Polyacrylonitrile-based fiber modified with thiosemicarbazide by microwave irradiation and its adsorption behavior for Cd(II) and Pb(II)

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Abstract:

A novel thiosemicarbazide modified adsorbent (PAN_{MW}-TSC) based on polyacrylonitrile fiber was successfully synthesized under microwave irradiation, which was applied for the uptake of Cd(II) and Pb(II) from aqueous solution subsequently. Microwave irradiation method is a new approach to achieve the modification and it turns out that just a 30 min process is enough for the anchoring of functional groups in the fiber matrix. The surface characterization was performed by fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) elemental analysis (EA) and thermogravimetric analysis (TGA), indicating that the modification was successfully accomplished. Batch adsorption experiments including equilibrium isotherms, kinetics and the effects of pH and temperature on the adsorption of Cd(II) and Pb(II) were systematically studied. Among three kinetic models, the pseudo-second-order kinetic model provides the best correlation for the process. The nonlinear resolution of the Langmuir isotherm equation has been found to show the closest fit to the equilibrium data. Thermodynamic parameters, involving ΔG , ΔH and ΔS were also calculated from graphical interpretation of the experimental data, which suggest that metal ions adsorption onto PAN_{MW}-TSC fibers is spontaneous and exothermic. Regeneration of PAN_{MW}-TSC fibers loaded with metal ions was efficiently done with 0.5 M HNO₃, by which the investigated adsorbent could be used reproductively for five times with a small decrease in sorption capacity. The feasible preparation of PAN_{MW}-TSC fibers with high adsorption capacities opens a new perspective in the potential application for wastewater treatment.

Keywords: Microwave irradiation; Polyacrylonitrile fiber; Adsorption; Cadmium; Lead.

1. Introduction

Nowadays, with the rapid development of industry, heavy metals have been abundantly discharged into the environment through industrial wastewater, which has become a worldwide environmental threat due to their non-biodegradability and carcinogenicity [1, 2]. Discharged toxic metals typically including cadmium and lead could be accumulated into human body through food chains, causing serious diseases and disorders even at low concentrations [3, 4]. Cadmium, for example, is associated with a higher incidence of nephrotoxic effects while lead causes kidney damage, anaemia and detriment to the reproductive system. Thus, it is critical to remove Cd(II) and Pb(II) from wastewater in the perspective of environment and health. Several technologies and processes have been developed and applied for the removal of heavy metal ions from different aqueous solutions, such as chemical precipitation, ion exchange, membrane separation and electrochemical treatment [5-7]. Whereas, few satisfactory removal results could be achieved by the above-mentioned techniques on account of their low efficiency, high cost, disposal of sludge and sometimes might bring secondary pollution into the environment. Comparatively, adsorption technology with chelating ligands has received considerable attention due to its remarkable simplicity, high efficiency and availability of different adsorbents. Among various adsorbents such as chitosan [8], activated carbon [9], silica nanocomposite and magnetite particles [10, 11], the adsorbents based on polyacrylonitrile fiber (PANF) possess many desirable superiorities in solvent resistance, thermal and mechanical stability. The raw PANF shows no metal binding ability towards metal ions, nevertheless, the ability can be activated subsequently by modified with manifold low-molecular weight ligands [12, 13]. Xiong et al. [14] reported that the 2-amino-1,3,4-thiadiazole functionalized PANF containing N and S atoms can be used for the selective adsorption of Hg(II) from mixed metal solutions. Zhao et al. [15] found that phosphorylate PAN nanofiber mat exhibit high adsorption performance towards Pb^{2+} , Cu^{2+} , Ag^+ and Cd^{2+} ions. According to the principle of hard and soft acids and bases, sulfur-containing groups are regarded as soft bases and therefore it is

reasonable to use sulfur functionalized PANF to interact with such soft acids like Cd(II) and Pb(II) through a coordinate bond in the side chain of the polymer.

