Adsorption performance of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) by aminated solution-blown polyacrylonitrile micro/nanofibers

Huiqing Lou, Xianzhong Cao, Xin Yan, Lina Wang and Zengbin Chen

ABSTRACT

In this work, we prepared amidoxime-functionalized polyacrylonitrile (APAN) micro/nanofibers by modifying solution-blown PAN fibers with hydroxylamine hydrochloride, and investigated the adsorption performance of the APAN fibers for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) from aqueous solutions. Batch experiments and quantitative analysis were conducted considering initial pH and contact time as controlling parameters. The equilibrium data were better explained by the Langmuir model with maximum adsorption capacities of 185, 204, 105, 104, 345 and 91 mg/g for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II), respectively. The adsorption kinetics were found to follow the pseudo-second-order kinetic model. The calculated thermodynamic parameters demonstrated that the adsorption of metal ions onto APAN fibers is feasible, spontaneous and endothermic. The five adsorption-desorption cycle experiments showed that APAN micro/nanofiber adsorbent exhibits good reusability, and has a potential application for the removal of heavy metals from wastewater. 

Key words | adsorption, adsorption capacity, APAN micro/nanofibers, metal ions, solution-blown

INTRODUCTION

Heavy metal pollution in wastewater poses a serious threat to ecological systems and public health because of the highly toxic, non-biodegradable and carcinogenic properties even at very low concentrations (Saeed et al. 2008; Kampalanonwat & Supaphol 2010; Li et al. 2011; Neghlani et al. 2011; Ihسانullah et al. 2016). Heavy metal ions are commonly removed by chemical precipitation, ion exchange, solvent extraction, chemical oxidation-reduction and adsorption. Among these methods, adsorption is one of the most economical, effective and widely used techniques due to the great advantages of convenient operation, low energy consumption, low generation of residues, high capacity and reusability (Hua et al. 2012; Raji et al. 2015; Ahmad & Hasan 2016).

Nowadays, most adsorbents developed for the removal of heavy metal ions depend on the interaction of target substances with the functional groups present on the adsorbent surfaces. Therefore, adsorbents with large specific surface areas and adequate binding sites are essential for adsorption affinity and capacity (Min et al. 2012; Qu et al. 2013). Due to the characteristics of large surface area, chemical resistance, thermal stability, low flammability as well as good mechanical properties, modified amidoxime-modified polyacrylonitrile (PAN) nanofibers have been recognized as highly efficient materials for the removal of toxic metal ions from solutions, with their high adsorption capacity and fast adsorption equilibrium (Saeed et al. 2008; Neghlani et al. 2011).

Saeed et al. (2008) prepared PAN nanofibers by combining the electrospinning technique and the chemical modification of the nitrile group in the PAN copolymer to remove Cu(II) and Pb(II) from water, with saturation adsorption capacities for Cu(II) and Pb(II) of 52.70 and 263.45 mg/g. Kampalanonwat & Supaphol (2010) studied the preparation and adsorption behavior of aminated electrospun PAN nanofiber mats to adsorb Cu(II), Ag(I), Fe(II), and Pb(II), and the adsorption of these metal ions fitted well with the Langmuir equation and maximal adsorption capacities of 150.6, 155.5, 116.5, and 60.6 mg/g. Neghlani et al. (2011) compared the adsorbability of the aminated-PAN nanofibers and microfibers, and they found the saturation adsorption capacity of aminated-PAN nanofibers for Cu(II) obtained from the Langmuir model was

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116.522 mg/g, which is five times more than that of amidoxime-functionalized polyacrylonitrile (APAN). Huang et al. (2015) prepared hydroxyamine-modified electrospun-PAN nanofibers to adsorb Cu(II) and Fe(III). The adsorption data of Cu(II) and Fe(III) fitted particularly well with the Langmuir isotherm, and the maximal adsorption capacities of Cu(II) and Fe(III) were 215.18 and 221.37 mg/g. Chaúque et al. (2016) prepared modified nanofibers (EDTA-EDA-PAN) to remove Cd(II) and Cr(III), and the modified nanofibers showed effective sorption affinity for both Cd(II) and Cr(III), with maximum adsorption capacities of 32.68 and 66.24 mg/g. Lee et al. (2017) prepared hydrolyzed oxidized polyacrylonitrile (H-PAN) nanofibrous webs to adsorb harmful heavy metal ions; the adsorption rate of the H-PAN nanofibers followed pseudo-second-order kinetics, and the maximum adsorption amounts of Pb(II) and Cd(II) were 116.2 mg/g and 85.7 mg/g.

