Recycling of precious materials by modified electrospun membranes

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ABSTRACT

In this study, adsorption of gold (Au) and platinum (Pt) ions by electrospun polyacrylonitrile (PAN) natural keratin-modified membranes with high sulfur content and affinity toward precious metals were investigated. Different adsorption parameters, sorbent amount, contact time, temperature and pH of solution on adsorption (%) were studied in detail in batch sorption. First, a PAN nanofiber membrane was fabricated by an electrospinning technique as a low-cost method for producing nanofiber membranes and was then modified with the natural keratin (human hair) by hydrolysis in a basic solution. A PAN–keratin nanofiber membrane was characterized by Fourier-transform infrared spectroscopy and scanning electron microscopy (FTIR and SEM, respectively). FTIR verified the modification of PAN with keratin in which the spectrum of the resulting membrane showed significant changes, by using this modified nanofiber membrane, Au adsorption of 99% was achieved while the Pt adsorption showed a maximum of 37%. The reason for this finding may be because the electronegativity of Au is higher than Pt. When the adsorption isotherms were investigated, it was noted that the Langmuir isotherm fit better than the Freundlich isotherm. 1.0 M thiourea solution was used as a desorption reagent for both Au and Pt ions. Reusability studies showed that the adsorption capacity can remain up to 90 % after four times of usage. This finding indicates that the adsorption process of precious ions onto the electrospun membrane is a monolayer adsorption process.

Keywords: Electrospinning; Adsorption; Gold; Platinum; Nanofiber membrane; Keratin

1. Introduction

Gold (Au) and platinum (Pt) are important as precious metals. They are used in catalytic applications, electronic devices, and plating materials among others. The primary platinum group metal (PGM) deposits are located in only South African, Russia, the United States, and Canada [1]. PGM deposits number only 66,000 tons worldwide, and the demand for PGMs is 590 tons on a yearly basis.

However, only 150 tons of PGM can be recovered from secondary sources [2]. Due to the limited nature of the raw resources and the high demand, the recovery of Pt and Au from secondary sources has attracted growing interest from the academic and industrial communities [3–5].

Several appropriate technologies are available for the recovery of precious metals from the aqueous solutions, including precipitation [6], solvent extraction [7], membrane filtration [8], ion exchange [9], and adsorption [10].

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Comparatively, adsorption seems to be the most suitable recovery method as large volumes of very dilute wastes can be treated economically, and nearly no waste residue is produced. A number of adsorbents, such as membranes [11], and chelating resins [9], have been developed and tested for the recovery of precious metals. In recent years, chelating sorbents have received increasing attention as adsorbents for the removal of metal ions from contaminated water/wastewater. Using chelating sorbents for adsorption can be more effective and economical and also provides a potential for the removal, recovery, and recycling of metals from industrial wastewater [1]. Adsorbents based on fibers and fabric materials have low costs, are easily scalable, and allow industrialization [12].

Electrospinning is commonly used to make nanofibers ranging from ~10 nm to several hundred nanometers in diameter. Electrospinning relies on electrostatic forces to draw ultrafine solid threads from solutions of polymers of sufficiently high molecular weight and does not require coagulation chemistry or high temperatures. Fiber mats produced by electrospinning are lightweight and characterized by high porosity, small inter-fiber pore size, and large surface area. Electrospun nanofiber membranes have a wide range of applications, including drug delivery, scaffolding in tissue engineering, clothing protection, and sensing in addition to adsorption and filtration [13]. Among fiber-based adsorbents, polyacrylonitrile (PAN) shows good chemical resistance, thermal stability, low flammability and very good mechanical properties and has been extensively studied [14,15]. PAN can be successfully used as a polymer matrix for obtaining complexing sorbents. Chelating sorbents based on PAN are easily prepared and abundant. Active nitrile (CN) groups present in PAN make it possible to introduce new functional groups via special reactions [1]. These active groups make PAN efficient at metal ion adsorption through coordination. Over the past few years, significant achievements in the chemical modification of polyacrylonitrile have occurred. To increase adsorption capacity of PAN toward precious metals, a variety of functional groups can be introduced. Since compounds with N and S atoms are known to promote the selective adsorption of precious metal ions, modified sorbents with hydroxylamine [16], hydrazine [16], ethylenediamine, thioamide [11], and thiosemicarbazide [17] were prepared by the researchers.

