The Applications of Populus Fiber in Removal of Cr^(VI) from Aqueous Solution

Miaomiao Li, Yumei Gong^{*}, Aichao Lyu, Yuanfa Liu^{*}, and Hong Zhang^{*}

School of Textile and Material Engineering, Dalian Polytechnic University, Dalian, 116034, China.

Fax: +86 411 86323438, Tel: +86 411 86323131

Corresponding author:

Yumei Gong

Email: ymgong@dlpu.edu.cn

Yuanfa Liu

Email: morning309@126.com

Hong Zhang

Email: zhang_hong1234@sina.com

ABSTRACT. The surface modification of natural materials to be applied in removal of $\text{Cr}^{(\text{VI})}$ from aqueous solutions has attracted much attention. A natural sorbent for $\text{Cr}^{(\text{VI})}$ based on natural populus fibers (PF) is prepared by transforming the cyano groups (AN) in polyacrylonitriles (PAN) grafted from PF into amidoxime groups (AO), which has strong ability to attract and chelate heavy metal ions. The prepared sorbent is characterized by Fourier Transform Infrared Spectra (FT-IR), thermogravimetric analysis (TGA), solid-state nuclear magnetic resonance (^{13}C -NMR) and scanning electron microscope (SEM). As potassium dichromate solution ($\text{K}_2\text{Cr}_2\text{O}_7$) is used as a target solution for detecting adsorption capacity of the sorbent, the adsorption kinetics of the sorbent for chromium is consistent with the pseudo-second-order kinetic model by analyzing the adsorption amount as a function of the sorbent dispersed duration in solution at $\text{pH} = 2$. The expected adsorption mechanism is that the $\text{Cr}^{(\text{VI})}$ in anionic ions $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- are adsorbed through electrostatic attraction but when $\text{Cr}^{(\text{VI})}$ is reduced to $\text{Cr}^{(\text{III})}$ by AO, the electronegative nitrogen and oxygen in AO chelate it through coordination bond. The as-prepared PF derivant with high adsorption efficiency of chromium 180.5 mg/g (3.47 mmol/g), low cost, reusability and greenly preparation process suggests that the development of natural PF as a sorbent in removal of $\text{Cr}^{(\text{VI})}$ from aqueous solutions is a destined significant approach.

Keywords: populus fibers; surface modification; amidoxime; chromium sorbent

1. Introduction

Pollution of surface and underground water resources with toxic $\text{Cr}^{(\text{VI})}$ has been one of the major causes for the deterioration in water quality [1-10]. $\text{Cr}^{(\text{VI})}$ is used in various industries including metallurgy, leather tanning, electroplating and wood preservation [1, 2, 10]. There are number of treatment methods available to remove heavy metal ions and extending to remove $\text{Cr}^{(\text{VI})}$ from waste water such as chemical precipitation [11, 12], ion-exchange [13], membrane separation [14], electrocoagulation [15], solvent extraction [16], reverse osmosis [17] and adsorption [18, 19]. Among these methods, adsorption is one of the simplest, most effective, and lowest costly. Various materials, including amorphous silica [20], MWCNTs [36], polymers [21, 22] and zeolites [23] have been studied for using as sorbent. However, these materials have various disadvantage such as high cost, low mechanical, poor removal efficiency etc. Therefore, the development of new materials and/or derived from existing materials as sorbents is very significant.

Naturally derived and renewable materials are very interesting in many applications because they are environmental friendly and naturally available. Among natural and renewable materials, cellulose is one of the promising resources because it can be easily gained and lots of hydroxyl groups on the chain can be functionalized for special applications [24-30]. Cellulose has been applied in waste water treatment [24-27], reinforcing composite materials [28], as well as in bio-derived and bio-inspired materials [29, 30]. Populus fibers (PF), a kind of natural cellulose, produced from poplar seeds, has been treated as waste or used as a cheap fertilizer because the fibers are soft and short, with low intensity and longitudinal torsion [31]. Nature PF consists of 41-44 wt% cellulose, 19-21 wt% hemicellulose, 29 wt% lignin and 4-9 wt% extractives [31]. In early June, a broad area of poplar planting appears a large number of air catkins, like snow. Since the fibers are water-insoluble, they float on water for so long time that they seriously pollute the environment.

