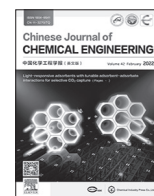




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Full Length Article

A core-shell amidoxime electrospun nanofiber affinity membrane for rapid recovery Au (III) from water

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ABSTRACT

An affinity membrane was prepared by coaxial electrospinning and amidoxime (AONFA), and it was applied to selectively recovery Au (III) from an aqueous solution. The static adsorption results showed that, when pH at 5, the maximum adsorption capacity of AONFA membrane for Au (III) was 509.3 mg·g⁻¹. AONFA membrane exhibit much higher affinity and selectivity towards Au (III) than other metal cations. The membrane could be regenerated effectively by mixture solution of thiourea and HCl, and the desorption ratio reached almost 100% after 4 hours desorption. The dead-end filtration results showed that, the membrane utilization efficiency and adsorption capacity can be improved by increasing the flow rate, while increasing the concentration shorted the breakthrough process and had little impact to adsorption capacity. We can flexibly adjust the flow rate and concentration according to the situation to obtain the maximum utilization efficiency of the membrane in filtration process. The dynamic adsorption capacity is higher than the static adsorption capacity. The adsorption mechanism for Au (III) is electrostatic adsorption and reduction. Thus, AONFA membrane filtration was demonstrated to be a promising method for continuous recover Au (III) from wastewater.

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1. Introduction

Gold has been a global currency since ancient times [1]. In recent years, gold has been applied to more fields such as aerospace technology, catalysis, electronic industry and medical technology. Growing demand for gold makes it crucial to recover the gold from industrial wastewater [2–4]. China is the largest producer of e-waste in the world, therefore, effectively recovering gold from electronic waste water or second resources has great economic and resource conservation value [5]. However, Au content in industrial wastewater is limited, and it always contains a large amount of other base metal ions. The selective extraction of gold from industrial wastewater is still a challenge.

The separation and enrichment of metal ions from solution is of great significance for resource recovery. Adsorption has incomparable advantages in this work due to its economic and high efficiency [6,7]. Electrospinning nanofiber membrane is an ideal adsorption material, which is characterized by high porosity,

micron-size and interconnection of void regions, and has been widely concerned in the field of adsorption and separation. Compared with traditional adsorbents, the binding sites of the nanofiber membrane were exposed to the surface and pore wall, which makes the membrane more likely to bind with the solute and significantly reduce the reaction time [8]. Especially in the ion filtration, the affinity membrane can make the ion recovery process more continuous. In addition, compared with the traditional adsorption bed, the affinity membrane module is smaller in size and easier to operate [9,10]. A mixed matrix nanofiber membrane was prepared as a flow-through adsorber by Park, and it can continuously recover Li⁺ from seawater [11]. Li *et al.* developed a spiral wound membrane (SWM) module of electrospun chitosan nanofiber affinity membrane for treating Cr (VI) contaminated water, which can effectively reject Cr (VI) from water [12]. Affinity membranes have been explored by researchers for metal ion recovery and separation include precious metals [13,14].

Affinity membranes designed specifically for Au (III) adsorption have been reported in literatures [8,15]. Functionalized polymer membrane incorporated chelating groups, ion exchange groups or affinity ligands such as CN—, —NH₃, thiourea. Among them, cyanide have very good affinity to Au, and were widely used in the

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extraction of gold in the past years [16–18]. However, cyanide has a strong toxicity to human, and caused serious environment pollution, this contradicts the concept of cleaner production [19,20]. Thiourea group can chelate with gold. Li *et al.* [21], developed a PVDF membrane modified with thiourea or thiosemicarbazide for Au (III) recovery from aqueous solution, but the membrane prepared by traditional non-solvent induced phase separation method caused low porosity, which limit the adsorption capacity of the membrane. Amidoxime (AO), one of the most effective structure towards chelating a wide group of metal ions [22–24], and can be easily fabricated by reaction between nitrile group and hydroxylamine (NH_2OH). However, as far as we know, few studies have reported the adsorption effect of AO containing polyacrylonitrile (PAN) on gold, this may be related to the decrease of mechanical strength of the modified PAN. Many studies have reported that the macrostructure of PAN changes with the conversion of nitrile groups [25,26]. Therefore, if we can keep the PAN structure and mechanical strength unchanged at a high nitrile conversion rate, AOPAN can be a good alternative to other polymers mentioned above for Au (III) recovery from aqueous solution.

In this work, a core-shell nanofiber membrane was prepared by coaxial electrospinning. PAN polymer was selected as shell polymeric material due to its hydrophilicity while PVDF polymer was selected as core polymeric material due to its flexibility and chemical stability, and the membrane was functionalized with amidoxime to introduce AO groups which will keep the certain flexibility and adsorption capacity. The fabricated affinity membranes will be used for the selective recovery of gold from the liquid. Both static and dynamic adsorption performances of affinity membranes to gold were evaluated. Moreover, the membranes were further characterized by FTIR spectroscopy, water contact angle, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy. It is noted that, the amidoxime nanofiber affinity (AONFA) membrane was used for the first time to extract gold from solution, and the dynamic adsorption performance of AONFA membrane for gold has not been reported in the literature. The work presented here is expected to provide an alternative to affinity membranes for selectivity extract gold from waste water.

2. Experimental

2.1. Materials

N,N-Dimethylacetamide ($\geq 99.5\%$ DMAc), Polyacrylonitrile (PAN) with a weight-average molecular weight (Mw) of $150000 \text{ g}\cdot\text{mol}^{-1}$ and hydroxylamine Poly(vinylidene fluoride) (PVDF) with a weight-average molecular weight (Mw) of $350000 \text{ g}\cdot\text{mol}^{-1}$ was bought from Kureha Chemical Industries (Osaka, Japan). hydroxylamine hydrochloride ($\geq 98.5\% \text{ NH}_2\text{OH}\cdot\text{HCl}$), hydrochloric acid (GR 36%–38% HCl), sodium hydroxide ($\geq 96\% \text{ NaOH}$), cadmium nitrate ($\geq 99\% \text{ Cd}(\text{NO}_3)_2$), Zinc chloride ($\geq 99\% \text{ ZnCl}_2$) were from Sinopharm Chemical Reagent Co., Ltd. (China). Gold ions (Au (III)) solution was purchased from National Standard Research Center. Nickel chloride ($\geq 98\% \text{ NiCl}_2$) was obtained from Xilong Scientific Co., Ltd. (China). Sodium carbonate ($\geq 99.8\% \text{ Na}_2\text{CO}_3$) was from Hunan Huihong Reagent Co., Ltd. Lead nitrate ($\geq 99\% \text{ Pb}(\text{NO}_3)_2$) was provided by Tianjin Kemiu Chemical Reagent Co., Ltd. (China). Copper chloride ($\geq 99\% \text{ CuCl}_2$) was from Tianjin HengXing Chemical Reagent Co., Ltd. (China). All chemicals were used without further purification.

2.2. Preparation of AONFA membrane

Polyacrylonitrile (12%(mass)) and polyvinylidene fluoride (12%(mass)) powder were initial dissolved into DMAc under magnetic

stirring at 60°C for 4 h respectively, until a homogeneous solutions are formed. Then transfer solutions into two 10 ml syringes and then delivered into the electrospinning apparatus. Adjusting apply voltage at 14 kV and outer and inner layer flow rate were $0.5 \text{ ml}\cdot\text{h}^{-1}$ respectively, the electrospinning process lasts for 2 h and the membrane was collected and dried at 60°C for 12 h. Complete details of electrospinning condition were provided in Table 1.

AO groups were introduced into the PAN surface through hydrothermal reaction as follows. 4 g Hydroxylamine hydrochloride and 3 g sodium carbonate were added into 100 ml deionized water. The membranes attached to non-woven support temporarily were fixed by clamps to prevent shrinkage and then immersed into the solution at 70°C for 120 min durations. After reaction, the AONFA membrane were washed three time with deionized water in order to remove the residual chemicals, and then freeze-dried under vacuum for 4 h.