Keratin is a naturally occurring polymer. It is biorenewable, biocompatible, biodegradable and found in all epidermal tissues, such as hair and nails [18]. Each year 300,000 tons of keratin waste is produced. Keratin-based materials in the form of electrospun fibers, films, hydrogels, and powders, especially for biomedical applications or as a reinforcement material for electrospun fibers, have been reported in the literature [19]. Keratin has a high sulfur content (>3%) [20,21], and this high sulfur content can be used to modify electrospun membranes to increase their adsorption capacities toward precious metals. Aluigi et al. [22] used wool-derived keratin for the fabrication of electrospun membranes that are capable of being used to recover heavy metals from aqueous solutions. Their study showed that keratin-based electrospun fiber has an adsorption capacity of 11 mg/g for Cu(II) and adsorption based on ion-exchange reactions. Aluigi et al. [22] used a blend of wool keratin in polyamide 6 nanofibers and showed that Cu(II) ion adsorption increased as a result of an increase in the specific surface area. Ki et al. [23] studied wool keratin and silk fibroin blends together for modifying electrospun membranes. The adsorption capacity of fabricated membranes was maintained for several cycles of the recycling process of adsorption and desorption. Jin et al. [24] used wool keratin/polyethylene terephthalate (PET) composite nanofibers to adsorb Cr(VI) in acidic solutions. This study showed that these membranes had a maximum capacity of 75.86 mg/g for Cr(VI) adsorption. The blending of wool keratin caused an increase in hydrophilicity and membrane pore ratio.

To the best of our knowledge, no Au and Pt adsorption studies have reported the use of human hair-based keratin modified PAN electrospun membranes. In this work, we prepared a chelating adsorbent modified with keratin and applied it to the adsorption of Pt and Au from aqueous solutions. The effects of various parameters, such as pH, amount of sorbent, contact time, and temperature, on adsorption were investigated. Fourier-transform infrared spectroscopy and scanning electron microscopy (FTIR and SEM, respectively) were used to characterize the modified nanofiber membranes.

2. Experimental

2.1. Materials

PAN with a molecular weight of 150,000 g/mol was supplied by Sigma-Aldrich (Germany). Dimethyl fluoride (DMF) from Merck (Germany) was used as a solvent. Thiourea (TU), HCl and NaOH were purchased from Merck (Germany) and used to adjust the pH of the adsorption solution. For the wet chemical analyses, distilled water was used. Natural undyed hair was donated in order to extract the natural keratin. Potassium gold chloride powder (99.9%, Sigma-Aldrich, Germany) was dissolved in the distilled–deionized water and then diluted with distilled–deionized water (TKA Smart2Pure, Germany). The Pt-containing solutions for the experiments were prepared from a hexachloroplatinic acid (H_2PtCl_6) standard solution (Merck, Germany). The concentrations of Au and Pt present in the solution were determined using the atomic absorption spectrometer, Anayltic Jena, (Germany). The initial metal ion concentrations were set to 100 mg/L. The pH of the solution was adjusted in the range of 1.50 to 4.50. In some experimental series, increasing the modified-PAN nanofiber membrane quantities from 10 to 30 mg per 10 mL solution was done.

2.2. Preparation of PAN electrospun membrane

The electrospun membrane solution was prepared by slowly adding 10 g of PAN powder into DMF and dissolving at 80°C. Then the prepared solution was placed in a syringe. The metallic tip of the syringe was connected to the positive terminal of a high-voltage power supply while the negative terminal was connected to a conductive collection drum for the nanofibers. A voltage of 25 kV with a tip-to-target distance of 15 km at a speed of 0.1 mL/h was applied to the solution. The nanofiber membranes were collected on the PET support.

2.3. Modification and characterization of PAN electrospun membranes

Hair (10 g) was dissolved into the alkaline solution that had a pH of approximately 12. For membrane modification, the resulting electrospun PAN membrane was immersed in the basic NaOH solution containing natural keratin for 2 h at 35°C. After immersion, the PAN membrane was washed with distilled water and dried at 40°C under a vacuum atmosphere.

For characterization of the nanofiber membranes, attenuated total reflectance (ATR)-FTIR and SEM were used. In order to determine the characteristic peaks of the functional groups on the prepared membranes, an ATR-FTIR spectrometer (Spectrum 100, Perkin Elmer, USA) was used in the wavenumber region of 4,000 to 650 cm^{-1}. The surface morphology of the electrospun membrane was examined using SEM (FEI, Quanta FEG 250).

2.4. Au/Pt adsorption tests

An adsorption study was conducted in a batch system by varying one factor at a time. For each experiment, 10 mL of the solution containing Au and Pt was placed into contact with the nanofiber membrane in a falcon tube. The shaking rate was adjusted to 100 rpm. The initial metal ion concentrations were set to 100 mg/L. Effects of several parameters were studied in detail on Au and Pt adsorption (%): (1) sorbent amount, (2) contact time, (3) temperature, and (4) pH of the solution. The adsorption percentage was calculated using the following equation:

$$\text{Adsorption \%} = \left[\frac{\left(C_0 - C_t\right)}{C_0}\right] \times 100 \tag{1}$$

where C_0 and C_t (mg/L) are the metal ions concentration present in the solution before and after adsorption, respectively.