In the present work, the PAN micro/nanofibers were fabricated by an alternative and economically feasible method, namely solution blowing, and the hydroxyamine-modified PAN micro/nanofibers were utilized for removal of six metal ions: Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II). The effects of contact time and initial pH were investigated in detail to obtain the optimum conditions for the maximum adsorption capacity of metal ions. Furthermore, the nature of the adsorption process with respect to adsorption isotherms, kinetics modeling and adsorption thermodynamics were also evaluated in a series of batch experiments. Finally, the desorption and reusability of amidoxime-functionalized polyacrylonitrile (APAN) micro/nanofibers adsorbents were determined based on five adsorption–desorption cycles.

**EXPERIMENTAL METHODS**

**Materials and apparatus**

Polyacrylonitrile (PAN, average MW ≈ 70,000), a copolymer of acrylonitrile (91.4 mol%) and methylacrylate (8.6 mol%), were obtained from Hangzhou Bay Acrylic Fiber Co., Ltd, Zhejiang, China. N,N-Dimethylacetamide (DMAc), Na2CO3, NH2OH-HCl, Cd(NO3)2, Cr(NO3)3, Cu(NO3)2, Ni (NO3)2, Pb(NO3)2, and Zn(NO3)2 were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. All the chemicals were analytical grade or above and used as received without further purification. Stock solutions of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) were prepared by dissolving appropriate amounts of the corresponding chemical compounds in Milli-Q water (Milli-Q Academic A10 system, Millipore Co., MA, USA). All other reagent solutions were made of analytic grade reagents with Milli-Q water.

The micrographs of the PAN and APAN micro/nanofibers were analyzed using a scanning electron microscope (SEM; Hitachi TM-3000, Tokyo, Japan). A Nicolet 8700 Fourier transform infrared spectroscopy (FT-IR), operating at a wavenumber range of 4,000 to 400 cm⁻¹ with the resolution of 4 cm⁻¹, was used to characterize the neat and modified solution-blown PAN fibers, based on the KBr method. The amounts of metal ions were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES) (Thermo iCAP 6000, Thermofisher Co., MA, USA).

**Solution blowing PAN micro/nanofibers**

Solution-blown PAN micro/nanofibers were prepared according to our previous studies (Lou et al. 2013, 2014). Briefly, the PAN solution was injected into a coaxial high-speed isothermal gas jet, and then attenuated by aerodynamic force with solvent evaporation and bending instability; at the same time, the polymer fibers deposited on the collector. Prior to further use, these PAN fiber mats were placed in vacuum drying oven at room temperature (25 ± 1 °C) to remove the solvent.

**Functionalization of PAN micro/nanofibers**

APAN micro/nanofibers were synthesized based on the procedure of Saeed et al. (2008). Briefly, about 0.1 g of the solution-blown PAN micro/nanofibers were placed in a sealed chamber containing 5.5 g of Na2CO3, 3.5 g of NH2OH·HCl, and 100 mL of Milli-Q water. The reaction temperature and time were fixed at 70 ± 2 °C and 2–8 hours. After this, the obtained fiber mats were washed several times with deionized water to remove the remaining salts, and then dried in a vacuum oven at 50 °C.

The conversion of the PAN nitrile group was calculated as follows:

\[
C_{n} = \frac{W_{1} - W_{0}}{W_{0}} \times \frac{M_{0}}{M_{1}}
\]  

(1)

where \(C_{n}\) is the conversion rate of the nitrile group in PAN into an amidoxime group, \(W_{0}\) is the weight of the PAN nanofiber mat before reaction, \(W_{1}\) is the weight of the PAN nanofiber mat after reaction, \(M_{1}\) is the molecular weight of the amidoxime group, \(M_{0}\) is the molecular weight of the PAN nitrile group, and \(W_{1} - W_{0}\) is the weight loss caused by the conversion of the PAN nitrile group.

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weight of hydroxylamine and $M_o$ is the molecular weight of the acrylonitrile monomer.

**Effect of initial pH**

The effect of initial pH on the adsorption of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) onto APAN fibers was evaluated in the pH range of 2.0–6.5. To avoid precipitated metal ions, a pH of greater than 6.5 was not studied. Then, 10 mg of APAN fiber mats was added to 100 mL of metal ion solutions and the mixture was shaken at 25 ± 1 °C for 24 hours.