2.3. Characterization

The morphology of the membranes was analyzed by field emission scanning electron microscope (JEOL, JSM-7900F, Japan). The components of the membrane after the adsorption was investigated by the Energy-dispersive X-ray spectroscopy (EDS) in the same FESEM instrument. The functional groups of the nanofiber membranes were recorded on a Fourier transform infrared spectrometer (FTIR) (Bruker, TENSOR27, USA). The wide-angle X-ray diffraction (WAXD) patterns were detected by an X-ray diffractometer (West Germany's Siemens Company, D500, Germany). The TEM images were observed by Spherical aberration Transmission electron microscope (FEI, Titan G2 60-300, USA). The concentrations of metal ions in the samples were analyzed by inductively coupled plasma spectrometer (NYSE: A, TCP5100-VDV, Malaysia). Surface information of membranes was detected by X-ray photoelectron spectrophotometer (XPS) (Thermo Fisher Scientific, K-ALPHA, England).

2.4. Batch adsorption experiments

The effect of AONFA membrane for Au extraction was evaluated through a series of batch adsorption experiments. Specifically, it includes equilibrium adsorption, adsorption kinetics, Au (III) selectivity and reusability.

Batch adsorption experiments were performed as follows: membranes were added in Au (III) solutions with different concentrations, and the mixture was oscillated at different temperatures. After that, the supernatant is sampled and analyzed at an interval to determine the concentration of Au (III) in the mixture. The adsorption capacity (q) of the samples was determined by Eqs. (1) and (2) [27,28].

Table 1

The conditions of core-shell nanofiber membrane prepare by coaxial electrospinning

Parameters	Values/Information
Dope solution	
Outer layer solution	12%(mass) PAN
Inner layer solution	12%(mass) PVDF
Solvent	DMAc
Electrospinning conditions	
Voltage/kV	14
Outer layer flow rate/ $\text{ml}\cdot\text{h}^{-1}$	0.5
Inner layer flow rate/ $\text{ml}\cdot\text{h}^{-1}$	0.5
Roller speed/ $\text{r}\cdot\text{min}^{-1}$	300
Duration time/h	2
Needle outer diameter/ μm	534
Needle inner diameter/ μm	374
Needle tip-collector distance/cm	15

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where q_t and q_e ($\text{mg} \cdot \text{g}^{-1}$) are the adsorption capacity of membranes at time t and equilibrium, respectively; C_0 ($\text{mg} \cdot \text{L}^{-1}$) is the initially concentration of the solution; C_t and C_e ($\text{mg} \cdot \text{L}^{-1}$) are the concentration of the solution at time t and equilibrium, respectively; V (ml) is the volume of the solution; m (g) is the mass of the membrane used.

Equilibrium Au (III) adsorption isotherms were evaluated according to Langmuir and Freundlich models, which are described in the Eqs. (4) and (5), respectively [29,30].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n \ln C_e} \quad (4)$$

where q_m ($\text{mg} \cdot \text{g}^{-1}$) is the Langmuir maximum adsorption capacity; K_L is the adsorption energy constant, K_F is the Freundlich adsorption capacity, while n is the adsorption intensity.

Adsorption kinetic were determined by two common kinetic models, pseudo first-order (Eq. (5)) and pseudo second-order (Eq. (6)) models as following showed [31,32].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where k_1 and k_2 are the first- and second-order rate constants, respectively.

The selectivity of AONFA membrane on Au (III) were performed as follows: Au (III) and other ions were mixed in the solution with the molar ratio of (1:1), then, a certain amount of membranes was added into the mixture to extract Au (III), the supernatant is sampled and analyzed at an intervals. The Au (III) selectivity was calculated using Eqs. (7) and (8) [33,34].

$$\alpha = \frac{K_{D(\text{Au})}}{K_{D(\text{M})}} \quad (7)$$

$$K_D = \frac{(C_0 - C_e) \times V}{C_e \times m} \quad (8)$$

where α is the selectivity constant, and K_D is the ion distribution coefficient.

The reusability of the AONFA membrane was evaluated in Au (III) solution. The AONFA membrane after adsorbed was eluted by the mixture hydrochloric acid and thiourea with different concentration. Then the membrane was washed with deionized water until neutral and reused for another adsorption cycle. The desorption efficiency is calculated by Eq. (9) [35].

$$R_d = \frac{C_d \times V_d}{(C_0 - C_e) \times V} \times 100\% \quad (9)$$

where R_d is the elution efficiency; C_d ($\text{mg} \cdot \text{L}^{-1}$) is the concentration of Au (III) in the desorption solution; V_d (ml) is the volume of the desorption solution.

2.5. AONFA membrane in dead-end filtration experiments

Schematic diagram of the dead-end membrane filtration system is shown in Fig. 1 AONFA membrane was mounted on the fixtures with effective diameter of membrane is 4 cm. The feed solution was fed into the membrane cell by peristaltic pump at a certain speed. The filtrates were collected at a definite interval, and the concentration of Au (III) in filtrates were detected by ICP-OES. Take the ratio of the effluent concentration and feed concentration as the Y-axis, and plot the time as the X-axis to obtain the breakthrough curves. The dynamic adsorption capacity of the membrane was calculated by Eq. (10) [12,36].

$$Q = \frac{\int_0^t (C_0 - C_t) v dt}{m} \quad (10)$$

where C_0 is the initial concentrations of Au (III) solution ($\text{mg} \cdot \text{ml}^{-1}$); C_t is the concentration of the filtrate at time t ($\text{mg} \cdot \text{ml}^{-1}$); v is the flow rate of the filtrate ($\text{ml} \cdot \text{min}^{-1}$) and m is the amount of the membrane (g).

In this study, breakthrough and saturation points of the membrane are defined as the time elapsed for the effluent concentration to reach 10% and 90% of the feed concentration. The membrane utilization efficiency η is defined as the ratio of breakthrough point and saturation which was determined using the following equation [12,36]:

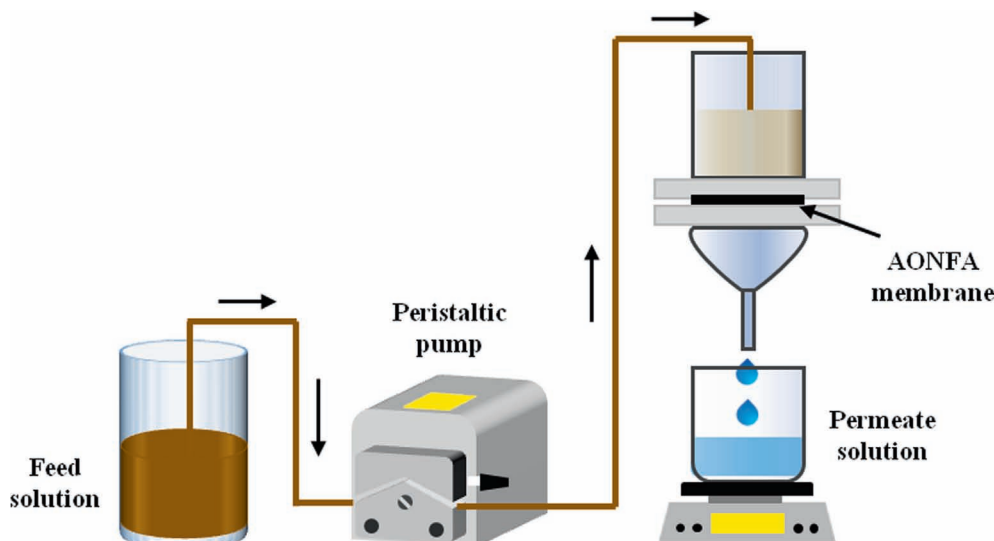


Fig. 1. Schematic diagram of the dead-end membrane filtration system.