Moreover, the PF also can easily enter the human respiratory system, and accordingly cause allergies [32]. However, the chemical structure, microtube morphological structure and high specific surface area imply that PF still may serve as a modified skeleton for waste water sorbent.

Cellulose derivants called as chelating resins [33, 34] have been reported that they have widely application in removal of $\text{Cr}^{(\text{VI})}$ from aqueous solutions. It is known that the chelating resins containing amidoxime groups show selective adsorption for heavy metal ions from waste water. These chelating resins are usually obtained through grafting polyacrylonitrile (PAN) from cellulose, and then the cyano groups converted into amidoxime groups [33-37]. It has been reported that KMnO_4 [33], Ce^{4+} [10, 34] and high-energy radiation [35, 36] can be used in initiating polymerization of acrylonitrile. Ce^{4+} as an initiator has advantages of short reaction time, mild reaction conditions and high rate of grafting [34].

Thereby, in this study, PF will be used as the original material, from which polyacrylonitrile (PAN) is grafted by using Ce^{4+} as the initiator. Then, the cyano groups on the grafting PAN are converted into amidoxime groups which exhibit high adsorption efficiency for $\text{Cr}^{(\text{VI})}$ 180.5 mg/g (3.47 mmol/g) in aqueous solution. This kind of sorbent with low cost, reusability and greenly preparation suggests that the development of natural PF as sorbent in removal of $\text{Cr}^{(\text{VI})}$ from aqueous solutions is a destined significant.

2. Experimental

2.1. Materials

Populus fibers (PF) were collected during the blooming period in June from plants in Shandong, China. N,N-dimethylformamide (DMF), Ceric ammonium nitrate (CAN), and HNO_3 were purchased from Sigma-Aldrich. Acrylonitrile (AN) was purchased from Tianjing Fuchen

Chemical Reagent Factory (China). NaOH and hydroxyl amine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) were purchased from Chengdu Kelong Chemical Reagent Co., Ltd. (China). All the chemicals were analytical grade and were used without further purification.

2.2. Preparation of populus fiber-graft-poly(amidoximated acrylonitrile) (PF-g-PAO)

Purification of PF. 6 g PF were mixed with 40 mL 5 wt% NaOH solution under stirring for 1.5 hr at 60 °C followed by washing with water to remove the hemicellulose and lignin in PF. After this process, a dilute acetic acid solution was applied to neutralize the NaOH. Then, a mixed solution including 0.5 mol/L acetic acid and 0.1 mol/L sodium chlorite in 100 mL water was used to bleach the PF at 75 °C for 1 hr followed by washing with water and dried at 60 °C [10].

Synthesis of PF-g-PAO. The amidoximated polyacrylonitrile grafted populus fibers (PF-g-PAO) was synthesized through a two-step approach, as shown in Sch 1. Typically, 0.8 g PF was dispersed in 40 mL NaOH solution (5 wt%) and stored at 25 °C for 6 h for activation and then washed thoroughly by water. Then the activated PF were dispersed in 50 mL water under stirring at room temperature followed by adding initiator (0.073 mol/L CAN and pH = 1) under N_2 protection. Next, 3 mL of acrylonitrile monomer was added into the above mixture dropwise to make it polymerized under N_2 for 60 min. The reaction mixture was separated by centrifugation at 6000 rpm for 15 min and the precipitate was washed in turn with DMF and water to remove homo-polyacrylonitrile, dried at 60 °C in vacuum for 24 h to result in PF-g-PAN. Subsequently, PF-g-PAN was dispersed in NaOH/ $\text{NH}_2\text{OH}\cdot\text{HCl}$ (1:1 in mole ratio) aqueous solution (50 mL) and stirred for 12 h at 50 °C, during this period the cyano groups changed into amidoxime groups to result in PF-g-PAO [38]. The reaction mixture was separated by centrifugation at 6000 rpm for 15 min and the precipitate was washed with water to remove all the soluble components.