In recent years, microwave (MW) irradiation, as an alternative method, has been utilized in graft copolymerization in substitution of conventional heating methods due to its ability to ensure rapid and uniform heating in chemical reaction [16]. Basically, MW irradiation can penetrate the material and supply energy while heating can be initiated by transferring electromagnetic energy to thermal energy efficiently which results in volumetric heating [17]. Consequently, the processing time of the reaction was reduced and the product quality was enhanced. In our recent report, the iminodiacetic acid (IDA) functionalized chelating fiber was prepared by MW irradiation method which displayed a high adsorption efficiency for Cu(II) and Hg(II) [18].

In the present study, we prepared a sulfur-bearing adsorbent based on PANF in two step graft modification process through MW irradiation method. The obtained fibrous material was systematically explored as adsorbent for removal of Cd(II) and Pb(II) from aqueous solution by batch adsorption experiments. To further understand the adsorption process, the adsorption kinetics, isotherms and the thermodynamic properties of the adsorption of Cd(II) and Pb(II) on the synthetic fiber were also clarified. Moreover, the recovery of Cd(II) and Pb(II) and reusability of the adsorbent were investigated.

2. Experimental

2.1. Materials and methods

The polyacrylonitrile fiber (PANF) made by 100% acrylonitrile was purchased from Beijing Rongnai Industry Material Co., Ltd. (Beijing, PR China). Diethylenetriamine (DETA), thiosemicarbazide (TSC), N,N-dimethylformamide (DMF) were all supplied by Aladdin Chemical Reagent Co., Ltd. (Shanghai, PR China). Cadmium ion (500 mg·L⁻¹) and lead ion (500 mg·L⁻¹) solution were prepared by dissolving appropriate amount of CdCl₂·2.5H₂O and Pb(NO₃)₂ (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, PR China) in deionized water, respectively.

2.2. Crosslinking reaction of PANF

The PANF (1.0 g), DETA (40 mL) and deionized water (20 mL) were added into a 250 mL round bottomed flask and then ultrasonic treated for 5 min. The reaction was carried out in MW reactor (COOPLEX-E with output power 1200 W, purchased from Preekem Scientific Instruments Co., Ltd, China) and the parameters of time and temperature were set up at 15 min and 388 K, respectively. The external and internal feature of the MW reactor are illustrated in Fig. S1 in supporting information (SI). After reaction, the product was washed with anhydrous ethanol and thermal deionized water until neutral, suction filtered, and dried in a vacuum oven at 343 K overnight. The crosslinked PAN fibers were named as PAN_{MW}-DETA. The grafting percentage (*GP%*) was calculated by gravimetry through following equation:

$$GP\% = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 and m_1 are the weights of raw polyacrylonitrile fiber and PAN_{MW}-DETA, respectively.

2.3. Modification of PAN_{MW}-DETA

The final fibrous product was synthesized by adding PAN_{MW}-DETA (1.0 g), TSC (8.0 g), DMF (100 mL) into a 250 mL round bottomed flask. The reaction was refluxed for 15 min at 398 K under continuous mechanical stirring in MW reactor. Then the modified fibers were removed and washed with anhydrous ethanol and thermal deionized water until neutral, suction filtered and dried in a vacuum oven at 343 K overnight. Due to the slightly side effects in the modification process by MW irradiation, the DMF solvent could be used repeatedly for at least 10 times. The modified fibers grafted TSC were named as PAN_{MW}-TSC.

Schematic presentation for the synthetic steps of the PAN_{MW}-TSC is shown in Scheme 1.

Scheme 1. Synthesis routine of PAN_{MW}-TSC based on polyacrylonitrile fiber.

2.4. Characterization and analysis

The concentration of metal ions was determined using an inductively coupled plasma optimal emission spectrometer (ICP-OES; Perkin-Elmer Optimal 8300). Fourier transform infrared spectroscopy (FT-IR) experiments of PAN_{MW}-TSC were performed via a FT-IR spectrometer (Perkin-Elmer spectrum 100), and the spectra was recorded in the wave number ranging from 400 to 4000 cm⁻¹. Surface morphology of PAN_{MW}-TSC was observed by scanning electron microscope-energy dispersive X-ray spectroscopy (SEM/EDX; FEI QUANTA 200). Thermogravimetric analysis (TGA) in a range of temperature 30-500°C by 10°C min⁻¹ under the protection of nitrogen on a TGA instrument (METTLER TOLEDO; TGA/SDTA851).