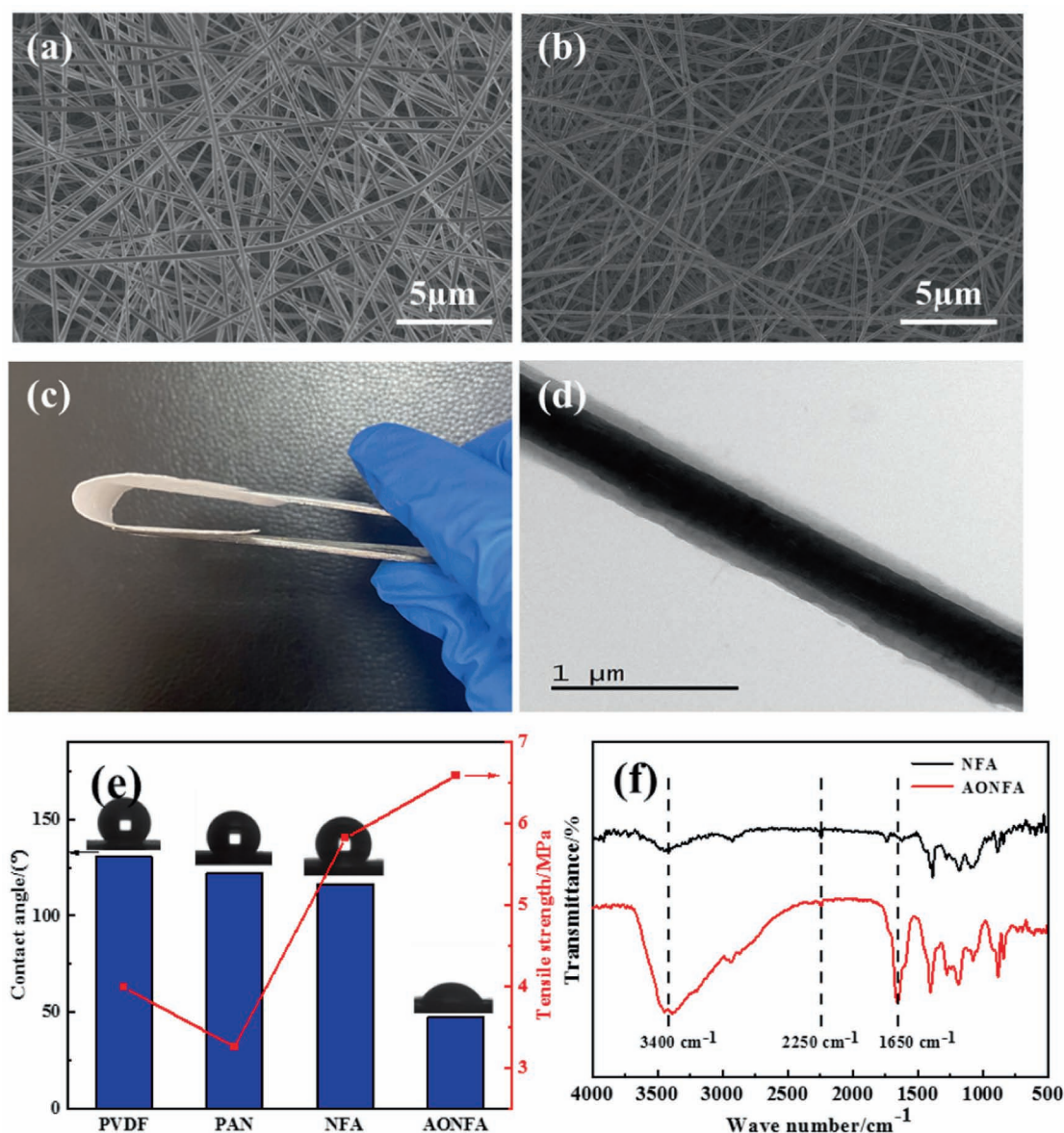


Fig. 2. (a) The SEM image of NFA membrane; (b) the SEM image of AONFA membrane; (c) digital photo of AONFA membrane; (d) the TEM image of AONFA fiber; (e) the water contact angle and tensile strength of different nanofiber membrane; (f) FTIR spectra of NFA and AONFA membrane.

$$\eta = \frac{Q_{t_b}}{Q_{t_s}} = \frac{\int_0^{t_b} (C_0 - C_{t_b}) v dt}{\int_0^{t_s} (C_0 - C_{t_s}) v dt} \times 100\% \quad (11)$$

where Q_{t_b} and Q_{t_s} are the dynamic adsorption capacity of the membrane at breakthrough time and saturation time ($\text{mg} \cdot \text{g}^{-1}$); t_b and t_s are the time to reach breakthrough and saturation point (min); C_{t_b} and C_{t_s} are the concentration of the effluent at t_b and t_s ($\text{mg} \cdot \text{L}^{-1}$).

2.6. Dynamic recovery Au (III) from mixtures by AONFA membrane

The setup in Fig. 1 was operated to demonstrate the selectivity and long-term performance of AONFA membrane for Au (III) recovery. Au (III) and other ions were mixed in the solution with the molar ratio of (1:10). The mixture solution was fed into the membrane cell by peristaltic pump and the filtrates were collected for elemental analysis (ICP-OES). The setup was operated until the concentration of Au (III) $C_p/C_f = 0.95$ was reached.

3. Results and Discussion

3.1. Preparation and characterization of AONFA membrane

It can be seen from the SEM (Fig. 2) images that the morphology of the fibers was maintained after modification, which is related to the two layers observed in TEM picture. The inner layer of PVDF does not participate in the reaction and provides support for the nanofiber membrane. Notably, AONFA membrane did not shrink in modification, they are still flexible and usable as a flow-through membrane adsorber. The high specific surface area and

Table 2
The fiber diameter, porosity and surface area of membranes

	Fiber diameter (d)/ μm	Porosity (ϵ)/%	Surface area/ $\text{m}^2 \cdot \text{g}^{-1}$
NFA	0.244	95.8	32.574
AONFA	0.265	94.6	32.855

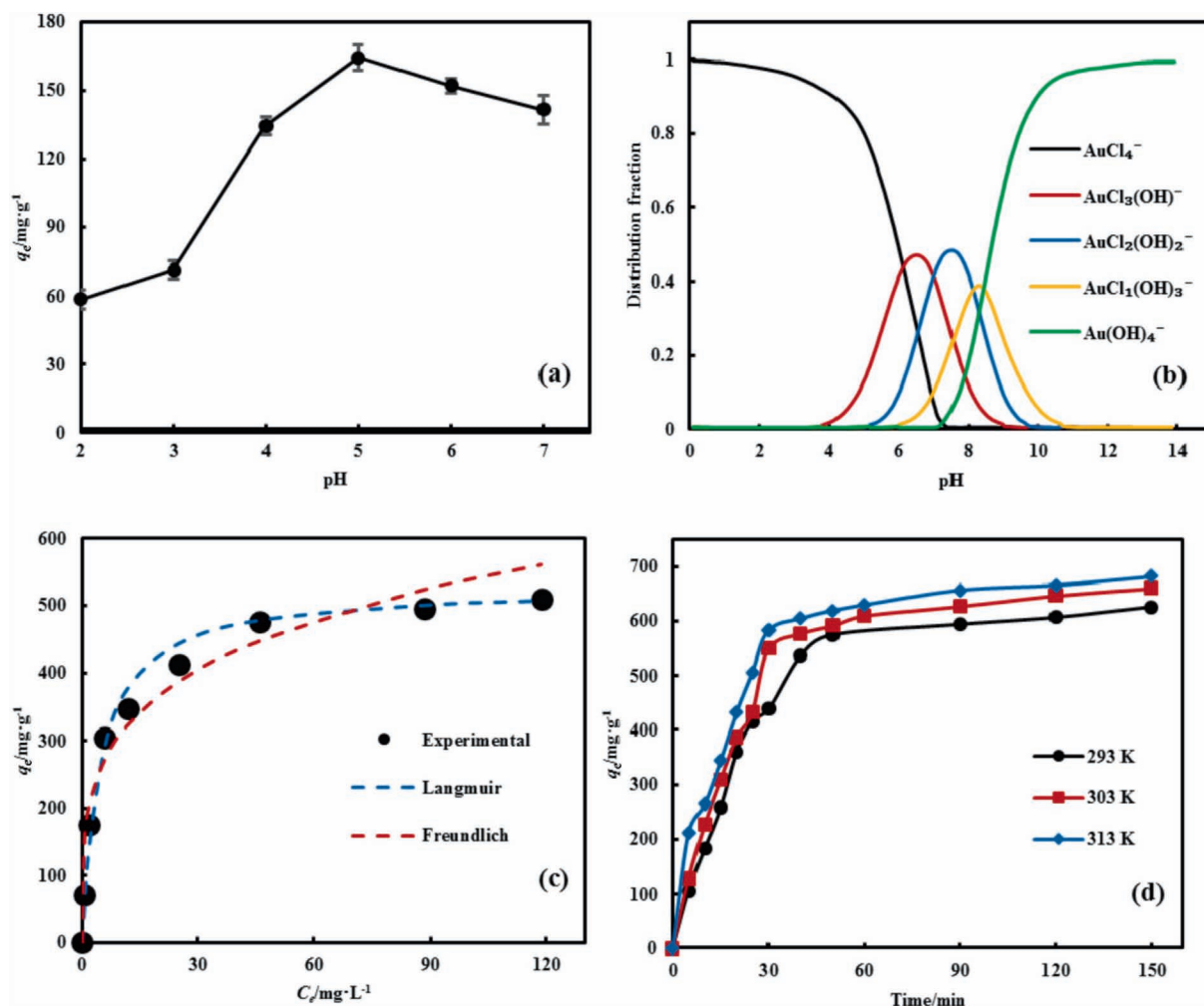


Fig. 3. Batch adsorption experiments: (a) adsorption capacity of AONFA in different pH value; (b) influence of pH on distribution fraction of Au (III); (c) adsorption isotherms of Au (III) on AONFA and fitting by the Langmuir and Freundlich models; and (d) adsorption time profiles of Au (III) on AONFA membrane.