For the adsorption capacity of the ions the following equation was used:

$$q_e = \frac{\left[\left(C_0 - C_t\right) \times V\right]}{m} \tag{2}$$

where q_e is the amount of metal ions adsorbed at equilibrium per unit weight of membrane (mg/g), C_0 and C_t (mg/L) are the concentrations of the ions present in the solution before and after adsorption, respectively, V is the volume of the solution (in L), and m is the amount of membrane (g) used in the adsorption experiments.

To understand the adsorption mechanism, adsorption isotherm experiments were conducted with different initial precious metal ion concentrations at temperatures of 25°C, 35°C, and 45°C.

2.5. Au/Pt desorption and reusability test of electrospun membrane

Desorption and the electrospun membrane reusability experiments were carried out with 1.0 M TU solution which consists of N, S and O atoms having an affinity towards precious metals [25]. First, the Pt and Au ions adsorbed on the modified PAN membrane was washed with deionized water several times, then introduced into 25 mL of desorption solution at 25°C for 120 min. The first adsorption–desorption cycle was followed by four other cycles using the same modified PAN membrane batch in order to examine the potential reusability of the electrospun membrane. The desorption percentage was calculated as follows:

$$\text{Desorption, \%}: \left[\frac{\left(C_d \times V_d\right)}{\left(C_0 - C_t\right) \times V}\right] \times 100 \tag{3}$$

where C_d (mg/L) is the concentration of the solutes in the desorption solutions; V_d (in L) is the volume of the desorption solution; C_0 and C_t (mg/L) are the metal ions' concentrations present in the solution before and after adsorption; V is the volume of the solution (in L).

3. Results and discussion

The interaction of PAN with hair-based keratin in basic solution is illustrated in Fig. 1. According to this interaction, FTIR spectra support the hydrolysis of PAN membrane with keratin. In Fig. 2, the characteristic peak at 2,243 cm^{-1} was assigned to C≡N stretching, while the other peaks were attributed to C–H stretching and C–H bending at 2,922 and 1,454 cm^{-1}, respectively. As seen in Fig. 2, the most relevant bands are related to the N–H stretching vibration that gave rise to the amide. A band and the O–H stretching of keratin in the range of 3,200 to 3,300 cm^{-1}. The characteristic adsorption bands of the keratin, assigned mainly to the peptide bonds (–CONH–) at the 3,276 cm^{-1} bands was connected with the stretching vibration of N–H bonds. The symmetric and asymmetric vibrations of the CH$_3$ and CH$_2$ occurred at 2,920 and 2,850 cm^{-1}, respectively, and the CO and N–H stretching of amide I and amide II at 1,635 and 1,530 cm^{-1}, respectively. The CH$_X$ scissoring of the keratin backbone occurred at 1,470 cm^{-1}. The C=S group, which is attached to a sulfur atom, showed absorption bands in the 1,010 to 1,234 cm^{-1} stretching region. After the modification of PAN with keratin, the spectrum of the resulting membrane showed many significant changes. The peak at 2,243 cm^{-1} (C≡N) shrank, and the peaks belonging to the keratin were seen on the spectrum of the modified PAN.

The SEM images of nanofiber membranes are shown in Fig. 3. The membranes were composed of numerous, randomly oriented nanofibers. The pure PAN nanofibers were smooth and uniform with an average diameter of 200 nm. The modified PAN nanofiber membrane showed some differences on the surface as their surfaces were still smooth. The average diameter was approximately 200 nm.