**Effect of contact time**

To investigate the effect of contact time, the initial pH of the testing solutions was chosen from the optimal pHs that brought about high adsorption capacity. In each case, 1 mL of each testing solution was withdrawn at predetermined time intervals and diluted with a proper amount of Milli-Q water. The adsorption capacity of each fiber mat specimen ($q_e$, mg/g) was calculated using the equation:

$$q_e = \frac{(C_0 - C_e)V}{M}$$  \hspace{1cm} (2)

where $C_0$ and $C_e$ are the initial and equilibrium concentrations of metal ions in the testing solution (mg/L), $V$ is the volume of the testing solution (L), and $M$ is the weight of the adsorbent (g).

**Adsorption equilibrium**

Adsorption equilibrium studies were carried out by placing 10 mg of APAN adsorbents with 100 mL of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) solutions with varying initial concentrations (10–300 mg/L) in 250 mL stopper conical flasks at temperatures of 15–45 °C and the optimal pHs. The mixture was shaken at 125 rpm for 8 hours. After they reached adsorption equilibrium, 1 mL of each of the testing solutions was diluted with a proper amount of Milli-Q water.

**Kinetic study**

Kinetic experiments were implemented by placing 10 mg APAN fiber mats with 100 mL Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) solution in 250 mL conical flasks at the temperature of 25 ± 1 °C and the optimal pH. Samples were withdrawn at predetermined time intervals to analyze the remaining metal concentrations in the aqueous solution.

**Desorption and reusability experiments**

10 mg of APAN fiber mats were separately added to 100 mL of 20 mg/L Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) solutions, buffered at optimum pH and constantly stirred for 8 hours. The metal ion-APAN fiber complexes were collected and washed several times with deionized water to remove any unabsorbed metal ions. Then the adsorbent samples containing each metal ion were placed in contact with 50 mL of HNO₃ (1 mol/L) solutions and constantly stirred for 2 hours. The adsorbed and desorbed amounts of metal ions were quantified by ICP-OES. After each cycle of the adsorption–desorption process, APAN fiber mats were washed thoroughly with deionized water to neutralize and recondition them for the next cycle. The adsorption–desorption experiments were conducted in five consecutive cycles.

Desorption efficiency was calculated based on the percentage of the ratio between the desorbed and the initial, pre-adsorbed amounts of the metal ions; the equation was expressed as:

$$\text{Desorption} \% = \frac{\text{amount of metal ions desorbed}}{\text{amount of metal ions adsorbed}} \times 100$$  \hspace{1cm} (3)

All experiments were conducted with single metal ion solutions. All the sample solutions were filtered through 0.45 μm filters, and the metal ion concentrations in the filtered solution were measured by ICP-OES. All experiments were conducted in triplicate and mean values were used in data analysis. Blank experiments were performed to ensure that no adsorption occurred on walls of the apparatus used.

**RESULTS AND DISCUSSION**

**Characterization of APAN micro/nanofibers**

**FT-IR characterization of APAN micro/nanofibers**

FT-IR spectra of the neat PAN and APAN micro/nanofibers are shown in Figure 1. The neat PAN spectra (curve a) show the absorption peaks of stretching vibrations at 2,245 cm⁻¹ (C≡N), 1,738 cm⁻¹ (C=O), and 1,159–1,060 cm⁻¹ (C–O), which indicate that the PAN is a copolymer of acrylonitrile and methylacrylate (Neghlanl et al. 2011); and the C = O and
C–O bands come from methylacrylate comonomer. The spectra of the APAN fibers (curve b) exhibit correlative characteristic bands of amidoxime at 3,081 cm$^{-1}$, 1,649 cm$^{-1}$, 1,580 cm$^{-1}$, 1,238 cm$^{-1}$ and 1,043 cm$^{-1}$, corresponding to the stretching vibrations of O–H, C=N, N–H, C–N and N–O in amidoxime group, respectively. The intensity of the C≡N peak (2,245 cm$^{-1}$) of the APAN fibers decreased as the conversion of the nitrile to the amidoxime group increased. The reduction of the C=O peak (1,738 cm$^{-1}$) of the APAN fibers suggests the hydroxylamine group was incorporated by chemical treatment of methylacrylate comonomer. From the FT-IR spectra of the APAN micro/nanofibers, the introduction of amidoxime group on solution-blown PAN fibers was clear. Accordingly, the mechanism of reaction between PAN and NH$_2$OH·HCl was proposed as Figure 2.