Table 3

Parameters of Langmuir and Freundlich models for Au (III) adsorption by AONFA membrane

Langmuir			Freundlich		
q_m	K_L	R^2	K_F	$1/n$	R^2
526.32	0.2135	0.9991	179.11	0.2392	0.9323

complex pore structure of electrospun nanofiber membrane leads to a higher water contact angle [37]. The treated membranes appeared more hydrophilic due to the introduction of amino group. The physic strength of nanofiber membrane increases compared with pure material, which have two reasons: on the one hand, the diameter of fibers increases; on the other hand, the modification take place at 70 °C, and high temperature has positive effect on enhancing the mechanical strength [38]. The detail information of the membrane before and after amidoxime are shown in Table 2. Overall characterization results reveal that the desired mechanical, structural, and surface properties of a suitable affinity membrane were achieved in the fabricated AONFA membrane.

The FT-IR spectra (Fig. 2) revealed the changes of the groups in membrane before and after modification. The peak in 2250 cm⁻¹ is decreased after modification which are owing to nitrile consumption in modification. The additional peaks of AONFA membrane at 3400 and 1650 cm⁻¹ are caused the stretching vibration of —NH₂ and C=N groups in amidoxime, respectively [25,39]. From the

FT-IR spectra of the AONFA membrane, the introduction of amidoxime groups on nanofibers was confirmed.

Table 4

Comparison of adsorption capacity of different adsorbents

Adsorbents	Adsorption capacity/ mg·g ⁻¹	Adsorption time/ min	References
MNP-G3	3.58	240	[42]
PS-APD	300.8	720	[43]
DACS-TA	298.5	1200	[17]
BHJC	425.5	200	[44]
SiO ₂ -DETA	145.8	60	[45]
Chitosan	167.5	100	[46]
PA-Lignin	384	100–200	[47]
Metal-organic polymer	1317	2880	[40]
UiO-66-NH ₂	495	180	[48]
A-PGMA polymer	440.5	180	[49]
AONFA membrane	509.3	120	This work

Table 5
Kinetic data of Au (III) adsorption by AONFA membrane

Temperature	$q_{e,exp}/\text{mg}\cdot\text{g}^{-1}$	Pseudo-first order			Pseudo-second order		
		k_1/min^{-1}	$q_{e,cal}/\text{mg}\cdot\text{g}^{-1}$	R^2	k_2	$q_{e,cal}/\text{mg}\cdot\text{g}^{-1}$	R^2
293 K	626.3	0.0128	456.9	0.9105	0.000154	714.28	0.9846
303 K	659.9	0.0370	454.46	0.9310	0.000136	769.23	0.9914
313 K	681.9	0.0133	398.47	0.9158	0.000280	769.23	0.9957

3.2. Batch adsorption experiments

The adsorption performance of AONFA membranes were evaluated by adsorption capacity, adsorption kinetics, Au (III) selectivity and regeneration

3.2.1. Au (III) adsorption capacity

The effect of solution pH on Au (III) adsorption is presented in Fig. 3a. As the initial pH of the solution increased from 2 to 5, the adsorption capacity increased and the optimal pH for Au (III) adsorption by AONFA membrane was 5. Low metal adsorption capacity at low pH can be attributed to the competition adsorption between Cl^- and AuCl_4^- [27,40]. And then, the adsorption capacity decreased with the pH value continue increased, which may be related to the change of Au form in the solution [41]. The Au (III) distribution fraction under different pH range shown in Fig. 3b, the hydrolysis of AuCl_4^- to $\text{AuCl}_3(\text{OH})^-$, $\text{AuCl}_2(\text{OH})_2^-$, and $\text{AuCl}(\text{OH})_3^-$ was proceeded when pH above 5, which would decrease the Au (III) adsorption on AONFA membrane. Based on the results, the optimum pH of 5 was adopted for all further adsorption experiments.

The effect of initial concentration on the adsorption capacity of Au (III) was investigated at room temperature and the adsorption isothermal data were fitted with two conventional models. The Langmuir model assumes the monolayer adsorption occurred on a homogenous surface while the Freundlich model is usually used to describe the adsorption process occurring on a heterogeneous surface. As shown in Fig. 3c, the adsorption capacity of Au (III) increases with the initial concentrations. The maximum uptake

quantity of Au (III) on AONFA membrane was $509.26 \text{ mg}\cdot\text{g}^{-1}$. Herein, Langmuir and Freundlich isotherms are employed to further understand the adsorption process. As presented in Fig. 3c and Table 3, the isotherms data can be better described by Langmuir model ($R^2 = 0.9991$) than Freundlich model ($R^2 = 0.9323$), which indicates that the adsorption of Au (III) on AONFA membrane is a monolayer adsorption due to the homogeneous distribution of binding sites on the surface of the AONFA membrane. The equilibrium adsorption capacity calculated by Langmuir model is $526.32 \text{ mg}\cdot\text{g}^{-1}$, which is close to the experimentally data (q_e , $509.26 \text{ mg}\cdot\text{g}^{-1}$). In addition, the Au (III) adsorption capacity of AONFA membrane is much higher than most of adsorbents reported in previous reference (see Table 4).

3.2.2. Kinetics of Au (III) adsorption

Kinetics of Au (III) adsorption on AONFA membrane at different temperature are shown in Fig. 3d. The Au (III) capture in AONFA membrane was rapid within the first 50 min and then slowed down considerably as adsorption reached equilibrium. This suggests that Au (III) could be rapidly adsorbed by the exterior active sites of AONFA membrane. It can also be seen from Fig. 3d, increasing temperature is conducive to increasing adsorption capacity. Results fitted in the two reaction rate models are shown in Table 5, and the correlation coefficient (R^2) is used to evaluate the fitting degree of the experimental results with models. Pseudo-first-order assumes that adsorption is limited by diffusion, and that physical reactions occur during the adsorption process. Pseudo-second-order assumes that the adsorption rate is controlled by chemical action [50]. In contrast, the pseudo-second model ($R^2 \geq 0.9846$) gave a higher R^2 value than the pseudo-first model ($0.931 \geq R^2 \geq 0.9105$) in our research, which indicate chemical action occurred during the Au (III) adsorption process.

3.2.3. Selectivity performance

Selectivity of an adsorbent is extremely important for Au (III) recovery. In mixed solution, Au (III) is mixed with cations at molar ratio of 1:1, and the adsorption capacity is showed in Fig. 4. The K_D sequence $\text{Au (III)} \gg \text{Cu (II)} > \text{Pb (II)} > \text{Cd (II)} > \text{Ni (II)}$ and α values verifies the affinity of the AONFA membrane to Au (III) (Table 6). This is due to the gold mainly exists in the form of AuCl_4^- in hydrochloric acid solution. The amino protonation on the fibers forms a positively charged membrane surface, which generates electrostatic adsorption with anions AuCl_4^- . However, metal cations have electrostatic repulsion with protonated amino groups, so it is difficult to approach the fiber surface. Interestingly, the adsorption performance of amidoxime adsorbent to cations have been reported in previous literatures [24,51,52], and in our study, it is found that Au (III) could be adsorbed priority by AONFA membrane in cations mixed solution.

