as a function of reciprocal of temperature ($1/T$) for the adsorption of Au(III) by Au-C-PTS and NI-C-PTS fibers.

Selectivity Study

The selectivity studies were carried out in a multi-component mixture containing Cu(II), Cd(II), Hg(II), Fe(III), and Au(III). The competitive adsorption onto both Au-C-PTS and NI-C-PTS were accomplished by agitating 0.03 g of the desired fibers with 30 mL of the solution on a shaker at 150 rpm, pH 5 for 3 h at 30°C. After this period, the residual content of each metal was measured and eqs. (4–6) were utilized for estimation of the selectivity parameters. As can be seen in Table VII, the ion imprinted Au-C-PTS fibers exhibited an obvious ability to selectively remove Au(III) ions compared with the non-imprinted NI-C-PTS fibers. These results confirm that the imprinting process creates a selective recognition sites, which match the geometry, size and charge of Au(III) ions.

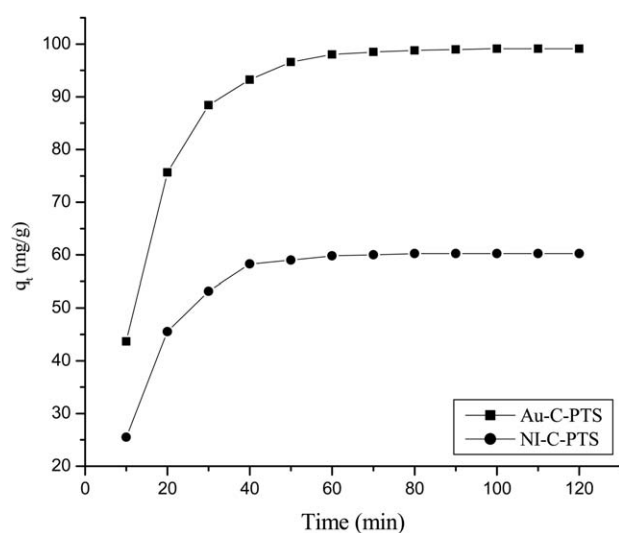


Figure 7. Effect of contact time on the uptake of Au(III) ions by Au-C-PTS and NI-C-PTS fibers (initial concentration 150 mg/L, adsorbent 1 g/L, pH 5.0, shaking rate 150 rpm, 30°C).

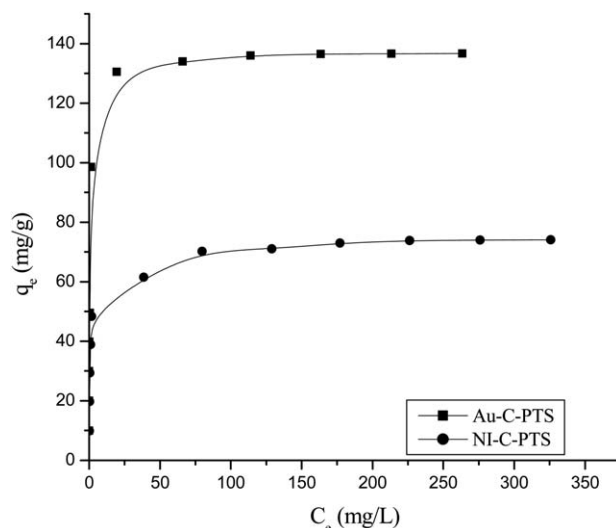


Figure 8. Adsorption isotherms of Au(III) ions by Au-C-PTS and NI-C-PTS fibers (initial concentration 10 to 400 mg/L, adsorbent 1 g/L, pH 5.0, shaking rate 150 rpm, 30°C).