2.5. Batch adsorption experiments

The prepared PAN_{MW}-TSC fibers were used as adsorbents for the removal of Cd(II) and Pb(II) from aqueous system. All batch adsorption experiments were performed on a model SHA-C shaker (Ronghua instrumental manufactory Co., Ltd., China) with a shaking speed of 100 rpm. The adsorption kinetics of the two metals were carried out with the initial concentration of 300 mg·L⁻¹ at 298 K and lasted for 180 min.

Adsorption isotherm for each heavy metal were conducted with initial concentration ranging from 20 to 300 mg·L⁻¹ at 288 K, 293 K, 298 K, respectively. The effect of pH value on adsorption was studied as pH ranged from 3 to 6.4 with the initial concentration of 300 mg·L⁻¹. Citric acid/sodium citrate buffer solution was used to adjust the pH value. The concentration of the metal ions in solution was determined by ICP-OES spectrometer. The adsorption capacity of the metal ion adsorbed onto each sample, q_e (mg·g⁻¹), was calculated on the basis of the following equation:

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

Where C_0 and C_e are the initial and the equilibrium concentration of the metal ions in the test solution (mg·L⁻¹), respectively, V is the volume of the testing solution (L), and m is the weight of the adsorbent (g). For regeneration of the fiber adsorbents, the fibers were washing with 0.5 M HNO₃ and then washed several times with deionized water. The adsorption/desorption cycle was repeated five times using the same PAN_{MW}-TSC fibers.

3. Result and discussion

3.1. Preparation and characterization of PAN_{MW}-TSC fibers

In our previous work, we have demonstrated highly time and energy efficient synthesis of IDA functionalized chelating fiber by using MW irradiation method [18], in which water acts as the mainly MW adsorber. To obtain TSC modified fibers in the present research, water was also introduced as the solvent in the reaction mixture firstly, but there is nearly no TSC immobilized on the fiber after the reaction. According to some previous researches [19, 20], DMF was suitable for the grafting reaction of TSC into different substrates such as active carbon and PVDF membrane. During MW irradiation process, the ability of a specific substance to convert electromagnetic energy into heat at a given frequency and temperature is determined by the so-called loss factor $\tan\delta$. Solvent with a high $\tan\delta$ value is required for efficient absorption, and consequently, for rapid heating [21]. Compared with water, DMF possess more sufficient ability of energy transforming on account of its higher $\tan\delta$ value. In application of DMF as solvent instead of water in the reaction under

MW irradiation, the *GP%* of PAN_{MW}-TSC fibers reached 35% in 15 min at 398 K and carmine fibers were obtained finally.

Meanwhile, for comparison of conventional heating with MW irradiation method, the immobilization of TSC experiment was performed at thermostatic magnetic heating agitator (CL-3, Gongyi City Yuhua Instrument Co., Ltd., China) under the same conditions and the grafting results are shown in Table 1. It is obviously to observe that the functionalization rate was dramatically accelerated and the outcome products by MW irradiation gained nearly nine times as much as those by conventional heating. The unique heat way and mass transfer characteristics of MW irradiation might be the reason of fast modification and high yield of PAN_{MW}-TSC fibers [22].

Table 1

Comparison of different heating types for preparation of PAN_{MW}-TSC fiber.