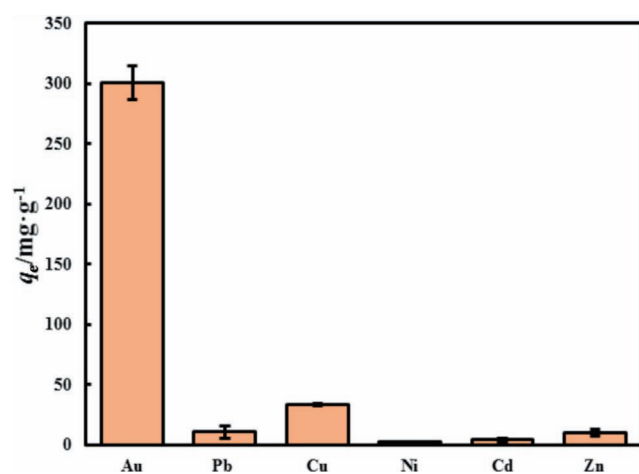


Fig. 4. Competitive metal ion adsorption properties of AONFA membrane.

Table 6
The K_D values of metal ions and α values of metal ions to Au (III)

Metal ions	Au (III)	Cd (II)	Cu (II)	Ni (II)	Pb (II)	Zn (II)
$K_D/\text{ml}\cdot\text{g}^{-1}$	23.946	0.062	1.139	0.018	0.064	0.392
α	1	388.95	21.026	1315.434	372.362	61.002

3.2.4. Regeneration

Reusability of the adsorbents is of great significance for their potential applications. Hence, in this study, the mixture of HCl and thiourea with various of concentration are tested to desorb Au (III) from AONFA membrane. AONFA membrane after adsorption are mixed with 20 ml of desorption solutions. As shown in

Fig. 5a and b, the desorption efficiency (R_d) increased with the increase of the concentration of HCl and remained unchanged when HCl concentration exceeded $1.5 \text{ mol} \cdot \text{L}^{-1}$. The same pattern is shown with increasing of thiourea concentrations. The results showed that the desorption efficiency (R_d) of the saturated AONFA membrane reached 99.37% in a mixture of $1.5 \text{ mol} \cdot \text{L}^{-1}$ and 10%

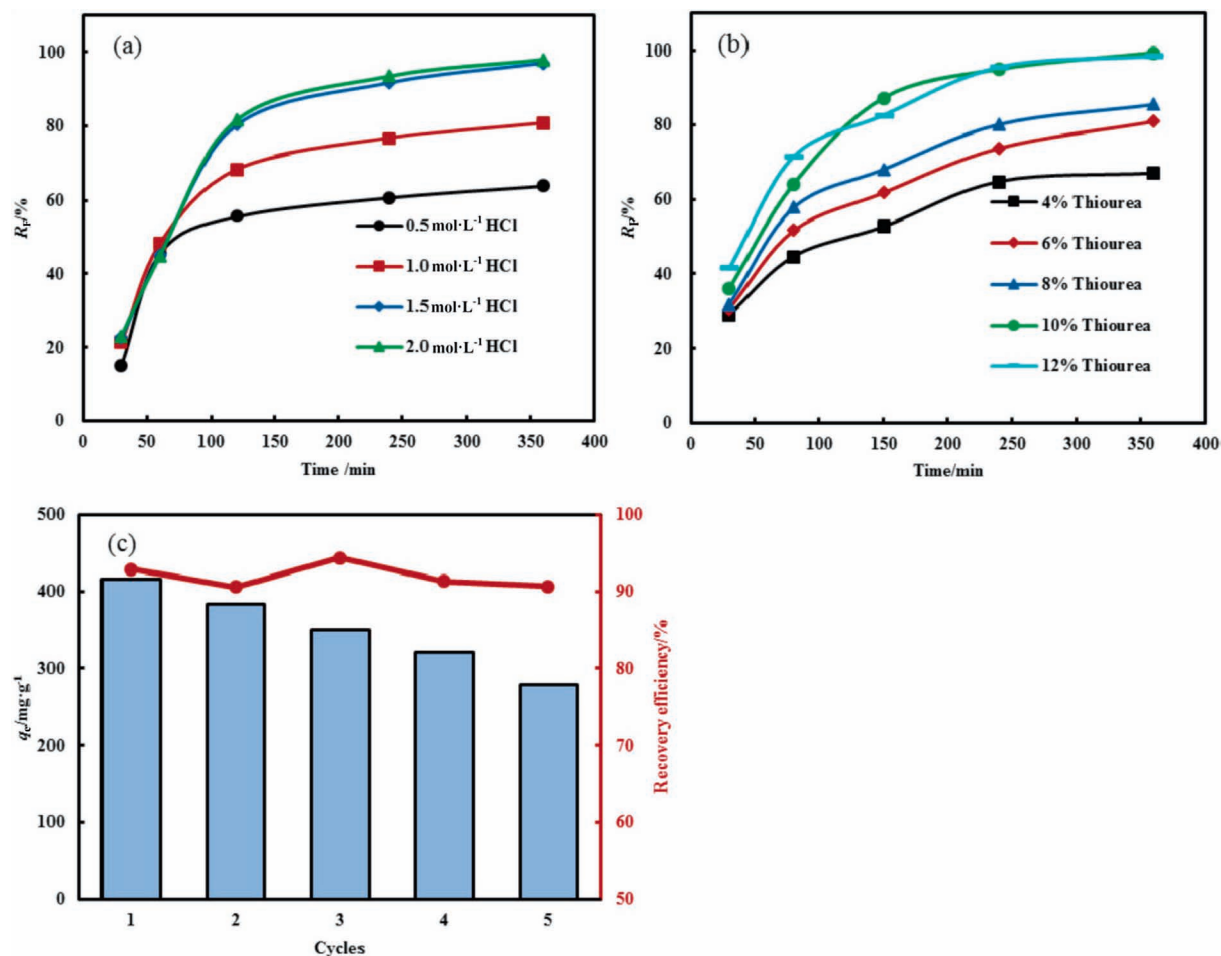


Fig. 5. Regeneration of AONFA membrane: (a) regeneration properties with different concentration of HCl mixed 10% thiourea; (b) regeneration properties with different concentration of thiourea mixed $1.5 \text{ mol} \cdot \text{L}^{-1}$ HCl; (c) reusability and recovery efficiency of AONFA membrane.

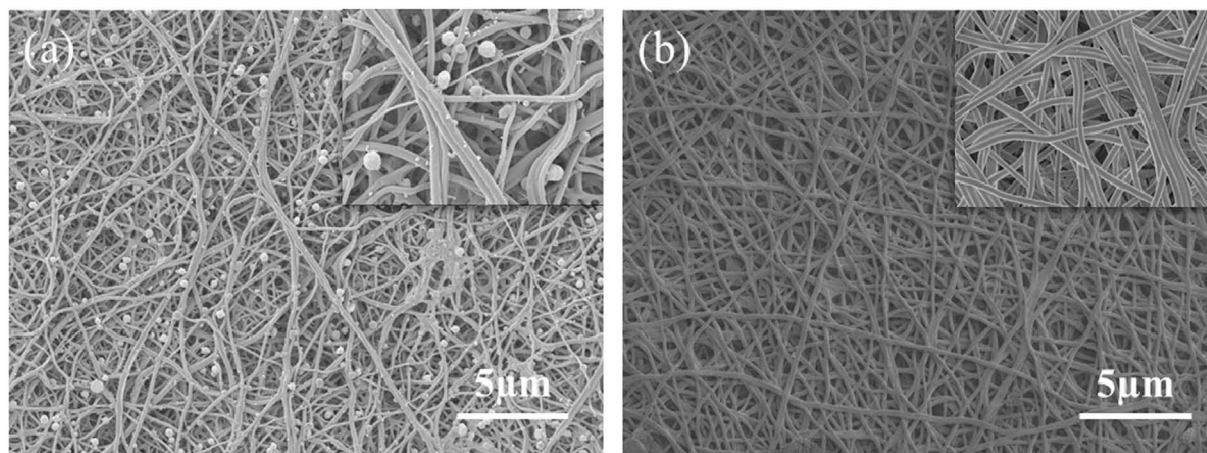


Fig. 6. SEM images of AONFA membrane after adsorption and desorption.

thiourea, and the desorption equilibrium reached within 4 h. After five adsorption–desorption cycles, the adsorption capacity remained 67% of the original membrane (Fig. 5c). From SEM images in Fig. 6a and b, large number of spherical Au crystals formed on the surface of the adsorbed fibers, and it became smooth after desorption, which verified the elution performance, moreover, the morphology of the fibers did not change significantly.