2.3. Determination of the Grafting Fraction

The degree of substitution of PF (DS_{AN} and DS_{AO}) defined as the average amount of grafted acrylonitriles and amidoximes from a glucose unit for PF-*g*-PAN and PF-*g*-PAO, respectively. The mass fraction of grafted acrylonitriles W_{PAN} and conversion efficiency (η) from PF-*g*-PAN to PF-*g*-PAO can be estimated from the ^{13}C -NMR spectrum. The DS_{AN} , DS_{AO} , W_{PAN} and η are calculated by the following equations [33, 38]

$$DS_{AN} = \frac{I_{CN}}{I_{C6}} \quad (1-1)$$

$$DS_{AO} = \frac{I_{AO}}{I_{C6}} \quad (1-2)$$

$$W_{PAN} = \frac{DS_{AN} \times M_{AN}}{M_C + DS_{AN} \times M_{AN}} \quad (1-3)$$

$$\eta = \frac{DS_{AO}}{DS_{AN}} \quad (1-4)$$

Where I_{CN} and I_{AO} are the integrated intensity of polyacrylonitriles and amidoxime, respectively; I_{C6} is the integrated intensity of C_6 in six-carbon sugar and is used as carbon referencing; M_C and M_{AN} are the molecular weights of hexose in PF and acrylonitrile in PAN, respectively.

2.4. Adsorption experiments

50 mL of potassium dichromate solution ($\text{K}_2\text{Cr}_2\text{O}_7$) in water with concentration (1.7×10^{-3} mol/L) in orange color was selected as the source of hexavalent chromium. 50 mg PF, PF-*g*-PAN and PF-*g*-PAO were dispersed into the solution under stirring under 25 °C for a certain time (1 ~ 700 min) respectively. The initial pH of $\text{Cr}^{(VI)}$ solution was adjusted to 2.0 by 0.5 mol/L HCl. By using flame atomic absorption spectrophotometry the concentration of supernatant residue chromium ions were determined. The adsorption capacity q_e (mg/g) was calculated according to the following equations [34-36].

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (1-5)$$

Where C_0 and C_e (mg/mL) denote the concentration of equilibrium chromium ion before and after adsorption respectively. V (mL) denotes the volume of the heavy metal solutions. W (g) denotes the mass of the adding PF-g-PAO.

The adsorption capability of PF-g-PAO for chromium solutions with the initial pH = 1.0 to 6.0 under 25 °C was also studied.

2.5. Characteristics

The surface functionalized groups of PF were characterized by Fourier Transform Infrared (FT-IR) Spectra which was performed on a Bruker-Equinox 55 FT-IR spectrometer by KBr-disk. In order to investigate the status of graft polyacrylonitrile (PAN), solid-state nuclear magnetic resonance (^{13}C -NMR) was carried out by a Bruker DMX 400 NMR instrument. The morphology of the fibers was characterized by a JEOL, JSM-6460LV scanning electron microscopy (SEM). The thermogravimetric analysis was performed on a TGA meter (TG Q-50, America) at heating rate 10 °C/min protected under N_2 . To determine the adsorption capacity of the as prepared PF-g-PAO, atomic absorption spectrometry (AAS) was carried out on HITACHI 180-80. To further explore the mechanism of adsorption, X-ray photoelectron spectroscopy (XPS) was carried out on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromated Al $K\alpha$ radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

3. Results and discussion

3.1. Characterization of the PF, PF-g-PAN, and PF-g-PAO

3.1.1. FT-IR

Fig 1 shows typical FT-IR spectra of PF, PF-g-PAN and PF-g-PAO. For PF, the peaks appeared at wave numbers 3338 cm^{-1} and 2908 cm^{-1} correspond to stretching vibrations of -O-H and -C-H on cellulose molecular chain, respectively. Compared to the profile of PF, the sharp peak appeared at 2243 cm^{-1} on the spectrum of PF-g-PAN comes from the stretching vibration of -CN in cyano groups, indicative of the successfully grafting of acrylonitrile from the fiber surface [22]. However, this peak disappears after amidoximation, which can be obviously seen from the spectra of PF-g-PAO compared with that of PF-g-PAN. Meanwhile, a new peak at 1660 cm^{-1} corresponding to -C=N- stretching vibrations in amidoxime groups -C(NH₂)=N-OH appears [37]. The local magnification of this peak can be obviously seen in the inserted figure under the profile of PF-g-PAO in Fig 1. It suggests that the -C≡N groups are converted into -C(NH₂)=N-OH groups after treated by NaOH/NH₂OH·HCl, and the conversion efficiency is calculated in the following part ¹³C-NMR. Moreover, the peak at 3338 cm^{-1} of the stretching vibration of -O-H on the FT-IR profile of PF-g-PAO becomes broader than those of PF and PF-g-PAN due to the presence of -NH₂ groups in PF-g-PAO [38].