**Conversion rate and component analysis of APAN**

The conversion rate of the nitrile group in PAN micro/nanofibers increased as the reaction time increased, and the conversion rate was 19.6%, 32.5% and 71.1% respectively when the reaction time was 2 hours, 4 hours and 8 hours. However, the softness of the micro/nanofibers decreased as the conversion increased. According to Saeed et al. (2008), the micro/nanofibers became brittle when conversion was higher than 35%, and increasing brittleness of the PAN micro/nanofibers with increasing conversion was also reported by McComb & Gesser (1997). So we chose 4 hours as the optimal reaction time.

The components of the micro/nanofibers before and after being functionalized are showed in Table 1. The carbon and nitrogen weight percentage changed from about 65.33 wt% and 22.58 wt% in the PAN to 55.57 wt% and 25.45 wt% in the APAN, respectively, which corresponded to about 32.5% of nitrile groups in the PAN being translated into amidoxime groups.

**Morphological properties of the PAN and APAN micro/nanofibers membrane**

SEM images of the PAN and APAN micro/nanofibers are shown in Figure 3. The fiber diameters of nanofiber membrane mats were analyzed by Image J processing software (National Institutes of Health, Bethesda, MD, USA). Figure 3(a) indicates the solution-brown PAN micro/nanofibers membrane have a main fiber diameter of 500–700 nm. Figure 3(b) shows an SEM image of the APAN micro/nanofiber, and the fiber structure was similar to that of the initial

<table>
<thead>
<tr>
<th>Nanofiber membrane</th>
<th>Carbon (wt%)</th>
<th>Nitrogen (wt%)</th>
<th>C:N (mole ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>65.33</td>
<td>22.58</td>
<td>3.38:1</td>
</tr>
<tr>
<td>APAN</td>
<td>55.57</td>
<td>25.45</td>
<td>2.54:1</td>
</tr>
</tbody>
</table>

**Figure 1** | FT-IR spectra of the (a) PAN and (b) APAN micro/nanofibers.

**Figure 2** | Chemical reaction between PAN and hydroxylamine hydrochloride.

**Figure 3** | SEM images of the PAN and APAN micro/nanofibers membrane.
solution-blown fibers, even though the fiber diameter increased due to being modified with hydroxylamine. The surface of the APAN micro/nanofibers did not show any serious cracks or degradation and presented an almost similar morphology to that of pure PAN micro/nanofibers.

**Adsorption study**

**Effect of initial pH**

Figure 4 shows the effect of solution pH the adsorption capacities of APAN micro/nanofibers. The sorption amounts increased with increasing pH, and approached a plateau between pH 5.5 and 6.0 for all cases. The changing trends of uptake quantity could be ascribed to the competitive adsorption between H\(^+\) and metal ions (Deng et al. 2015). At pH < 3.0, adsorption of the six metal ions except Pb(II) was almost not observed due to competition between the prevalently available H\(^+\) and the metal ions in terms of binding sites (Huang & Chen 2009; Kampalanonwat & Supaphol 2010; Wan & Chen 2010). Equation (i) indicates the protonation reactions of the \(-\text{NH}_2\) groups of APAN micro/nanofibers in the mixed solution, where \(M^{n+}\) \((n = 2\) or 3) represents the metal ion and R is the polymer structure of the PAN. As more \(-\text{NH}_2\) groups were converted to \(-\text{NH}_3^+\), there were fewer \(-\text{NH}_2\) sites available on the surface of the APAN micro/nanofibers for adsorption of metal ion by Equation (ii), which expresses the formation of surface complexes of \(M^{n+}\) ions with the \(-\text{NH}_2\) group via the interaction of metal ions with the unpaired electrons of nitrogen atom. Moreover, the positive charges due to protonation of the \(-\text{NH}_2\) produced a strong electrostatic repulsive force with the positively charged metal ions. Both of these factors go against the adsorption of metal ions. As the pH was increased, the \(-\text{NH}_2\) groups were free from protonation and available to capture metal ions through Equation (ii), thus the adsorption quantities of metal ions, especially of Pb(II), Cr(III) and Cd(II) clearly increased. At higher pH conditions, the combination of OH\(^-\) from the solution through hydrogen bond interaction occurred (Equation (iii)), resulting in reduction of adsorption \(M^{n+}\) ions through surface complexation (Equation (ii)). However, adsorption of \(M^{n+}\) ions through electrostatic attraction as indicated in Equation (iv) proceeded gradually (Neghali et al. 2011; Soltanzadeh et al. 2014). This helps to explain the lower adsorption rate when solution pH was greater than 5.5. Therefore, the pH was set 6.0 for subsequent investigation of the adsorption process.