TSC Modification	MW irradiation	Conventional heating
<i>GP%</i>	35	4
Time (h)	0.25	12

The FT-IR spectra of the raw PANF, PAN_{MW}-DETA and PAN_{MW}-TSC fibers are shown in Fig. 1. A sharp and distinct adsorption band at 2243 cm⁻¹ in PANF, PAN_{MW}-DETA and PAN_{MW}-TSC fibers attributed to C≡N group in the polyacrylonitrile fiber. Although the fiber was claimed to be made of 100% acrylonitrile, the adsorption at 1683 cm⁻¹ still confirmed the existence of methyl acrylate or methyl methacrylate [23]. After crosslinked by DETA, the adsorption intensity of C≡N group reduced and disappeared entirely at the peak of 1683 cm⁻¹. Moreover, two new peaks at 1566 cm⁻¹ (C=O) and 1651 cm⁻¹ (-NH₂) appeared, suggesting the happening of the crosslinking reaction [24]. In the infrared spectrum of PAN_{MW}-TSC fibers, three new peaks occurred. The band at 1372 cm⁻¹ and 1507 cm⁻¹ attribute to stretching vibrations of C=S and N-C=S [25, 26]. The band at 1640 cm⁻¹ indicated the presence of C=N bond [27]. These results are all coordinated with the Scheme. 1 presented above.

The results of the elemental analysis of C, N, O, S of the fibers are given in Table 2. The C value of PAN_{MW}-DETA and PAN_{MW}-TSC fibers decreased after the

crosslinking and modification, which may attribute to the lower carbon content of DETA and TSC. Due to the hydrolysis of $C\equiv N$ group into $O=C-OH$, the N value decline was found in PAN_{MW}-DETA fibers. About 10.21% of sulfur content newly appeared in PAN_{MW}-TSC fibers, indicated that the thiosemicarbazide group has been successfully attached onto it and it coordinated to the results of FT-IR. Both FT-IR spectrum and EA analysis confirmed that the TSC functional group has been anchored expectantly on the surface of PAN_{MW}-TSC fibers.

The morphologies of fibers obtaining from different reaction steps were observed by SEM and the results are shown in Fig. 2. It can be seen that the surface of PANF was smooth and neat, barely with crack on it. Inspiringly, after crosslink reaction, the smooth surface of PANF fibers was substituted with creased appearance and the fibers were shrunk simultaneously. Compared with PANF, both PAN_{MW}-DETA and PAN_{MW}-TSC fibers showed an increase in diameter which may due to the introducing of DETA and TSC chains onto the fiber [28]. Additionally, all the fibers kept well in shape and did not show any serious cracks or degradation while the color altered from faint yellow to crimson. Therefore, the immobilization of DETA and TSC was expected to change the properties of the pure fiber and then affect metal ion adsorption.

The thermal stabilities of the raw PANF, PAN_{MW}-DETA and PAN_{MW}-TSC fibers were performed and compared, and the results are shown in Fig. 3. The PAN_{MW}-DETA and PAN_{MW}-TSC fibers exhibited three mainly steps transient of weight loss at temperature (i) 100°C, (ii) 280°C, and (iii) 450°C, which are ascribed to (i) evaporation of moisture and residue on the polymer, (ii) decomposition of the grafted functional groups, and (iii) degradation of the PANF backbone, respectively. Comparatively, the PANF showed tiny gravity loss under 280°C and the residue weight was higher than both PAN_{MW}-DETA and PAN_{MW}-TSC fibers. These results all indicated that the modification was successfully took place on the fiber.

Fig. 1. FT-IR spectrum of: (a) PANF, (b) PAN_{MW}-DETA and (c) PAN_{MW}-TSC.

Table 2

The dates of element analysis of PAN-Raw fiber, PAN_{MW}-DETA and PAN_{MW}-TSC.

Sample	Element content (%)				Grafting ratio (%)
	C	N	H	S	
PAN	64.97	27.53	5.41		
PAN _{MW} -DETA	55.26	25.89	7.85		45.33
PAN _{MW} -TSC	46.43	25.36	6.17	10.21	13.86

Fig. 2. SEM images of: (a) PANF, (b) PAN_{MW}-DETA and (c) PAN_{MW}-TSC.

Fig. 3. TGA curves of PANF, PAN_{MW}-DETA and PAN_{MW}-TSC fibers.