3.1.2. TGA

To further explain the component of the synthesized PF-g-PAN and PF-g-PAO, TGA is performed. Fig 2 shows TGA and the corresponding DTG curves for PF, PF-g-PAN and PF-g-PAO. From the curves of TGA, as shown in Fig 2a, the weight residue of the three samples after treated at 700 °C are different from each other. The residue of PF is $\leq 5\text{ wt\%}$, but the residue of PF-g-PAN is $\sim 30.8\text{ wt\%}$ and that of PF-g-PAO is $\sim 33.2\text{ wt\%}$. It indicates that the synthesized samples are different from the original PF. On the other hand, the weight loss of PF-g-PAO from 100 °C to 300 °C is larger than those of the other two samples PF and PF-g-PAN. When the temperature is as low as 150 °C, the PF-g-PAO starts to degrade rapidly and the degradation rate achieves peaks at 200 °C

and 252 °C (Fig 2b), which may correspond to the loss of water adsorbed by the hydrophilic amidoxime and amino groups and the decomposition of the amidoximated group in PF-*g*-PAO respectively [33]. That is, the amidoximation reaction increases the hydrophilicity but simultaneously decreases the thermal stability of PF.

Still from Fig 2a, as the temperature increases higher than 280 °C, the weight loss of all three samples is accelerated, the DTG curves in Fig 2b show that the fastest degradation of PF and PF-*g*-PAO take place at 355 and 347 °C, respectively, but that of PF-*g*-PAN takes place at 300 °C and 367 °C. The peak at 300 °C for PF-*g*-PAN corresponds to the decomposition of the grafted PAN, whereas all the three degradation peaks at 347 °C, 355 °C, and 367 °C of the three samples belong to the decomposition of cellulose in the three samples. It also indicates that the grafting of PAO onto PF decreases the cellulose thermal stability, but the grafting of PAN onto PF increases the cellulose thermal stability.

3.1.3. SEM analysis

The morphologies of the fibers are determined by SEM, and the typical images are shown in Fig 3. The original PF, as natural cellulose fibers, have a reasonably smooth surface, as shown in the SEM image in Fig 3a. After treated by aqueous NaOH solution, the surface of the fiber becomes rough, there form some stripes and bulges, as marked by arrows, which are remains of the damaged cellulose on the fiber surface, as shown in the SEM image in Fig 3b. While PAN is grafted from the fiber surface, these stripes are filled and the bulges are covered, the surface is still rough enough, as shown in the SEM image in Fig 3c. With the cyano groups transforming to amidoxime groups, the morphology of the fiber surface remains, the SEM image as shown in Fig 3d of PF-*g*-PAO is similar to that shown in Fig 3c of PF-*g*-PAN. The four images as shown in Fig 3 suggest that the surface of the PF destroys slightly by a series treatment of NaOH, grafting, and amidoximation. And hence it is

a reliable and mild approach to PF modification, which is consistent with the results obtained by Hu and co-workers [33-38].