For the adsorption experiments using the modified electrospun membrane, the first effect of the solution's pH was investigated with respect to the adsorption of Pt and Au. The pH of the solution was adjusted in the range of 1.50 to 4.50. According to Fig. 4, the optimum adsorption percentage of Au was obtained at 97.34% in the solution with a pH of 2.50 while it was 66.40% for Pt in a solution of pH of 2, both of which were selected for all subsequent adsorption experiments. Moreover, unmodified PAN electrospun
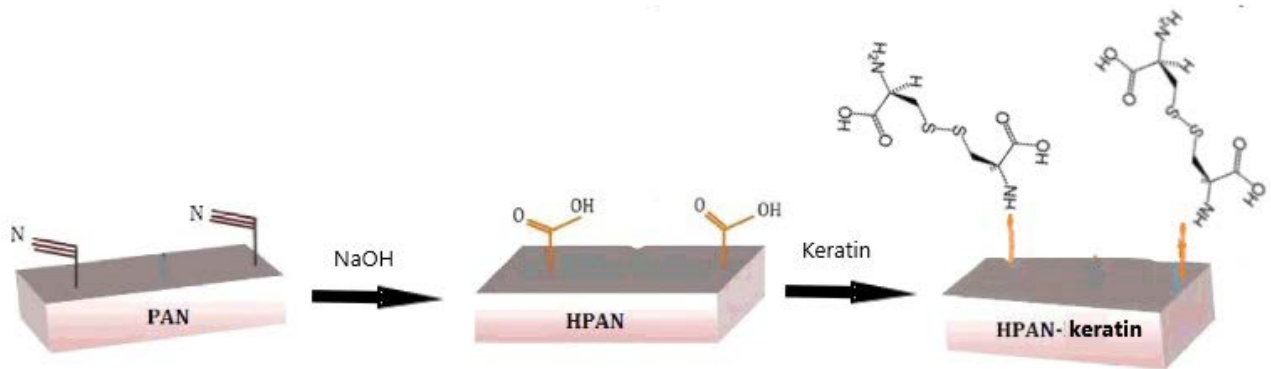
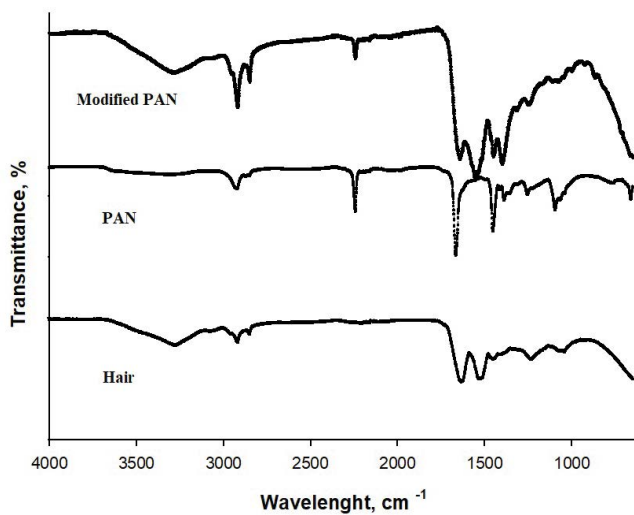Fig. 1. Hydrolysis of polyacrylonitrile modified with keratin.

Fig. 2. Fourier-transform infrared spectroscopy spectrum showing transmittance % vs. cm^{-1} of hair, polyacrylonitrile, and modified polyacrylonitrile.

membrane showed more than 2 times lower adsorption performance than keratin modified PAN membrane. It was understood that keratin had played a positive role in the adsorption of Pt and Au ions on the electrospun membrane because of having more S content which shows affinity toward these metal ions.

Fig. 5 shows the effect of the amount of electrospun membrane on Pt and Au adsorption in the solution that was investigated for a contact time of 60 min. In this experiment, increasing modified-PAN nanofiber membrane quantity from 10 to 30 mg per 10 mL solution resulted in an increase in the adsorption of Pt and Au from 20% to 34% and from 30% to 97%, respectively. The adsorption percentage was found to increase with an increasing amount of nanofiber membrane because adsorption reactions are thermodynamically more favorable when the sorbent-to-metal ion ratio is higher until the equilibrium point is reached. This result was expected because as the amount of adsorbent increases an increasing amount of surface area becomes available, which exposes more active sites for binding metal ions until the saturation point is reached. In this situation, all the active sites were occupied by all of
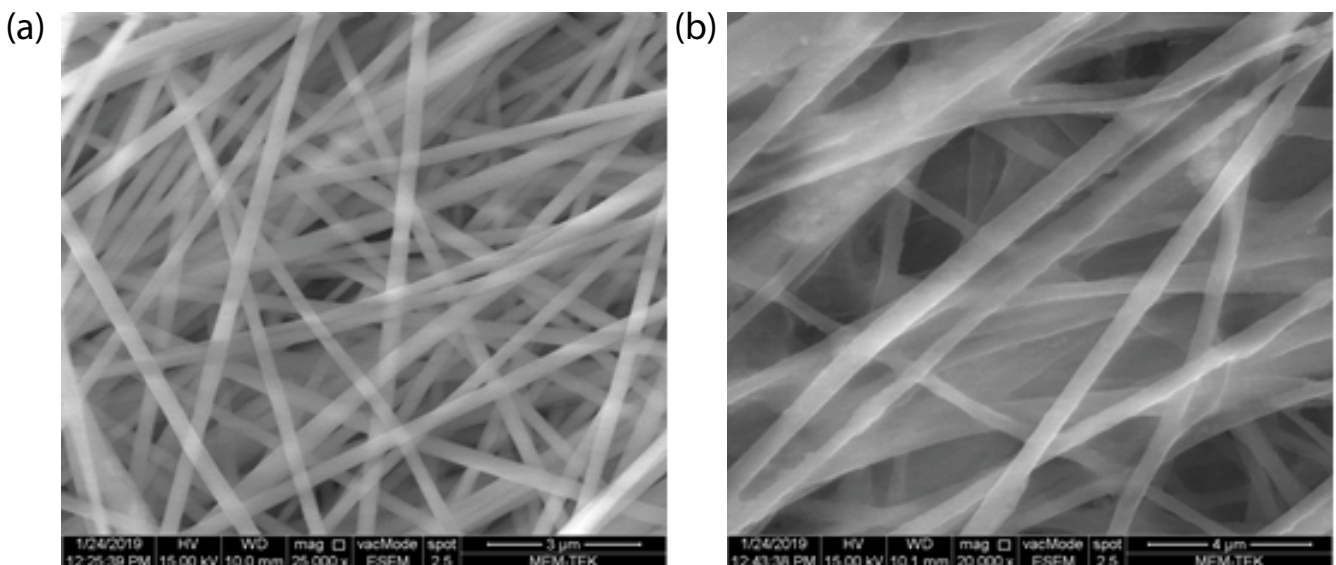