3.3. AONFA membrane as flow-through membrane adsorbers

3.3.1. Effect of feed concentration

For dynamic adsorption, the dead-end membrane filtration was performed using AONFA membrane as filtration membrane. As indicated in Fig. 7a, the profile of the breakthrough curves varies with feed concentration significantly, where the flow rate is fixed

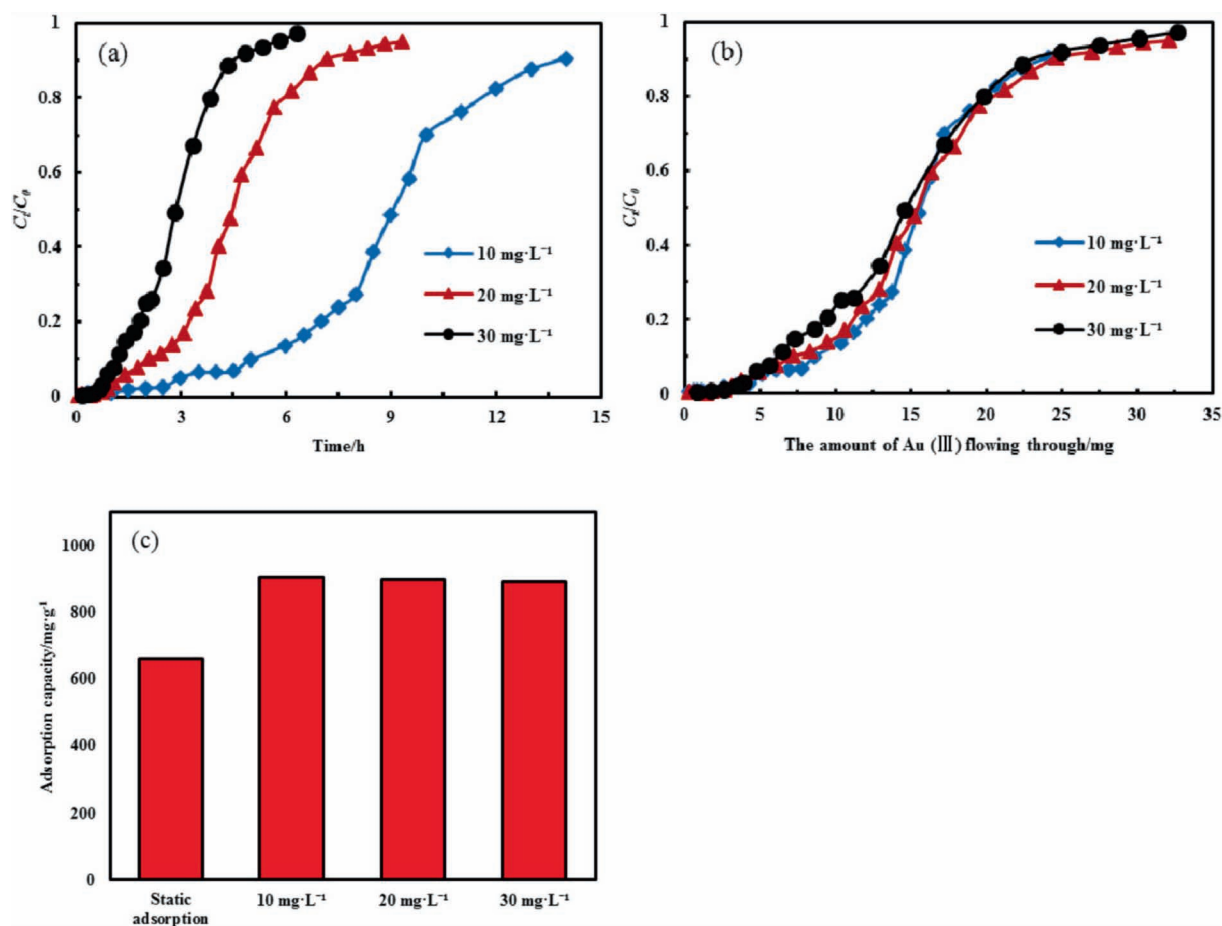


Fig. 7. Effect of feed concentration on dynamic adsorption (a) breakthrough as a function of time at different feed concentration (b) breakthrough as a function of the amount of Au (III) flowing through the membrane (c) static and dynamic adsorption capacity.

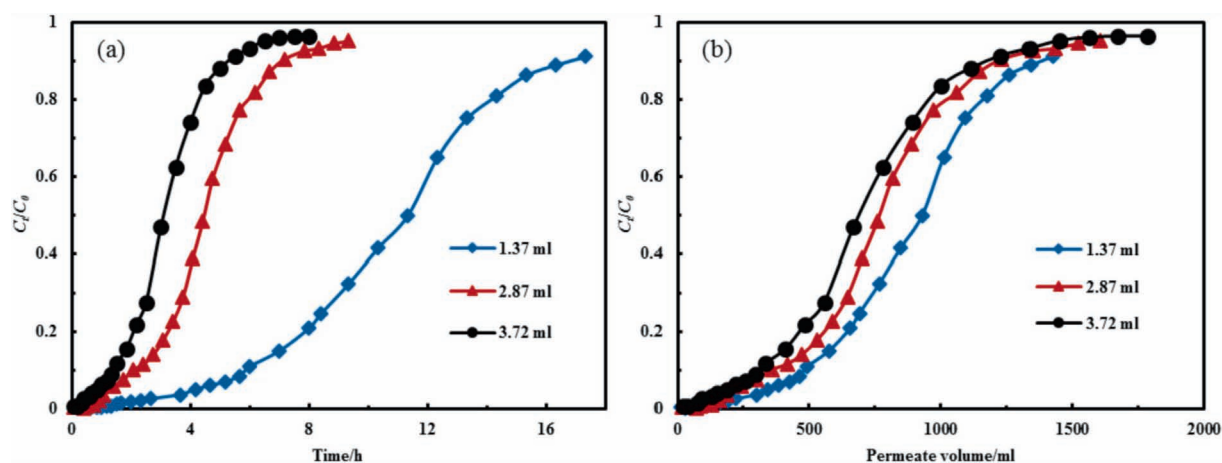


Fig. 8. Effect of flow rate on dynamic adsorption (a) breakthrough as a function of time at different flow rate (b) breakthrough as a function of the permeate volume.

Table 7

The adsorption capacity and utilization efficiency of AONFA membrane in static adsorption and dynamic adsorption.

	Static adsorption	Dynamic adsorption					
		10 mg·L ⁻¹	20 mg·L ⁻¹	30 mg·L ⁻¹	1.37 ml·min ⁻¹	2.87 ml·min ⁻¹	3.72 ml·min ⁻¹
Adsorption capacity/mg·g ⁻¹	509.3	904.74	899.18	894.41	1028.35	960.29	856.34
Membrane utilization efficiency		52.32%	43.69%	38.9%	52.07%	43.76%	40.76%

at 2.87 ml·min⁻¹. The breakthrough curves become steeper with the increases of feed Au (III) concentration, which means that breakthrough occurs faster. As the concentration increases, more Au (III) ions contact with the site on fibers, and reduce the time to reach equilibrium. When the amount of Au (III) ions flowing through the membrane was used as axis X to draw the breakthrough curves, the three curves basically overlap (Fig. 7b). By defining the breakthrough equilibrium point as the position where $C_t/C_0 = 0.9$, the dynamic adsorption capacity of the membrane was calculated, and the results are shown in Fig. 7c. This indicated that, the increase in concentration only shortened the breakthrough time and had little impact on the dynamic adsorption capacity. Compared with batch system, the membrane adsorption capacity was significant improved in dead-end filtration process. This is related to the degree of adsorption. Static adsorption occurs in a fixed volume solution and the fiber membrane floats in the upper solution due to lower density, which weakens the mass transfer process in the internal pore of fiber membrane, thus the adsorption mainly occurs on the surface of the membrane. Nevertheless, in dynamic adsorption, the solution flow through the membrane. On the one hand, Au (III) can fully contact with the adsorption site internal the membrane; On the other hand, the attached gold particles on the fiber surface provide attachment points for Au (III) in solution, which lead to more gold particle growth.