3.1.4. ^{13}C -NMR

To further analyze the degree of substitution (DS) of PF-*g*-PAN and the conversion efficiency (η) from PF-*g*-PAN to PF-*g*-PAO, ^{13}C -NMR was performed and the spectra are shown in Fig 4. The resonances peaks between chemical shifts $\delta = 60 - 110$ ppm corresponding to the carbons in cellulose are observed on the spectrum of PF [33], the top profile in Fig 4. For the sample PF-*g*-PAN, there exists a peak corresponding to the carbon in -CN group at $\delta = 121.18$ ppm [33], as shown on the middle profile in Fig 4. Whereas on the spectrum of PF-*g*-PAO as shown on the below profile in Fig 4, the peak at $\delta = 121.18$ ppm remains a little. Meanwhile, a new peak at $\delta = 158.34$ ppm corresponding to -C=N-OH in amidoxime groups appears [33], as shown in Fig 4. Moreover, the peaks between chemical shifts $60 \sim 110$ ppm corresponding to the carbons in cellulose on the spectra of PF-*g*-PAN and PF-*g*-PAO remain similar to those on the spectrum of PF. It also confirms that the conversion of the nitrile group to amidoxime group without severe damage to the chemical structure of cellulose. ^{13}C -NMR spectra further indicates the successfully preparation of PF-*g*-PAN.

On the other hand, from the profiles of the PF-*g*-PAN as shown in Fig 4, according to the equations (1-1) and (1-2), the calculated DS_{AN} and DS_{AO} are 3.63 and 3.57, respectively. The fraction of the grafted acrylonitrile W_{PAN} is 54.75%. The conversion efficiency from PAN to PAO is 98.35%.

3.2. Adsorption Behavior Studies

In general, the adsorption of heavy metal ions by sorbents is influenced strongly by the solution conditions such as pH, temperature and ion concentration in aqueous solutions. Here, we mainly examine the effect pH of the target $\text{K}_2\text{Cr}_2\text{O}_7$ solution on the adsorption capacity because the pH determines the chromium state in solution, as shown in equations 2-1 and 2-2. We examine the effect

of pH (1.0 ~ 6.0) on the adsorption capacity as PF-g-PAO is dispersed into the $K_2Cr_2O_7$ aqueous solution with concentration of 1.7×10^{-3} mol/L. The results are illustrated in Fig 5. It is observed that the adsorption capacity of chromium increases with increasing pH from 1.0 to 2.0. Then, the capacity decreases with increasing pH from 2.0 to 6.0. The optimum pH for the maximum adsorption capacity of chromium is 2.0. The reasons of the pH effect on the adsorption capacity of chromium can be expressed as follows:

In an acidic medium, the basic amino group $-NH_2$ in amidoxime group converts into NH_3^+ and $-N-OH$ [43], which decrease the coordination capacity of PF-g-PAO with metal cations. With the pH increasing, this negative effect of adsorption weakens and makes the PF-g-PAO surface positive. On the other hand, the $Cr^{(VI)}$ exists in the form of oxyanions such as $HCrO_4^-$ and $Cr_2O_7^{2-}$ in a strong acidic medium. The protonated PF-g-PAO surface electrostatically attracts these oxyanions and as a result the adsorption capacity increases with the pH increasing to 2.0. Whereas with the pH further increasing, the increasing of negative hydroxyl ions in solution makes the positivity of the PF-g-PAO surface and redox reaction in solution decrease, which causes the adsorption capacity to decrease.

At the same time, note the fact that the sorbent PF-g-PAO changed to greenish which clearly is not the color of $Cr^{(VI)}$, but certainly the color of $Cr^{(III)}$, a reduction form of $Cr^{(VI)}$. Therefore, during the process of $Cr^{(VI)}$ adsorption, there exists simultaneously the $Cr^{(III)}$ adsorption. That is, the adsorption of $Cr^{(VI)}$ by PF-g-PAO may involve a complex process such as the conversion from orange $Cr^{(VI)}$ to greenish $Cr^{(III)}$. The expected process of this conversion is the adsorbed $Cr_2O_7^{2-}$ acts as an oxidant to oxidize the $-C=N-OH$ in amidoxime group into $-C(NH_2)=O$ or $-COOH$ [43, 44], and get reduced itself from $Cr^{(VI)}$ to $Cr^{(III)}$, as shown in equations 2-1 and 2-2. Then, the cationic $Cr^{(III)}$

ions are chelated by -NH_2 and -OH groups in PF-g-PAO through coordination bond. The detail will be reported in future. The chelation between $\text{Cr}^{(\text{III})}$ and the -NH_2 and -OH groups is strong enough to make the sorbent remain greenish. However, it turns light greenish when the chromium loaded sorbent is immersed into a basic solution with $\text{pH} = 9.5$ and simultaneously the solution turns pale green. After desorption, the sorbent can be reused to adsorb chromium again.