3.2. Adsorption behaviors

3.2.1. Effect of pH on Cd(II) and Pb(II) adsorption

The pH value of the solution has been regarded as the most important factor during

adsorption process. In this perspective, the experiments were carried out at different pH conditions ranged from 2 to 6.4. The pH values were accessed using the pH meter (PHSJ-4F, Shanghai Yidian Co., Ltd., China) with pH electrode. Whereas, beyond pH 6.4, the tests were not proceeded due to the formation of cadmium hydroxide and lead hydroxide [29, 30].

Apparently, as presented in Fig. 4, the adsorption capacities on PAN_{MW}-TSC fibers were highly pH dependent and the maximum capacities of Cd(II) and Pb(II) increased steadily to 1.42 mmol·g⁻¹ and 0.95 mmol·g⁻¹ at pH value of 6.4, respectively. At this pH, the modified fibers acquired negatively charged surface which enhanced the electrostatic attraction between the fibers and metal ions followed by chelation [31]. The observed low uptakes at lower pH were attribute to the protonation of the subgroup of PAN_{MW}-TSC (-NH-), along with the existence of large amount of H⁺ in the solution, which prevented metal ions from approaching and adhering onto the fibers. These negative impacts were descended as the increasing of the pH which led to higher amount of capacities in PAN_{MW}-TSC fibers. Normally, the pH of naturel water polluted by metal ions was around 7 which indicated that PAN_{MW}-TSC fibers could be effectively used as suitable adsorbents for the removal of Cd(II) and Pb(II) from the polluted water.

Fig. 4. Effect of pH on the adsorption capacity of PAN_{MW}-TSC for Cd(II) and Pb(II) at 298 K.

3.2.2. Adsorption kinetics

Kinetic studies of Cd(II) and Pb(II) were carried out at 298 K and pH 6.4, and the dynamic adsorption results are presented in Fig. 5. It can be seen that the

adsorption process for these two metal ions were rapid which reached its half saturation at just 30 min and nearly 90% saturation at 60 min. The adsorption equilibrium was attained in 180 min, approximately. The fast adsorption rate may attribute to the fiber state of the adsorbent, in which the active adsorption sites were mainly located at the outer surface and thus the diffusion resistance of mass transfer during adsorption process would be negligible [32].

Fig. 5. Adsorption kinetics curve of Cd(II) and Pb(II) on PAN_{MW}-TSC at 298 K and pH 6.4.

The applicability of the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were tested for the adsorption of Cd(II) and Pb(II) onto PAN_{MW}-TSC fibers. The best fit model was selected based on both linear regression correlation coefficient (R^2) and the calculated q_e values. These three equations describe the kinetics of adsorption process are expressed as follows [33]:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

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

$$q_t = k_3 t^{0.5} \quad (5)$$

where q_e and q_t are the amount of heavy metal ions adsorbed ($\text{mg} \cdot \text{g}^{-1}$) at equilibrium and at time t (min), respectively, while k_1 , k_2 and k_3 are the rate constants of the

pseudo-first-order model (min^{-1}), pseudo-second-order model ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) and intraparticle diffusion model ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$).

As a statistical tool for the best explanation of an adsorption system, the nonlinear chi-square test has been utilized by judging the sum squares differences between the experimental and the calculated data with each squared difference is divided by its corresponding value [34, 35].

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,cal} - q_{e,exp})^2}{q_{e,exp}} \quad (6)$$

where $q_{e,cal}$ ($q_{e,calculated}$) equilibrium capacity obtained by calculated from model ($\text{mg}\cdot\text{g}^{-1}$) and $q_{e,exp}$ ($q_{e,experimental}$) was the equilibrium capacity from the experimental data ($\text{mg}\cdot\text{g}^{-1}$). The value of χ^2 calculated from the equation represents the similarity between the data from model and the data from experiment test. A small χ^2 value indicated similarities, while a larger number represents variation of the experimental data [36].