Fig. 3. Scanning electron microscopy images of (a) unmodified polyacrylonitrile and (b) keratin-modified polyacrylonitrile.
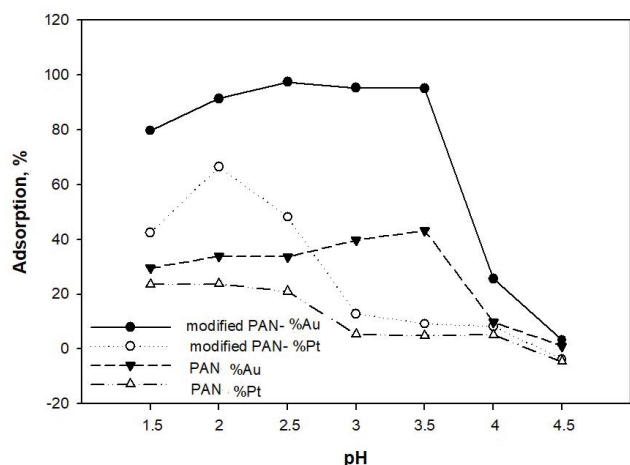
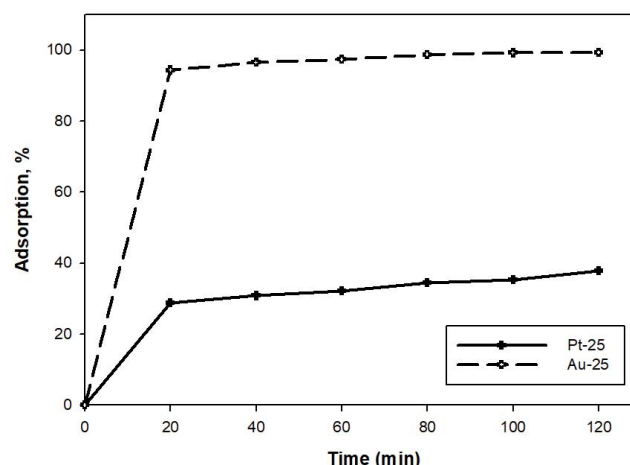Fig. 4. pH of solutions.

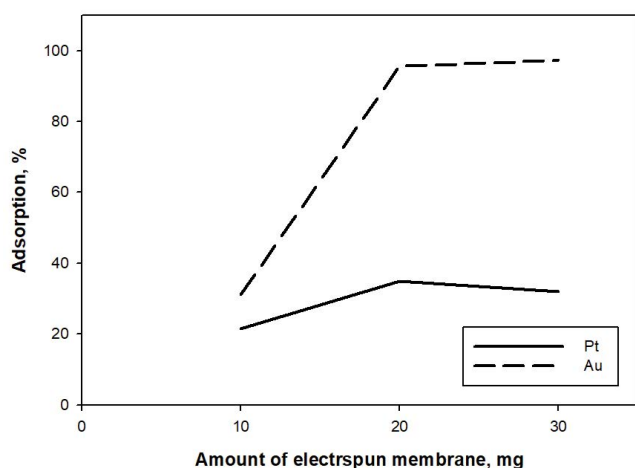Fig. 6. Effect of contact time on Pt and Au adsorption.

Fig. 5. Effect of the sorbent amount on platinum (Pt) and gold (Au) adsorption.

the binding metal ions. If an excess amount of metal ions had been added to the solution, the increasing trend would have continued.

Fig. 6 represents the effect of contact time on the adsorption percentages of Pt and Au by the modified-PAN nanofiber membrane in the range of 0 to 120 min. As shown in Fig. 6, the increasing contact time had a positive effect on Pt and Au adsorption (for example, the adsorption % increased with increasing time), and it reached equilibrium after 80 and 100 min for Pt and Au, respectively.