3.2.1. XPS

In order to make clear the mechanism of the adsorption of PF-g-PAO on $\text{Cr}^{(\text{VI})}$, XPS analysis is carried out for PF-g-PAO before and after chromium adsorption (denoted as PF-g-PAO-Cr) at solution $\text{pH} = 2$. Fig 6a shows the XPS survey spectra of PF, PF-g-PAN, PF-g-PAO, and PF-g-PAO-Cr, mainly consisting of carbon, oxygen, nitrogen and chromium. Compared the profiles of PF-g-PAN with PF, the peak of nitrogen is only seen on the profile of PF-g-PAN. The reason for this phenomenon is expected that PAN covers the surface of PF, which is consistent with the SEM image of PF-g-PAN as shown in Fig 3c.

In more detail, the observed spectra of N 1s and O 1s are simulated using two-component Gaussian-Lorentzian sum functions, as shown in Fig 6b and 6c. The N 1s spectra in PF-g-PAO composites could be separated into two peaks at binding energies 399.15 and 400.20 eV, corresponding to the nitrogen of the species amino group (-C-NH_2) and oxime group (-C=N-OH), respectively [36]. Compared with PF-g-PAO, the relative intensity of both amino nitrogen (-C-NH_2) and amidoxime nitrogen (-C=N-OH) in PF-g-PAO-Cr changes slightly but the peak positions of both two nitrogens shift to higher binding energies. The peak position of nitrogen in amino nitrogen (-C-NH_2) shifts to binding energy 399.39 eV and that of amidoxime nitrogen (-C=N-OH) shifts to binding energy 400.84 eV, as marked by the dashed lines as shown in the profile of PF-g-PAO-Cr in Fig 6b, indicative of the decrease in electron density for the nitrogen atoms due to chelating with chromium in PF-g-PAO-Cr [36]. This results suggests that the adsorption of chromium mainly

interacted with not only -C=N-OH but also -C-NH_2 of the amidoxime group.

Fig 6c shows the peak fitting of the O 1s spectra of PF-g-PAO and PF-g-PAO-Cr. As is shown, the O_{1s} spectrum in PF-g-PAO composites can be separated into three peaks at binding energies 532.94, 532.22 and 531.38 eV, which can be assigned to adsorbed H₂O, terminal -OH and bridging -OH, respectively [36]. Compared with PF-g-PAO, the peak positions of the three kinds of oxygen in PF-g-PAO-Cr remain but the relative intensity changes largely. The relative intensity for both peaks of adsorbed H₂O and terminal -OH decrease while that for peak of the bridging -OH increases largely. The result suggests that the adsorption capacity of the PF-g-PAO depends strongly on the terminal -OH located in oxygen-containing functional groups especially -C=N-OH , which can bind metal cations easily. As a subordinate result, the amount of the adsorbed H₂O decreases due to the hydroxyl chelating chromium mainly.

To better understand the valence of the adsorbed chromium ions, the chromium 2p_{3/2} core-level spectrum after chromium adsorption can be fitted into two peaks at binding energies of 576.65 and 579.06 eV, which can be attributed to Cr^(III) and Cr^(VI), respectively [19], as shown in Fig 6d. The results suggest that the PF-g-PAO shows strong ability to reduce Cr^(VI). About 48.34 mol% of Cr^(VI) ions are reduced to Cr^(III) (as shown in Fig 6d). Moreover, the adsorption of potassium dichromate solution on PF-g-PAO completes trivalent cations and hexavalent anions of chromium.

3.2.2. Kinetic studies

Adsorption kinetics is necessary to study in the removal of chromium, which demonstrates the adsorption efficiency of sorbents. The adsorption capacity as a function of the adsorption time can be estimated by fitting the pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models [39-41]. Fig 7a displays the chromium adsorption capacity on PF-g-PAO as a function of the adsorption time. It shows clearly that the amount of chromium adsorption increases rapidly during the first 30 min of adsorption time and then proceeds at a slow rate and finally reaches

equilibrium at 700 min, which accords with the phenomenon that the orange color of the solution of $\text{Cr}^{(\text{VI})}$ fades rapidly as PF-g-PAO are dispersed in it.