\[
\text{RNH}_2 + \text{H}^+ \rightarrow \text{RNH}_3^+ \quad \text{(i)}
\]
\[
\text{RNH}_2 + M^{n+} \rightarrow \text{RNH}_2M^{n+} \quad \text{(ii)}
\]
RNH₂ + OH⁻ → RNH₂OH⁻  
(iii)

RNH₂OH⁻ + Mⁿ⁺ (or MOH⁺) → RNH₂OH⁻ · · · Mⁿ⁺ (or RNH₂OH⁻ · · · MOH⁺)  
(iv)

Effect of contact time

The profiles of contact time versus adsorption amounts are plotted in Figure 5. As expected, the adsorption amounts increase sharply and then level off with increasing contact time. Adsorption equilibriums were reached within 8 hours for the Cd(II) and Zn(II) with sorption quantities of 130.47 and 52.38 mg/g; 4 hours for the Cr(III), Cu(II) and Pb(II) with sorption quantities of 150.84, 71.64 and 291.09 mg/g; and 6 hours for Ni(II) with a sorption quantity of 57.50 mg/g. There are two stages in the adsorption process as reported previously (Kampalanonwat & Supaphol 2010; Adebisi & Alaba 2017). In the initial stage, the adsorption rate increases rapidly due to the many adsorptive sites of the adsorbent and high concentration gradient of metal ions. Later, the adsorption process achieves equilibrium gradually, and the adsorption quantity tends to stabilize with the occupation of adsorptive sites and the decrease of metal ion concentration. To ensure the equilibratory adsorption of the metal ions onto the APAN micro/nano fibers, we chose the contact time of 8 hours for subsequent studies.

Adsorption mechanism

Adsorption isotherms

The Langmuir model assumes a monolayer adsorption on a homogenenous surface where the binding sites have equal affinity and energy, and no interaction between the adsorbed species (Li et al. 2011). The nonlinear and linear forms of the model are represented as:

\[ q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \]  

(4)

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{K_L q_m} \ln C_e \]  

(5)

where \( q_m \) is the maximum adsorption capacity of metal ions to form a monolayer on the adsorbent surface (mg/g); \( C_e \) is the equilibrium concentration of metal ion (mg/L); \( K_L \) is the Langmuir constant, which is related to the affinity of the binding sites (L/mg).

The Freundlich isotherm assumes that adsorption of metal ions occurs on a heterogeneous surface by multilayer adsorption and the sorption amount increases with increasing concentration (Li et al. 2011). The nonlinear and linear expressions of the model are:

\[ q_e = K_F C_e^{1/n} \]  

(6)

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  

(7)

where \( q_e \) and \( C_e \) are the maximum adsorption capacity of the adsorbent (mg/g) and the equilibrium metal ion concentration (mg/L); \( K_F \) (mg(1-1/n)·L1/n·g⁻¹) and \( n \) are Freundlich constants which indicate adsorption capacity and adsorption intensity, respectively.

The isotherm constants of Langmuir and Freundlich models along with the correlation coefficients (R²) are summarized in Table 2. For all studied systems, the Langmuir model gives higher regression correlation coefficients (R² > 0.99) than the Freundlich model, which indicates that the Langmuir isotherm model describes the experiment data better, suggesting a monolayer adsorption. The \( q_m \) of each metal ion increases with increasing temperature, confirming the sorption process is temperature dependent. Moreover, the higher values of \( K_L \) also indicate strong bonding of metal ions onto APAN micro/nanofibers under the conditions studied.

The non-linear relationships between the adsorption capacities versus the concentration of remaining metal ions in the solution at different temperatures are shown in Figure 6. As can be seen from the figure, the calculated adsorption amounts obtained from Langmuir isotherm are in good accordance with experimental values, which further
prove that Langmuir model fits the experimental data well. The $q_e$ of each metal ion increases with increasing equilibrium concentration and temperature, progressively saturating the adsorbent. The initial increase is due to large numbers of available adsorptive sites on the APAN micro/nano fiber surface. The maximal adsorption capacities for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II), and Zn(II) were 185, 204, 105, 104, 345 and 91 mg/g, respectively. The $q_m$ values obtained for Pb(II), Cr(III) and Cd(II) are higher than those for Ni(II), Cu(II) and Zn(II), showing the following capacity order: Pb(II) > Cr(III) > Cd(II) > Cu(II) > Ni(II) > Zn(II).