Table V. Parameters for Au(III) Ions Adsorption by Au-C-PTS and NI-C-PTS Fibers According to Different Equilibrium Models

Fibers			
Langmuir isotherm constants	K_L (L/g)	q_m (mg/g)	R^2
Au-C-PTS	29.3×10^{-2}	140 ± 1	0.9998
NI-C-PTS	15.4×10^{-2}	72 ± 1	0.9999
Freundlich isotherm constants	K_F	n	R^2
Au-C-PTS	29.208	4.112	0.8997
NI-C-PTS	20.789	3.545	0.8988

Desorption and Reusability Studies

The desorption and regeneration of the Au(III) loaded Au-C-PTS ion-imprinted fibers was performed using 0.1M HMO₃ solution, and then washed with distilled water several times for neutralization. The Au(III) free fibers were reused again and the

Table VI. Maximum Adsorption Capacities for the Adsorption of Au³⁺ onto Various Adsorbents

Adsorbent	Maximum adsorption capacity Au ³⁺ (mg/g)	Reference
Rice husk carbon	139.72	44
Hen eggshell membrane (ESM)	111.89	45
Dealginated Seaweed Waste	66.8	46
Alfalfa	30.06	47
Sulfur derivative of chitosan	534.4	6
Fucus vesiculosus	58.45	48
Lysine modified chitosan	70.34	49
Present study	140.54	

Table VII. Selective Adsorption of Au(III) from Multicomponent Mixtures by Au-C-PTS and NI-C-PTS (Initial Concentration 20 mg/L, Adsorbent 1 g/L, Shaking Rate 150 rpm, Solution pH 5.0, 30°C)

Metal	Distribution ratio (L/g)		Selectivity coefficient $\beta_{Au^{3+}/M^{n+}}$		Relative selectivity coefficient β_r
	Au-C-PTS	NI-C-PTS	Au-C-PTS	NI-C-PTS	
Au ³⁺	957.23	10.59	-	-	114.2
Cu ²⁺	6076	8.54	141.6	1.24	150.16
Cd ²⁺	6089	11.54	138.9	0.925	135.11
Hg ²⁺	7.87	11.76	121.6	0.900	111.27
Fe ³⁺	4.78	5.89	200.3	1.8	

adsorption-desorption cycles was carried out for five consecutive times. Table VIII lists the adsorption efficiency after each cycle, and as can be seen, after the fifth cycle the fibers still maintain about 96% of its original efficiency. These results indicate that the prepared fibers is promising for fast and selective Au(III) ions extraction.

CONCLUSION

This study focuses on extraction or recovery of Au(III) ions from aqueous solution using surface ion-imprinted Au-C-PTS chelating fibers as an effective adsorbent. The interest in using the IIP Au-C-PTS for the extraction or recovery of the Au(III) ions from aqueous solutions is driven by the possibility of obtaining high adsorption capacity along with excellent selectivity. The results demonstrated that the adsorption process was dependent on contact time, initial metal ion concentration, pH, and solution temperature. A short contact time was observed at the beginning of the adsorption process making these fibers suitable for online operation during the extraction process. Kinetic studies suggested that the adsorption reaction is a pseudo-second order. Equilibrium experiments fitted well with the Langmuir and Freundlich models. The imprinted fibers showed higher adsorption capacity for the Au(III) ions compared with the non-imprinted fibers due to a large number of cavities matching with gold ions by ion imprinting. Thermodynamic parameters obtained indicated that the adsorption process is an exothermic spontaneous reaction. The sorbent is efficient for Au(III) ion extraction in aqueous media containing other closely related ions, such as base metals and other precious metals. The selective adsorption of Au(III) ions by the Au-C-PTS from strongly complex mixture such as mining drainage and stimulated mining solutions indicates its applicability in preferential recovery of Au(III) ions from industrial solutions containing gold. Furthermore, 0.1M HNO₃ solu-

tion can effectively desorb Au(III) ions from the fibers. The regenerated adsorbents exhibited almost the same adsorption capacity as the fresh fibers. The latter is very beneficial in practical applications for the specific recovery of Au(III) ions from aqueous solutions.

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Table VIII. Desorption Efficiencies of Au(III) on Au-C-PTS Fibers from Five Adsorption-Desorption Cycles

Cycle number	Adsorption capacity (%)
1	100
2	99.5
3	98.8
4	98.2
5	97.5

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