Kinetic parameters and Chi-square values from all kinetic models have been calculated and listed in Table 3. It was observed that the calculated $q_{e,cal}$ values of both Cd(II) and Pb(II) obtained from the pseudo-second-order model are different from the experimental $q_{e,exp}$ values when compared with calculations from the pseudo-first-order model, which possibly resulted from the imprecise sampling and inaccurate testing within the error range. The χ^2 value of pseudo-second-order model for metal ions are the smallest which followed by those of pseudo-first-order model and intraparticle diffusion model, respectively. Additionally, according to the R^2 values, the pseudo-second-order model fits the experimental kinetic data better than the pseudo-first-order model and intraparticle diffusion model, suggesting that the adsorbent system can be well-described by the pseudo-second-order model. The pseudo-second-order model was developed on the assumption that the rate-determining step may be chemisorption promoted by covalent forces through electron sharing between adsorbent and adsorbate [37]. Thus, the result suggested that the adsorption of two metal ions on the PAN_{MW}-TSC fibers was mainly controlled by the chemically reactive adsorption.

Table 3Kinetic model constants for the adsorption of Cd(II) and Pb(II) onto PAN_{MW}-TSC fibers.

Metal ions	$q_{e,exp.}$ (mg·g ⁻¹)	pseudo-first-order model				pseudo-second-order model				intraparticle diffusion model		
		$q_{e,cal.}$	k_1	R^2	χ^2	$q_{e,cal.}$	$k_2 \times 10^4$	R^2	χ^2	k_3	R^2	χ^2
		(mg·g ⁻¹)	(min ⁻¹)			(mg·g ⁻¹)	(mg·g ⁻¹ ·min ⁻¹)			(mg·g ⁻¹ ·min ^{-1/2})		
Cd (II)	157.04	148.36	0.037	0.9678	10.95	174.22	2.47	0.9968	1.091	10.8	0.9138	29.33
Pb (II)	194.77	184.63	0.036	0.9665	7.349	217.41	1.89	0.9962	0.829	13.5	0.922	17.12

 $q_{e,exp.}$, $q_{e,experimental}$; $q_{e,cal.}$, $q_{e,calculated}$

3.2.3. Adsorption isotherms

To examine the effect of initial concentration of metal ions on the adsorption capacity, the adsorption isotherms of Cd(II) and Pb(II) at 288 K, 293 K, 298 K were undertaken to simulate the metal uptake by adsorbents. The pH value of Cd(II) and Pb(II) were adjusted to 6.4 by citric acid/sodium citrate buffer solution. The results shown in Fig. 6 indicated that the adsorption capacities of Cd(II) and Pb(II) improved with the increase of Initial concentration of metal ions until maximum adsorption were reached gradually.

The Langmuir and Freundlich isotherm models are the most frequently used models to describe and analyze the adsorption isotherms. The Langmuir isotherm model is derived to assume surface homogeneity of the adsorbent, such as identical active sites, monolayer adsorption and no interaction between the adsorbed species. The Freundlich isotherm model proposed based on the assumption of surface heterogeneous due to the diversity of the adsorption sites or the diverse nature of the metal ion-adsorbed, free, or hydrolyzed species. The Langmuir and Freundlich equations can be expressed as follows [38]:

$$q_e = \frac{q_m K_d C_e}{1 + K_d C_e} \quad (7)$$

$$q_e = K_f C_e^{\frac{1}{n}} \quad (8)$$

where q_e is the amount of metal ion adsorbed at equilibrium by the adsorbent (mmol·g⁻¹), C_e is the equilibrium concentration (mmol·L⁻¹), q_m is theoretical saturation adsorption capacity (mmol·g⁻¹), K_d (L·mmol⁻¹) is the equilibrium Langmuir constant, K_f (mmol·g⁻¹) and n are constants representing the adsorption capacity and

intensity of adsorption.

The fitting of equilibrium data at different temperature by Langmuir and Freundlich models was conducted and the results are presented in Fig. 6 and Table 4. As illustrated in Fig. 6, the equilibrium data are very well represented by Langmuir model and it can be observed from the parameters listed in Table 4 that the adsorption equilibrium data well fits Langmuir model with correlation coefficient values $R^2 > 0.99$. Additionally, the maximum adsorption capacities of Cd(II) and Pb(II) by PAN_{MW}-TSC fibers according to Langmuir model are highly agreed with the experimental value in each temperature. The better fit of equilibrium data by Langmuir isotherm model confirms the monolayer coverage of metal ions into the homogenous surface of the adsorbents.