Bode-Aluko et al. (2017) reviewed the adsorption capacities of modified PAN nanofibers for toxic metals such as Pb(II), Cd(II), Cr(III) and Cu(II). The adsorption capacities for Pb(II), Cd(II), Cr(III) were in the ranges of 60–263.45 mg/L, 32.68–99 mg/L and 33.2–133 mg/L, respectively. The adsorption capacities of modified PAN nanofibers for Cu(II) was in the range of 11.6–215.18 mg/L, but most of

| Table 2 | Isotherm parameters for the adsorption of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) onto the APAN micro/nano fibers at 25 °C |
|---------|---------------|---------------|----------------------|---------|
| Metal   | $q_m$ (mg/g)  | $K_L$ (L/mg)  | $R^2$               | $K_F$ (mg$^{1-n}$·1/n·L$^{n-1}$·g$^{-1}$·C$^0$) | $R^2$ |
| Cd(II)  | 185.19        | 0.1154        | 0.9989              | 11.22   | 108.84 | 0.9741 |
| Cr(III) | 204.08        | 0.0734        | 0.9973              | 10.24   | 111.23 | 0.9586 |
| Cu(II)  | 105.26        | 0.1412        | 0.9972              | 9.49    | 58.72  | 0.9789 |
| Ni(II)  | 104.17        | 0.1196        | 0.9982              | 6.69    | 46.74  | 0.9871 |
| Pb(II)  | 344.83        | 0.1593        | 0.9996              | 17.33   | 246.51 | 0.9828 |
| Zn(II)  | 90.91         | 0.1102        | 0.9975              | 6.69    | 40.50  | 0.9920 |

Figure 6 | Langmuir isotherm plots for sorption of (a) Cd(II), (b) Cr(III), (c) Cu(II), (d) Ni(II), (e) Pb(II) and (f) Zn(II) onto the APAN micro/nano fibers.
the results were in the range of 30–115 mg/L. Compared with the above results, the APAN micro/nanofibers prepared by this paper had good adsorption effect, and the adsorption capacities for Pb(II), Cd(II) and Cr(III) were higher than for the similar adsorbents.

The different $q_m$ are related to the physicochemistry of the metal ions including ionic radius, electronegativity, charge to radius ratio ($Z/r$), molecular weight and softness, as shown in Table 3. For divalent ions, one can infer that the highest adsorption capacity of Pb(II) is probably linked to the higher electronegativity, ionic radius and molecular weight of Pb(II) (Heidari et al. 2013; Hossain et al. 2014). Higher ionic radius and molecular weight also have a significant effect on adsorption of Cd(II) (Hossain et al. 2014). The adsorption sequence of Cu(II), Ni(II) and Zn(II) suggests that electronegativity and $Z/r$ also affect the adsorption capacity in case of similar ionic radii and molecular weights (Heidari et al. 2013). As for the trivalent Cr(III), the higher adsorption capacity may be related to the $Z/r$ and softness. The interaction between heavy metal ions and the $–\text{NH}_2$ group relies heavily on the hard and soft acids and bases (HSAB). The $–\text{NH}_2$ group of APAN is a hard base ligand, so the interaction between this ligand and the hard Lewis acid (Cr(III)) is easier.

**Adsorption kinetics**

The pseudo-first-order kinetic model is based on the approximation that adsorption rate relates to the numbers of unoccupied active sites (Kampalanonwat & Supaphol 2010). The nonlinear and linear forms of the model are expressed as:

$$q_t = q_e(1 - e^{-k_1t})$$

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

(8)

(9)

**Table 3 | Physicochemical properties of the metal ions**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ionic radius (Å)</th>
<th>Electronegativity</th>
<th>$Z/r$</th>
<th>Molecular weight</th>
<th>Softness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>0.97</td>
<td>1.69</td>
<td>2.06</td>
<td>112.40</td>
<td>Soft</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>0.64</td>
<td>1.66</td>
<td>4.69</td>
<td>51.996</td>
<td>Hard</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.72</td>
<td>1.90</td>
<td>2.78</td>
<td>63.546</td>
<td>Borderline</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>0.70</td>
<td>1.91</td>
<td>2.86</td>
<td>58.70</td>
<td>Borderline</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>1.32</td>
<td>2.33</td>
<td>1.51</td>
<td>207.2</td>
<td>Borderline</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>0.74</td>
<td>1.65</td>
<td>2.70</td>
<td>65.37</td>
<td>Borderline</td>
</tr>
</tbody>
</table>

where $k_1$ is the pseudo-first-order rate constant (min$^{-1}$), $q_e$ (mg/g) and $q_t$ (mg/g) are the adsorbed amounts of metal ion at equilibrium and time $t$ (min), respectively.