Dissolution and extraction of keratin is a difficult process compared to the extraction of other natural polymers, such as chitosan, starch, and collagen. This difficulty occurs because keratin fibers formed of crystalline rod-like components consisting of alpha-helices containing cystine in high quantity inside an amorphous matrix are in fact made of soluble proteins, which are active in a certain range of values of temperature and pH; thus, these alpha-helices of denatured protein can be found at temperatures below 80°C and in insoluble keratins above 100°C [26,27]. Several methods to solve the insoluble keratin exist, including the

use of lime and oxidative agents, such as peracetic acid, and reduction reactions (thermo-chemical treatments with various reducing agents, such as 2-mercaptoethanol, dithiothreitol, sodium m-bisulfite and sodium bisulfite followed by NaOH treatment for the extraction of keratin from duck feathers) among others [27,28]. In our study, the resulting electrospun PAN membrane was immersed in the basic NaOH solution containing natural keratin and extracted by high alkali treatment for 2 h at 35°C in order to modify the electrospun PAN membrane in these studies. The protein structure of the keratin denatured gradually at increasing temperatures and became unstable after which point decreases in Au and Pt ion adsorption occurred due to keratin deformation.

The effect of temperature on Pt and Au adsorption was studied in the range of 25°C to 45°C. The percentage adsorption of Pt and Au as a function of temperature is presented in Fig. 7. When the temperature was increased from 25°C to 45°C, the adsorption percentage of Pt decreased due to keratin deformation resulting from the effects of high temperature. The same behavior was observed for Au adsorption in which the adsorption decreased while temperature increased. This reason could be due to the degradation of natural keratin at high temperatures. Maximum metal ion adsorption was obtained at 25°C. Temperature increases clearly play an adverse role for Pt and Au adsorption by using modified PAN nanofiber membrane from the solution.

The adsorption isotherms were investigated in order to describe the adsorption system of the electrospun membrane. The equilibrium data were fitted to the Langmuir and Freundlich isotherm models. These isotherms yielded the relationship between q_e and C_e and the equation is shown below [29]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

$$\frac{C_e}{q_e} = \left[\frac{1}{(Q_{max} \times K_L)}\right] + \left(\frac{1}{Q_{max}}\right) \times C_e \tag{5}$$
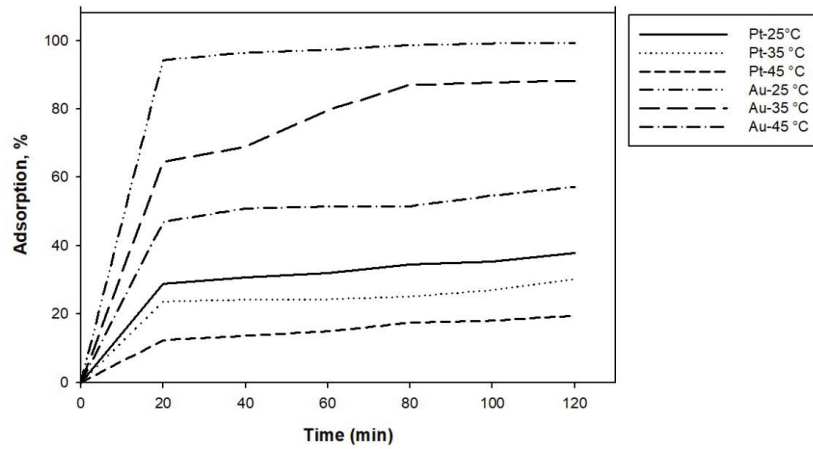
Fig. 7. Effect of temperature on Pt and Au adsorption.