The pseudo-first-order kinetics [18, 39], pseudo-second-order kinetics [18, 40, 41] and intra-particle diffusion models [42] are applied to estimate the experimental data in order to explore the mechanism of chromium adsorption process on PF-g-PAO. The linear forms of these three models can be expressed respectively as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1-6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (1-7)$$

$$q_t = k_{\text{id}} t^{1/2} \quad (1-8)$$

where q_t (mg/g) and q_e (mg/g) denote the amount of chromium adsorption per gram PF-g-PAO depending on time and at equilibrium, respectively; k_1 (/min), k_2 (g/mg·min), and k_{id} (mg/g·min^{1/2}) are adsorption constants of the pseudo-first-order adsorption kinetics, pseudo-second-order adsorption kinetics, and diffusion rate within the particles, respectively [18, 39-42].

The theoretical value of adsorption capacity is determined by doing $\log(q_e - q_t)$ as a function of t , t/q_t as a function of t , q_t as a function of $t^{1/2}$ curves to calculate the slope and intercept, respectively. The relevant kinetic parameters obtained from both the pseudo-first-order, pseudo-second-order kinetic models and diffusion rate within the particles are given in Table 1. The highest correlation coefficient value $R^2 \sim 0.99832$ of pseudo-second-order kinetics model and the closest $q_{\text{e,cal}}$ (193.4 mg/g) to $q_{\text{e,exp}}$ (180.5 mg/g) suggests that the pseudo-second-order adsorption is essentially chemisorption involved valence forces through sharing or exchanging of electrons between chromium and PF-g-PAO [41]. And a 5 plots t/q_t as a function of t fitting on pseudo-second-order kinetic model is shown in Fig 7b, in which q_t is the adsorption amount selected as the time prolongs every 5 min during the first 30 min.

Based on the above analysis, we can propose the adsorption mechanism of chromium on the sorbent PF-*g*-PAO that there may exist the adsorption of trivalent cations $\text{Cr}^{(\text{III})}$ (in Sch 2) and hexavalent anion. $\text{Cr}^{(\text{III})}$ forms a bidentate inner-sphere complex with $-\text{C}-\text{NH}_2$ and $-\text{C}=\text{N}-\text{OH}$ groups in PF-*g*-PAO, as shown in Sch 2 in which the PF1 and PF2 denote the same PF-*g*-PAO molecule or different PF-*g*-PAO molecules. The rich electron elements nitrogen in amino groups ($-\text{C}-\text{NH}_2$) and oxime groups ($-\text{C}=\text{N}-\text{OH}$) and oxygen in oxime groups ($-\text{C}=\text{N}-\text{OH}$) chelate $\text{Cr}^{(\text{III})}$ during the adsorption process. Furthermore, because the DS_{AN} of the PF-*g*-PAN is as high as 3.63, the sorbent PF-*g*-PAO is of high efficiency, with the adsorption of chromium 180.5mg/g (3.47 mmol/g). Compared with the sorbent prepared by Yin and coworkers [36] in which amidoxime grafted MWCNTs with the optimum adsorption of 0.61 mmol/g for uranium at a special pH (4.5), the adsorption capacity of PF-*g*-PAO is obviously much higher. In addition, the material of the present sorbent comes from waste and disgusting PF, the approach developed here is destined a low cost and green method. And hence the development of natural populus fiber as a sorbent in environmental pollution management is a significant approach.

4. Conclusions

In summary, we have prepared a natural sorbent PF-*g*-PAO of chromium from aqueous solution based on a natural material PF. PAN has been grafted from PF as ceric ammonium nitrate is used as an initiator, then the cyano groups in PAN are transformed into amidoxime groups to result in PF-*g*-PAO. The amidoxime groups can electrostatically attract the toxic $\text{Cr}^{(\text{VI})}$ and reduce and chelate the $\text{Cr}^{(\text{III})}$ ions so as to removing $\text{Cr}^{(\text{VI})}$ in aqueous solution. The maximum adsorption capacity for chromium is found at $\text{pH} = 2.0$. The adsorption of chromium kinetics is consistent with the pseudo-second-order kinetic model by analyzing the adsorption capacity as a function of the sorbent adsorption time in solution at $\text{pH} = 2.0$. The expected adsorption mechanism is that the $\text{Cr}^{(\text{VI})}$