The pseudo-second-order kinetic model assumes that adsorption capacity of the adsorbent is proportional to the numbers of active sites on its surface (Li et al. 2011). The nonlinear and linear forms of the model are given as:

$$q_t = \frac{k_2q_e^2t}{1 + k_2q_et}$$

$$t = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

(10)

(11)

where $k_2$ is the pseudo-second-order rate constant (g/(mg·min)), $q_e$ (mg/g) and $q_t$ (mg/g) are the adsorption amounts of metal ion at equilibrium and time $t$ (min), respectively. Herein, the initial sorption rate ($k_0$) is calculated as follows:

$$k_0 = k_2q_e^2$$

(12)

The kinetic constants of $k_1$ and $k_2$ are determined by plotting the slopes and intercepts of $(\log(q_e - q_t))$ versus $t$ and $(t/q_t)$ versus $t$ of Equations (9) and (11), respectively. As can be seen from Table 4 and Figure 7, the calculated $q_e$ values from the pseudo-second-order kinetic model are closer to the experimental data than those from the pseudo-first-order kinetic model, and the corresponding $R^2$ values are all greater than 0.979. These results verify the assumption that the rate-limiting step during adsorption of metal ions is chemisorption involving valence forces through exchanging or sharing electrons between adsorbents and metal ions (Ho 2006; Li et al. 2011; Song et al. 2015).

The adsorption rate $k_0$ values calculated from the pseudo-second-order kinetic model are higher for Pb(II) and Cr(III) than those for Cd(II) Cu(II), Ni(II) and Zn(II), suggesting that the $–\text{NH}_2$ group was easily accessible for Pb(II) and Cr(III). Moreover, fast adsorption rate will result in short equilibrium time as indicated in the ‘Adsorption mechanism’ section and, coupled with high adsorption capacity, they together illustrate the high affinity of APAN micro/nanofibers towards Pb(II) and Cr(III).

**Thermodynamic parameters**

The adsorption experiments at temperatures of 288, 298, 308 and 318 K were performed to evaluate thermodynamic
parameters, i.e., Gibbs free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$), which all play an important role in determining the degrees of spontaneity and feasibility of adsorption process. $\Delta G^0$ is the main criterion for a spontaneous process, which is calculated using the equation:

$$\Delta G^0 = -RT \ln K_L$$

(13)

where $R$ is the universal gas constant (8.314 J/(mol·K)) and $T$ is the absolute temperature (K). The thermodynamic equilibrium constant ($K_L$) is obtained from the Langmuir model (Liu 2009). The relationship between $K_L$ and $T$ is given by the linearized Van ‘t Hoff equation (Equation (10))

$$\ln K_L = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

(14)

where $\Delta H^0$ and $\Delta S^0$ can be obtained from the slope and intercept of the Van ‘t Hoff plot of $\ln K_L$ versus $1/T$.

Thermodynamic parameters are presented in Table 5. The $\Delta G^0$ values are negative for all the metal ions under the conditions studied. This clearly confirms that the feasibility and spontaneous nature of different metal ion sorption onto the APAN micro/nanofibers. Also, the $\Delta G^0$ values decrease with an increase in temperature, indicating higher temperatures are more favorable for the adsorption process. In combination with adsorption isotherms under different temperatures, adsorption capacities increase with rising temperature, and this phenomenon is ascribed to (1) the increasing quantity of surface active sites available for adsorption on the adsorbent and (2) the decreasing boundary layer thickness surrounding the adsorbents. Consequently, the mass transfer resistance of metal ions in the boundary layer decreases and the diffusion rate of metal ions in the external mass transport process increases, as reported by Coskun et al. (2006).