According to the Langmuir fitting, the maximum adsorption capacity was 1.47 mmol·g⁻¹ for Cd(II) and 1.01 mmol·g⁻¹ for Pb(II), respectively. The higher tendency toward Cd(II) than that for Pb(II) may be attributed to the anchoring of sulfur atom by the modification of thiosemicarbazide. Cadmium is considered as a soft Lewis acid due to its high polarizability, and according to the theory of hard and soft acids and bases, soft acid coordinate more strongly with ligands that have soft donor atoms [39]. This result was also proved by comparing the adsorption capacities between PAN_{MW}-DETA and PAN_{MW}-TSC fibers in Table S1 in supporting information.

Fig. 6. Adsorption equilibrium curve of Cd(II) and Pb(II) on PAN_{MW}-TSC at 288 K, 293 K and 298 K and pH 6.4.

Table 4

Adsorption isotherm parameters for the adsorption of Cd(II) and Pb(II) on PAN_{MW}-TSC at 288 K, 293 K and 298 K.

Metal ions	T (K)	Langmuir parameters			Freundlich parameters		
		q_m (mmol·g ⁻¹)	K_d (L·mmol ⁻¹)	R^2	n	K_f (mmol·g ⁻¹)	R^2
Cd(II)	288	0.967	7.96	0.9916	3.23	0.833	0.9317
	293	1.26	8.83	0.9924	3.13	1.13	0.9387
	298	1.47	11.07	0.9901	3.12	1.41	0.9324
Pb(II)	288	0.749	17.72	0.9913	3.01	0.851	0.9241
	293	0.913	20.97	0.9977	2.86	1.12	0.9393
	298	1.01	28.97	0.9918	2.99	1.33	0.9403

3.2.4. Thermodynamic analysis

An insight towards the spontaneity and energetics involved in the interaction between the modified fibers and the metal ions can be best explained through the Gibbs free energy change (ΔG), entropy (ΔS) and enthalpy (ΔH) which are determined by the following equations:

$$\Delta G = -RT \ln K_d \quad (9)$$

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

where K_d is the adsorption equilibrium constant obtained from Langmuir model, R is the universal gas constant (8.314 J·mol⁻¹·K⁻¹), T is the temperature (K). The values of ΔH and ΔS could be obtained as the slope and intercept from a linear plot between $\ln k$ versus $1/T$.

The obtained thermodynamic parameters for the adsorption process are presented in Table 5. The transport of metal ions from the solution phase to the adsorbent is partially dominated by the concentration gradient across the adsorbent-solution interphase which is reflected in the free energy difference. The increase in absolute ΔG value as temperature rising indicated that the adsorption process becomes more favorable at higher temperature and the positive values of ΔH and ΔS for the adsorption of Cd(II) and Pb(II) demonstrated the endothermic nature of this process, along with an increased randomness at the solid-liquid interface [40].

Table 5Thermodynamic parameters for the adsorption of Cd(II) and Pb(II) on PAN_{MW}-TSC.

Metal ions	ΔH (kJ·mol ⁻¹)	ΔS (J·mol ⁻¹ ·K)	ΔG (kJ·mol ⁻¹)		
			283 K	293 K	303 K
Cd(II)	23.48	99	-4.96	-5.31	-5.95
Pb(II)	30.03	150	-6.88	-7.41	-8.34