where q_e is the number of metal ions adsorbed at equilibrium per unit weight of membrane (mg/g), Q_{max} is the monolayer capacity of the adsorbent (mg/g), C_e is the equilibrium ion concentration present in the solution after adsorption, K_L (L/mg) and K_F (mg/g) are the constants in the Langmuir and Freundlich isotherm models, respectively, that are related to adsorption capacity, K_L (L/mg) is the constant in the Langmuir isotherm model related to the energy or net enthalpy of adsorption, and n is the constant in the Freundlich isotherm model that is used to measure adsorption intensity. In order to identify the adsorption isotherm and determine the maximum adsorption capacities, all parameters of the isotherms were calculated using the slopes and intercepts of the plots, respectively, as given in Fig. 8.
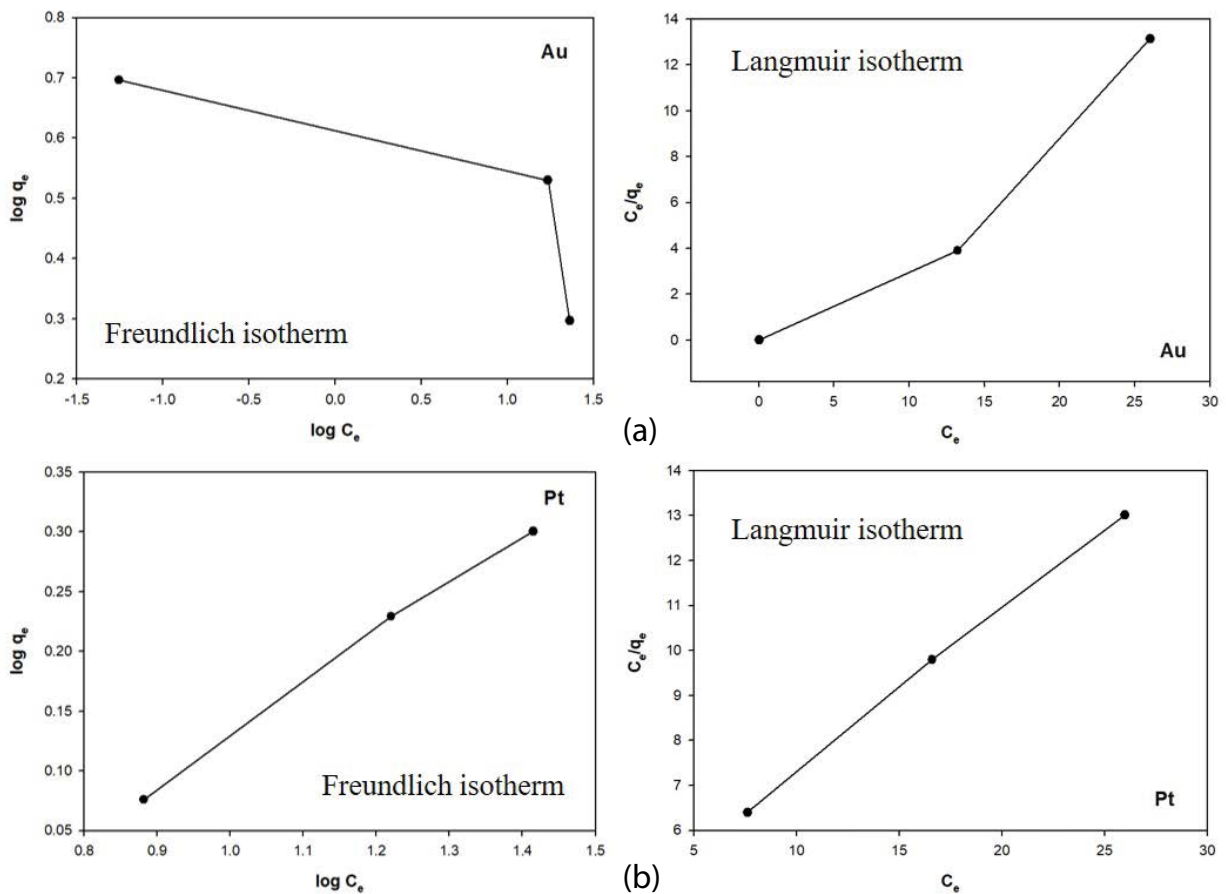

Fig. 8. Adsorption isotherms of (a) Au and (b) Pt on the modified polyacrylonitrile electrospun membrane.

A comparison of the correlation coefficient, R^2, showed that the Langmuir isotherm (R^2 = 0.99, linear plot) was a better fit than the Freundlich isotherm (R^2 < 0.99). This result indicates that the adsorption process of precious ions onto the electrospun membrane is a monolayer adsorption process.

In this study, the temperature range was chosen between 298 and 318 K. Thermodynamic parameters for the adsorption process, such as enthalpy change $\Delta H°$, entropy change $\Delta S°$, and the free energy of specific adsorption $\Delta G°$, are calculated using the following equations [30,31]:

$$K = \frac{C_{Ac}}{C_e} \quad (6)$$

where K is the equilibrium constant, C_{Ac} and C_e are the equilibrium concentrations (in mg L^{-1}) of the metal ion adsorbed and left in the solution, respectively. $\Delta G°$ is calculated from the following relationship:

$$\Delta G = \Delta G° + RT \ln K \quad (7)$$

At equilibrium, $\Delta G° = 0$, hence

$$\Delta G° = -RT \ln K \quad (8)$$

where T is the absolute temperature in Kelvin, and R is the gas constant.

$\Delta H°$ is calculated from the following equations:

$$\Delta G° = \Delta H° - T\Delta S° \quad (9)$$

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (10)$$

The enthalpy change $\Delta H°$ and the entropy change $\Delta S°$ are calculated from the slope and from the intercept in linear plots of $\ln K$ vs. $1/T \times 10^{-3}$ as shown in Fig. 9. The values of the calculated thermodynamic parameters, $\Delta H°$, $\Delta S°$, and $\Delta G°$, for the Pt and Au ions adsorption on the modified PAN electrospun membrane, are given in Table 1. The values of $\Delta H°$ for the Pt and Au ions adsorption were found to be −10.23 and −101.68 kJ mol^{-1}, respectively. The negative values of the free energy of specific adsorption $\Delta G°$ for the adsorption of Pt and Au ions on the electrospun membrane show that the process is spontaneous because adsorption decreased while temperature increased [31].