The positive values of $\Delta H^0$ further prove the endothermic nature of the heavy metal ion sorption onto the APAN micro/nanofibers. The positive values of $\Delta S^0$ suggest

<table>
<thead>
<tr>
<th>Metal</th>
<th>q_e,exp (mg/g)</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second-order model</th>
<th>q_e (mg/g)</th>
<th>k_1 (min^-1)</th>
<th>R^2</th>
<th>q_e (mg/g)</th>
<th>k_2 (g/mg·min)</th>
<th>R^2</th>
<th>k_0 (mg/g·min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>132.14</td>
<td>107.5</td>
<td>0.0083</td>
<td>0.9854</td>
<td>142.86</td>
<td>0.000133</td>
<td>0.9990</td>
<td>12.71</td>
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</tr>
<tr>
<td>Cr(III)</td>
<td>151.92</td>
<td>116.84</td>
<td>0.0170</td>
<td>0.9866</td>
<td>161.29</td>
<td>0.000296</td>
<td>0.9985</td>
<td>7.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td>72.73</td>
<td>62.46</td>
<td>0.0136</td>
<td>0.9756</td>
<td>78.13</td>
<td>0.000394</td>
<td>0.9924</td>
<td>2.41</td>
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</tr>
<tr>
<td>Ni(II)</td>
<td>58.87</td>
<td>51.44</td>
<td>0.0090</td>
<td>0.9734</td>
<td>62.89</td>
<td>0.000318</td>
<td>0.9896</td>
<td>1.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb(II)</td>
<td>297.27</td>
<td>236.16</td>
<td>0.0129</td>
<td>0.9380</td>
<td>303.03</td>
<td>0.000130</td>
<td>0.9907</td>
<td>11.94</td>
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</tr>
<tr>
<td>Zn(II)</td>
<td>53.64</td>
<td>44.17</td>
<td>0.0074</td>
<td>0.9899</td>
<td>58.48</td>
<td>0.000275</td>
<td>0.9982</td>
<td>0.94</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 7 | Adsorption kinetics for sorption of metal ions onto the APAN micro/nanofibers: (a) pseudo-first-order and (b) pseudo-second-order models.
the increased randomness of the solid–liquid interface during the adsorption process.

Desorption and reusability studies

The results of five cycles of adsorption–desorption of six single metal ions onto the APAN micro/nanofiber are graphically displayed in Figure 8. Figure 8(a) shows the desorption efficiencies of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) using 1 mol/L HNO₃ solution. After the fifth cycle, the desorption efficiency for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) are still 93%, 92%, 94.67%, 96%, 85% and 97%, respectively. Furthermore, the re-adsorption capacities of the APAN fibers as shown in Figure 8(b) are slightly decreased with increasing adsorption–desorption cycles, and more than 87%, 88%, 83%, 82%, 91% and 81% of the initial adsorption capacities for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) are attained after the fifth cycle. This result is probably attributed to: (1) desorption efficiency cannot reach 100% because of the involvement of non-electrostatic forces between the APAN fibers and the metal ions (Singh et al. 2007), thus certain binding sites are still occupied; and (2) the loss of some functional groups on the fibers due to acid hydrolysis (Aliabadi et al. 2013). The results indicated that the APAN micro/nanofibers can be reused frequently without appreciable losses in adsorption performance, and thus, they have potential application in industrial activities.

CONCLUSION

Amidoxime-functionalized solution-blown PAN micro/nanofibers were synthesized, characterized and utilized for the removal of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) in aqueous solution. Factors affecting the adsorption process, including pH and contact time, were studied. The optimal initial pH was identified as 6.0, and the APAN micro/nanofibers exhibited the highest adsorption capacity toward all six types of metal ions under this condition. Moreover, adsorption capacities increased with increasing contact time and equilibria were reached within 8 hours for Cd(II) and Zn(II), 4 hours for Cr(III), Cu(II) and Pb(II), and 6 hours for Ni(II). Comparison of isotherm models showed that the Langmuir model was better than the Freundlich model, with maximum adsorption capacities of 185, 204, 105, 104, 345 and 91 mg/g for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II), respectively. The kinetic data demonstrated that adsorption processes fitted the pseudo-second-order kinetic model, indicating that chemical sorption is the rate-limiting step. The thermodynamic parameters calculated from the equilibrium data showed the feasibility, endothermic and spontaneous nature of the metal ion adsorption process in the conditions studied. Decreasing ΔG° values with increasing temperatures suggested an increase in the
feasibility of the adsorption process at higher temperatures. Desorption and reusability of APAN micro/nanofibers were determined by five adsorption–desorption cycles, and the re-adsorption capacities were up to 80–91% of the initial adsorption values after five successive cycles of operation. The results obtained show the APAN micro/nanofibers' good adsorption performances with Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II). This shows the usefulness of the adsorption values after re-adsorption capacities were up to 80%.

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REFERENCES


McComb, M. E. & Gesser, H. D. 1997 Preparation of polyacryloamidoxime chelating cloth for the extraction of heavy metals from water. Journal of Applied Polymer Science 65 (6), 1175–1192.


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