is electrostatically attracted by PF-g-PAO and the reduction chromium $\text{Cr}^{(\text{III})}$ is chelated by the groups $-\text{NH}_2$ and $-\text{C}=\text{N}-\text{OH}$ in PF-g-PAO. The as-prepared PF-g-PAO with high adsorption efficiency of chromium 180.5 mg/g (3.47 mmol/g), low cost and greenly preparation process suggests that the development of natural PF as a sorbent in environmental pollution management is a destined significant approach.

Acknowledgement. This work was supported by the National Science Foundation of China (51103017) and Open Research Fund of State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (201513).

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Figure Captions

Sch 1. Schematic synthesis route for PF-*g*-PAO.

Fig 1. Typical FT-IR spectra of populus fibers (PF), PF-*g*-PAN, and PF-*g*-PAO.

Fig 2. TGA profiles (a) and the corresponding DTG (b) of PF, PF-*g*-PAN, and PF-*g*-PAO.

Fig 3. SEM images of the original PF (a), PF treated by aqueous NaOH solution (b), synthesized PF-*g*-PAN (c), and PF-*g*-PAO (d).

Fig 4. ^{13}C -NMR of original PF (top), synthesized PF-*g*-PAN (middle), and PF-*g*-PAO (below). The tables inserted in the middle and the below parts are the calculated data of the carbons on cyano groups $-\text{C}\equiv\text{N}$ and amino groups $-\text{C}(\text{NH}_2)=\text{N}-\text{OH}$ and C_6 on glucose units, respectively.

Fig 5. Histogram of the adsorption capacity depends on the pH of the initial solution.

Fig 6. (a) Typical XPS survey spectra for PF, PF-*g*-PAN, PF-*g*-PAO, and PF-*g*-PAO-Cr (a). High resolution XPS spectra of (b) N 1s, (c) O 1s, and (d) Cr for PF-*g*-PAO and PF-*g*-PAO-Cr, respectively.

Fig 7. The amount of chromium (mg) adsorbed per gram PF-*g*-PAO q_t versus t (a). $W = 50$ mg, $C_0 = 1$ mg/mL, $T = 298.15$ K, $\text{pH} = 2.0$, and $V = 50$ mL. The plot of t/q_t versus t (b). **Sch 2.** The proposed adsorption mechanism of cations $\text{Cr}^{(\text{III})}$ on PF-*g*-PAO in which PF1 and PF2 denote the same PF-*g*-PAO molecule or different PF-*g*-PAO molecules, based on the analysis of adsorption kinetics and XPS examination of the sorbent before and after adsorption for chromium.

Table 1. The kinetic parameters of the chromium adsorption on PF-*g*-PAO.

Sch 1. Schematic synthesis route for PF-g-PAO.

Fig 1. Typical FT-IR spectra of PF, PF-g-PAN, and PF-g-PAO.

Fig 2. TGA profiles (a) and the corresponding DTG (b) of PF, PF-g-PAN, and PF-g-PAO.

Fig 3. SEM images of the original PF (a), PF treated by aqueous NaOH solution (b), synthesized PF-g-PAN (c), and PF-g-PAO (d).

Fig 4. ^{13}C -NMR of original PF (top), synthesized PF-g-PAN (middle), and PF-g-PAO (below). The tables inserted in the middle and the below parts are the calculated data of the carbons on cyano groups $-\text{C}\equiv\text{N}$ and amino groups $-\text{C}(\text{NH}_2)=\text{N}-\text{OH}$ and C_6 on glucose units, respectively.

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Table 1. The kinetic parameters of the chromium adsorption on PF-*g*-PAO.

Pseudo-first-order	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (/min)	R^2
	180.5	71.4	0.0914	0.90918
Pseudo-second-order	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (g/mg·min)	R^2
	180.5	193.4	0.0018	0.99832
Intra-particle diffusion	$q_{e,exp}$ (mg/g)	k_{id} (mg/g·min ^{1/2})		R^2
	180.5	12.0017		0.82485