The desorption and reuse membrane were tested with a 1.0 M TU solution. The results exhibited that the first desorption ratios were 99.1% for Au ion and 98.7% for Pt ion as seen in Fig. 10. After four adsorption–desorption cycles of Au and Pt ions, the desorption ratios were below 85%. This result shows that the modified PAN membrane achieves well for repeated use of up to four cycles.
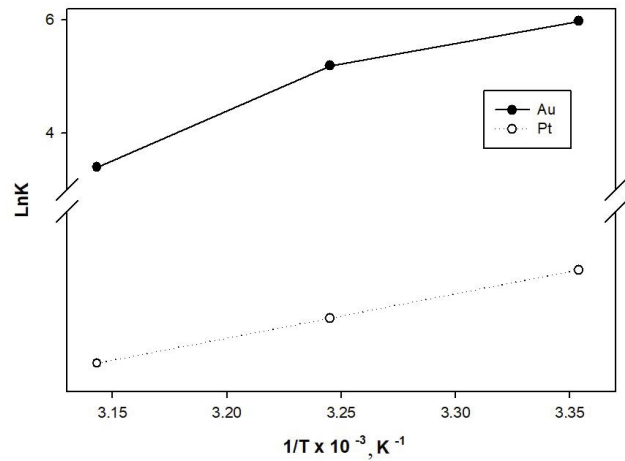

Fig. 9. ln$K$ vs. $1/T \times 10^{-3}$ on modified polyacrylonitrile electrospun membrane for Pt and Au ions.
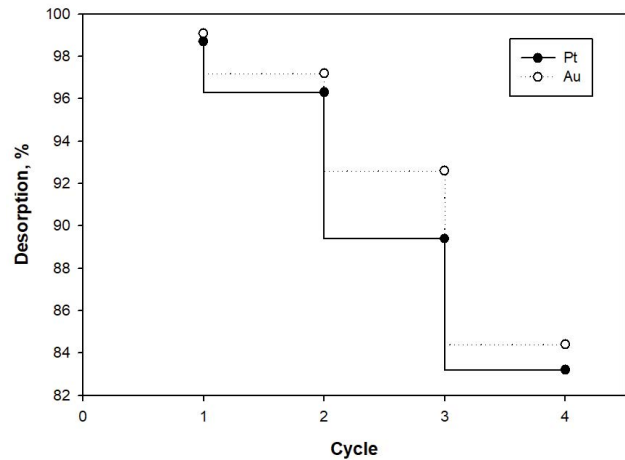

Fig. 10. Desorption and reusability performance of the modified polyacrylonitrile electrospun membrane.

Table 1
Thermodynamic constants for the adsorption of Pt and Au at different temperatures

	Pt			Au		
			Thermodynamic constants			
T/K	$\Delta G°$, (kJ mol^{-1})	$\Delta H°$, (kJ mol^{-1})	$\Delta S°$, (J mol^{-1}K^{-1})	$\Delta G°$, (kJ mol^{-1})	$\Delta H°$, (kJ mol^{-1})	$\Delta S°$, (J mol^{-1}K^{-1})
298	−8.66			−91.30		
308	−8.60	−10.23	−5.28	−90.95	−101.68	−34.85
318	−8.55			−90.60		

4. Conclusions

In this study, the modified PAN nanofiber membranes containing natural keratin were synthesized via the electrospin process. The nanofiber diameters of PAN nanofiber membranes were about 200 nm and had smooth surfaces. The modified PAN electrospun membrane showed efficient adsorption for Au ions, while it had a lower adsorption capacity for Pt ions under the same conditions. It was thought that this result may have been due to the fact that the electronegativity of Au is higher than that of Pt. The electrospun membrane was adversely affected by temperature during the adsorption experiments. It was noted that the PAN membrane containing keratin did not function well with an increase in temperature in the adsorption conditions because the keratin structure that had an active role in capturing the metal ions could be destroyed at high temperature. Moreover, it was understood that the adsorption process was spontaneous since the specific free energy was negative. The adsorption isotherm models show that the adsorption of these precious metal on the electrospun membrane was fitted Langmuir isotherm, indicating that it was a monolayer adsorption process. The reusability of modified PAN membrane was determined after four adsorption–desorption cycles. Consequently, the modified PAN nanofiber membrane appears to be a promising candidate for recovering precious metal ions in aqueous solutions, especially Au ions.

Acknowledgment

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