3.3.2. Effect of flow rate

The flow rate of filtrate is adjusted by controlling the speed of feed solution driven by peristaltic pump. The Au (III) dynamic adsorption behavior of AONFA membrane was also observed through a series of breakthrough studies at varied flow rate and the concentration of Au (III) was fixed at 20 mg·L⁻¹. It can be seen from Fig. 8a, the steeper of the breakthrough curve at higher flow rate. The higher flow rate suggested that the residence time of the

feed in the AONFA membrane might have been too short. This leads to early breakthrough and low Au (III) adsorption capacity. The relationship between breakthrough and permeate volume is shown in Fig. 8b. Lower flow rate (1.37 ml·min⁻¹) increased the adsorption capacity and membrane utilization efficiency. When the flow rate increases from 1.37 ml·min⁻¹ to 3.72 ml·min⁻¹, the membrane utilization efficiency decreases from 52.07% to 40.76% (Table 7). when the filtration at low flow rate, the hydraulic residence time of the solution is longer, which is conducive to the full contact and reaction between Au (III) and the fiber membrane. The results show that the membrane utilization efficiency can be improved by decreasing the flow rate. In combination with the experimental results, increasing the concentration of solution and reducing the flow rate can effectively reduce the time to equilibrium and improve the membrane utilization efficiency. We can flexibly adjust the flow rate and concentration according to the situation to obtain the maximum utilization efficiency of the membrane in filtration process.

3.3.3. Dynamic recovery Au (III) from mixtures by AONFA membrane

In process, trace Au (III) usually coexists with large number of other ions in the water. Keep the sensitivity to recovery trace Au (III) in complex water is a crucial performance for an affinity membrane. To simulate actual waste water, the selectivity of AONFA membrane in dynamic filtration is carried out in mixtures, which the molar ratio of Au with other cations (Pb, Cd, Cu, Ni · Zn) are fixed in 1:10. It can be seen from Fig. 9, the concentration of other cations increases rapidly at the initial stage of operation, while the shape of Au (III) breakthrough curve is basically consistent with early experiments (Section 3.2.1). Even if the concentration of other cations are much higher than Au (III), AONFA membrane still maintains a high selectivity to gold ion. This indicated that, AONFA membrane is highly sensitive to Au (III) and the process is not affected by other metal cations, which is a promising method for recovering trace Au (III) from mixtures.

3.4. The mechanism of recovery Au (III) by AONFA membrane

In order to understand the behavior of Au (III) on AONFA membrane, characterizations were used to detect the different between before and after adsorption. SEM images of membrane surfaces with different adsorption times are shown in Fig. 10. There are some particles formed on fibers within 30 s, and the number and size of particles gradually increase within 60 min. When the adsorption time reached 120 min, larger particles similar in shape to walnut were formed on the surface of the membrane. Three different positions on membrane surface are selected for elemental analysis include the walnut particle and the position where the particle is not fully formed, and the results are shown in Fig. 11. The results of EDS showed that the walnut particle is gold, while the non-walnut particle mainly consisted gold and chlorine. This suggested that Au (III) adsorption process on membrane surface possibly involved two steps: (1) AuCl₄⁻ attracted on the fiber surface by electrostatic force, and the concentrated solution around the fibers result in the precipitation of AuCl₃ and (2) The AuCl₃ particles on the fibers are aggregated into groups and reduced into

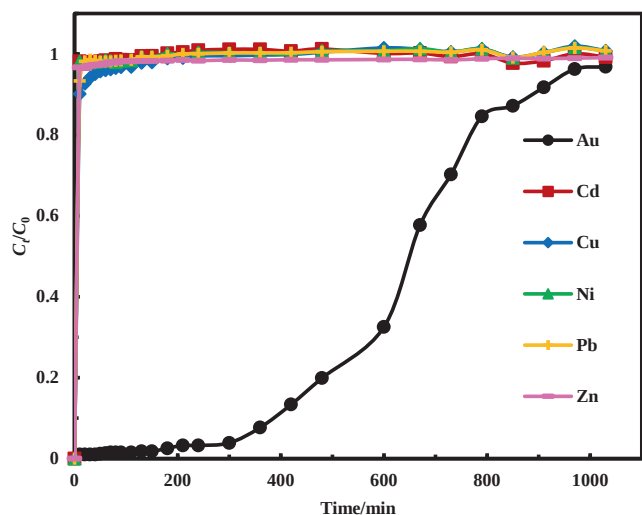


Fig. 9. The selectivity performance of AONFA membrane to Au (III) in dynamic filtration process.

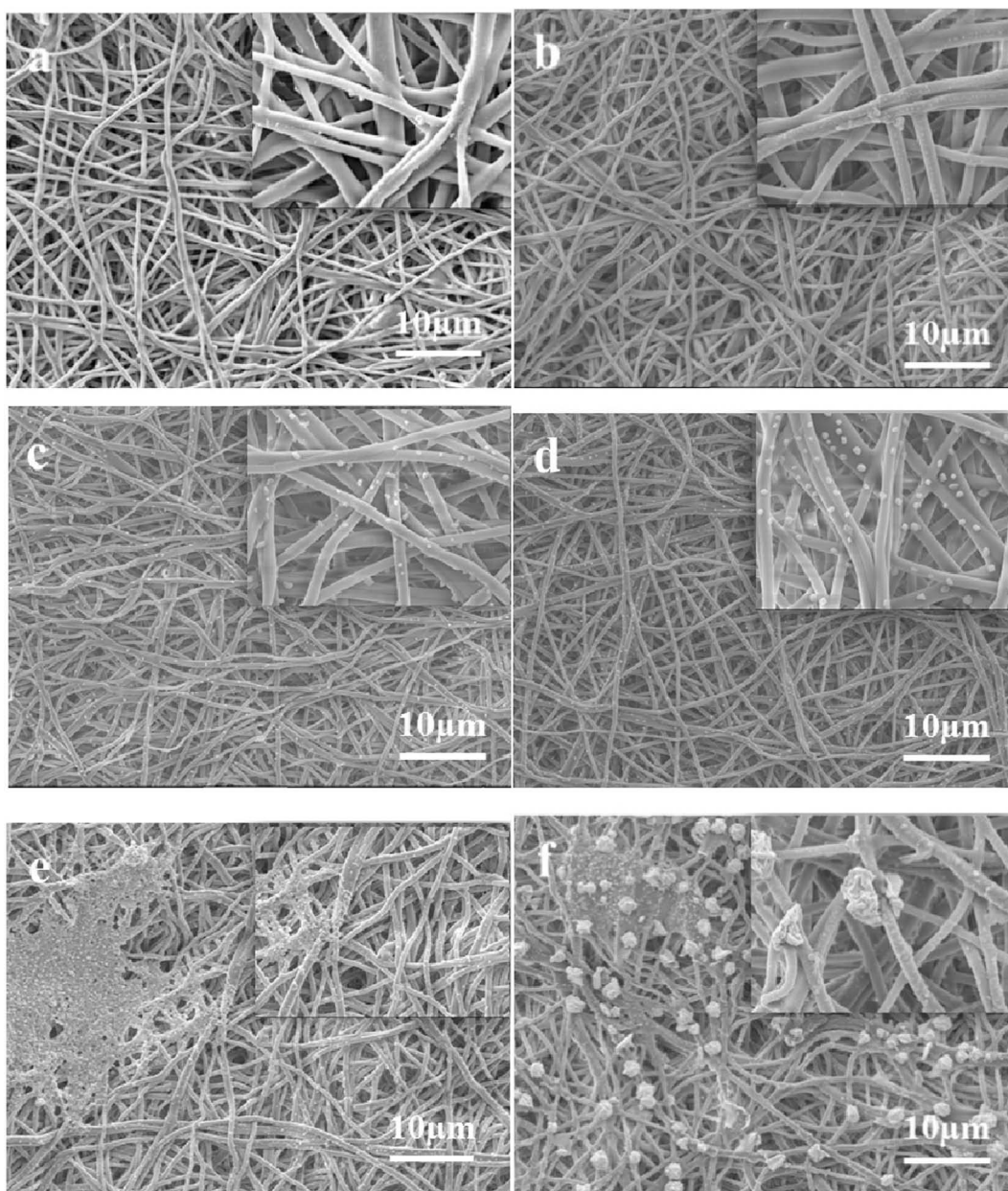


Fig. 10. The SEM images of AONFA membrane surface with different adsorption time (a)–(f) 30 s, 5 min, 10 min, 30 min, 60 min, 120 min.