3.2.5. Desorption experiment and reusability

In order to economize the application of adsorbent, it is imperative to evaluate the regeneration ability of PAN_{MW}-TSC fibers in the adsorption process. Thus, sorption-desorption cycles were performed repeatedly to examine the reusability and metal recovery efficiency of PAN_{MW}-TSC fibers. In the present study, 0.5 M HNO₃ solution was used to desorb the Cd(II) and Pb(II) adsorbed by PAN_{MW}-TSC fibers and this process repeated for five sorption-desorption cycles. Fig. 7 summarizes desorption efficiency for the five cycles. As depicted in Fig. 7, the desorption efficiency of heavy metal ions decreased slightly as the regeneration cycles progressed, which indicated that 0.5 M HNO₃ solution can effectively desorb from PAN_{MW}-TSC fibers. Moreover, at the end of the fifth cycle, the fibers still retained more than 85% of its original adsorption capacity for the metal ions which indicated that no appreciable loss in capacities over the five studied cycles. The results illustrated that PAN_{MW}-TSC fiber was expected to be a promising adsorbent for fast removal of Cd(II) and Pb(II) from aqueous solution, especially in emergency disposal of heavy metal pollution accidents.

Fig. 7. Different cycles on the desorption efficiency of Cd(II) and Pb(II) by PAN_{MW}-TSC fibers.

3.3. Comparison with other fibrous adsorbents

Compared with the reported fibrous adsorbents in Table 6 which were prepared

through conventional heating, the adsorption capacities of PAN_{MW}-TSC fibers for these two metal ions were higher, and the duration of functionalization process decreased incredibly by using MW irradiation. The consumed time declined from 5-29 h to 0.5 h with higher grafting rate of N and S atoms onto the fibers which both took effects in the adsorption process [41, 42].

The observed acceleration and high grafting rate of PAN_{MW}-TSC fibers might attribute to the combination of thermal and non-thermal effect of MW irradiation. In other words, MW irradiation is instantaneous which leads to shorter start-up and rapid internal heating during the functionalization process [43-45]. Importantly, as we mentioned above, the non-thermal effect of MW irradiation was taking effects through the distinct results from the conventionally heated counterpart at the same measured reaction conditions [46].

Table 6

Comparison of PAN_{MW}-TSC fiber adsorption capacities with other fibrous adsorbents.

Adsorbents	Reaction time (h)	Adsorption capacity (mmol·g ⁻¹)		pH		Reference
		Cd(II)	Pb(II)	Cd(II)	Cd(II)	
PAN/PPy/MnO ₂ nanofiber	12	—	0.83	—	6.0	[47]
phosphorylated PAN-based nanofiber	29	0.17	0.47	6.0	6.0	[15]
PAN _{ac} F	12	1.11	—	6.0	—	[48]
poly(p-phenylene terephthalamide) fibers	8	—	0.087	—	5.0	[49]
functionalized polyacrylonitrile	5-29	—	0.85	—	5.0	[50]
chitosan nanofibril	—	0.54	0.57	5.0	5.0	[51]
cellulose fiber	24	0.77	0.93	6.0	5.7	[52]
PAN _{MW} -TSC fiber	0.75	1.47	1.01	6.4	6.4	Present study

4. Conclusions

This work has shown that MW irradiation provided an effective approach to immobilize thiosemicarbazide onto polyacrylonitrile fiber, and the results indicated that the PAN_{MW}-TSC fibers obtained by MW possessed remarkable accelerated duration and high grafting rate. Thermal and non-thermal effect were convinced to make efforts in these two grafting steps. The adsorption capacities of the obtained PAN_{MW}-TSC fibers for Cd(II) and Pb(II) were found to be significantly improved with increasing pH value and reached the top at pH 6.4. The adsorption kinetics were found to follow pseudo-second-order model and the equilibrium data followed Langmuir isotherm model. The maximum adsorption capacities for Cd(II) and Pb(II) were 1.47 mmol·g⁻¹ and 1.01 mmol·g⁻¹, respectively, according to Langmuir model. The high adsorption capacity of PAN_{MW}-TSC fibers was attributed to the introduction of nitrogen and sulfur atom onto the surface of the adsorbent. The adsorption thermodynamics indicated that the adsorption process is spontaneous and endothermic. The regeneration experiments showed that the fabricated adsorbent had a good stability and reusability within five times regeneration. Overall, MW irradiation is a fascinating and promising tool for the preparation of functional fibrous adsorbent, which exhibits excellent prospect in heavy metal ions wastewater treatment.

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