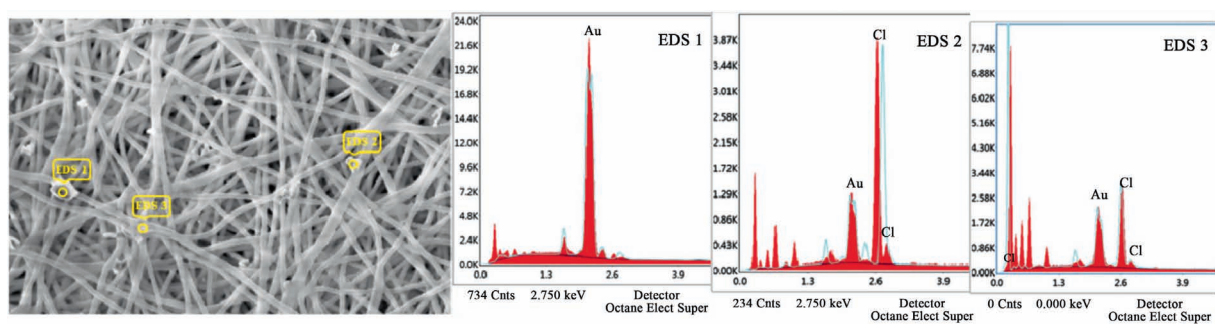


Fig. 11. The EDS analysis of AONFA membrane after adsorption.

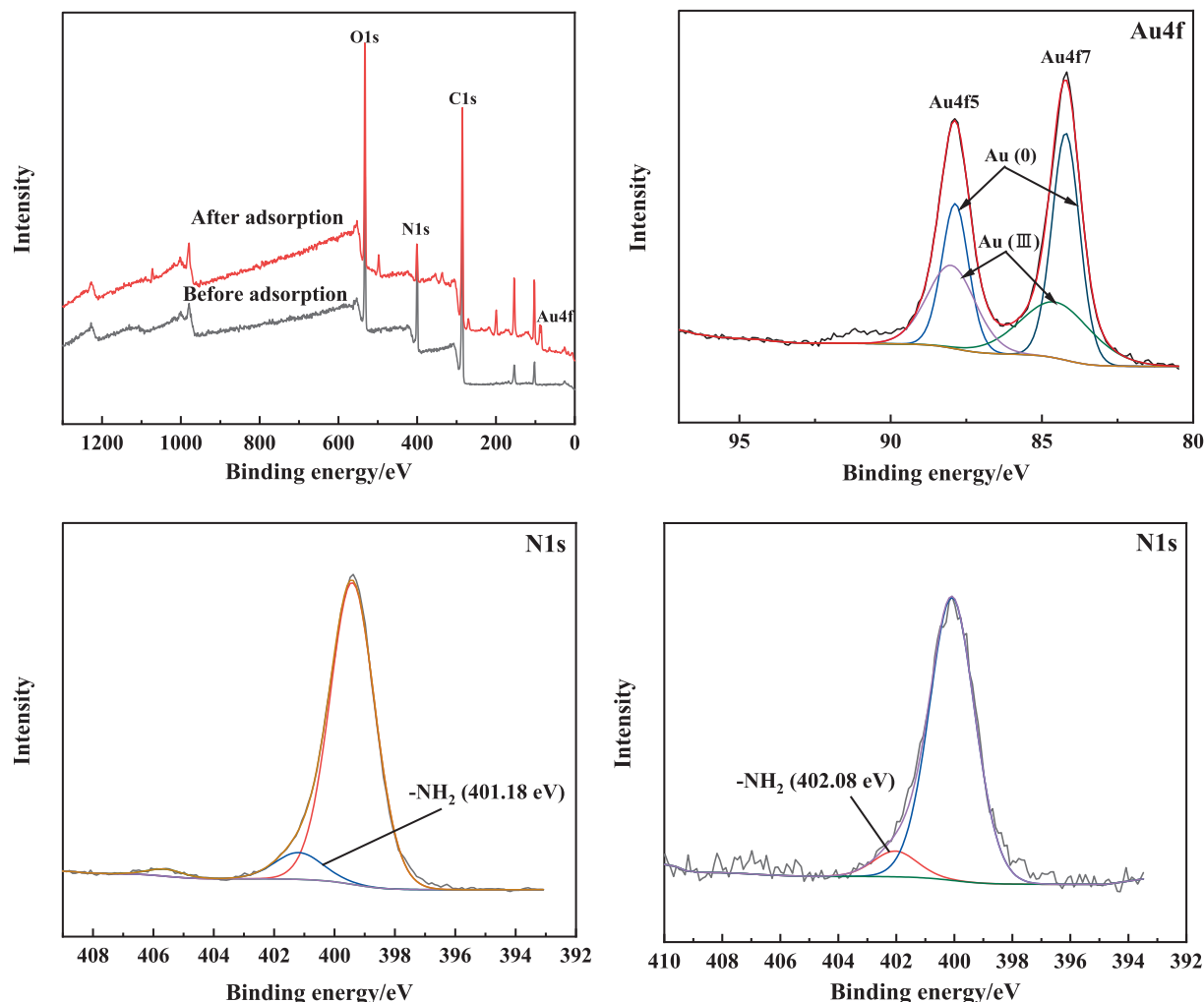


Fig. 12. XPS analysis of the full spectrum (a), Au4f spectra of AONFA membrane after adsorption (b), N1s spectra of AONFA membrane before adsorption (c) and after adsorption (d).

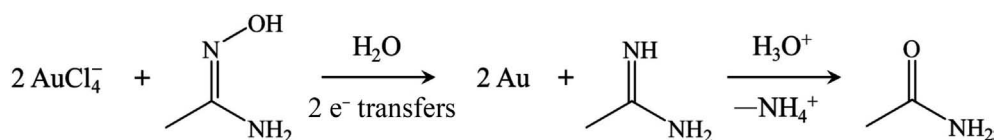


Fig. 13. Redox mechanism of amidoxime and AuCl₄⁻

gold. XPS was employed to analyze the surface composition of AONFA membrane before and after Au (III) adsorption. As shown in Fig. 12a, the peak of Au4f appeared after Au (III) adsorption. In other words, Au (III) was adsorbed by AONFA membrane. The spectrum of Au4f was listed in Fig. 12b, two strong peaks at 84.18 eV (Au4f7/2) and 87.88 eV (Au4f5/2) are related to Au (0). The peaks at 84.68 eV (Au4f7/2) and 88.08 eV (Au4f5/2) are assigned to Au (III) [41,53]. N1s XPS spectra of AONFA membrane before and after Au (III) adsorption are shown in Fig. 12c and d. A comparison between N1s XPS spectra before and after adsorption reveal major changes like the disappearance of the 405.68 eV peak (=N–) and the peak at 401.18 eV shifted to higher energy values. These indicates that =N– may be involved in the redox process of Au [18], and the type reaction of reductive deoxygenation of amidoximes occurs on the surface of AONFA membrane [54]. Besides, AuCl₄⁻ ions were reduced to Au [41]. Fig. 13 shows the possible redox mechanism between amidoxime and gold.

4. Conclusions

An amidoxime PAN nanofiber membrane based on core-shell structure was prepared by electrospinning and used for the selective recovery of Au (III) from aqueous solutions. The experimental results show that AONFA membrane was not only flexible, but also had high adsorption capacity (509.3 mg·g⁻¹) and excellent selectivity for Au (III). In addition, the adsorption reached equilibrium within 120 min, and AONFA membrane remained a high adsorption performance after five regeneration cycles. In dead-end filtration test, the dynamic adsorption capacity of the membrane was 1028 mg·g⁻¹, and the results showed that lower flow rate can improve the utilization efficiency of membrane and increase the solution concentration can accelerate the breakthrough process. We could flexibly select the flow rate and concentration to achieve the highest membrane utilization efficiency in the shortest time. The adsorption mechanism of Au (III) on AONFA membrane

was proved to be an electrostatic adsorption and reduction processes.

CRedit authorship contribution statement

Yang Chen: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Lanying Jiang:** Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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