Competitive adsorption and mechanism of hexahydroxy metallic system by aminated solution-blown polyacrylonitrile micro/nanofibers

Huiqing Loua, Siyu Lib, Xiangwei Fenga and Xianzhong Cao,c,*
a School of Textiles Engineering, Henan University of Engineering, Zhengzhou 450007, China
b School of Materials and Chemical Engineering, Henan University of Engineering, Zhengzhou 450007, China
c Henan Yuqing Environment & Safety Technology Co., Ltd, Zhengzhou 450007, China
*Corresponding author. E-mail: xianzhongcao@126.com

ABSTRACT

Adsorptive properties for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) onto amidoxime-functionalized polyacrylonitrile (APAN) micro/nanofibers were systematically investigated in a hexahydroxy metallic solution system using batch experiments. The interactive effect of multi-metal ions in multi-metal systems was antagonistic in nature, and the adsorption capacity in a multi-metal system was lower than that in a single-metal system. The Langmuir isotherm model could explain respectively the isotherm and kinetic experimental data for the hexahydroxy metallic system with much satisfaction. The maximum adsorption capacity in hexahydroxy metallic for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) was calculated to be 98 mg/L, 158 mg/L, 80 mg/L, 76.312 mg/L, and 58 mg/L individually. The APAN micro/nanofibers possessed good selectivity toward Pb(II) and Cr(III), over Cd(II), Cu(II), Ni(II), and Zn(II), having the highest selectivity coefficients at 17.52 and 6.07 in the test range. The five adsorption-desorption cycle experiments exhibited that APAN micro/nanofibers adsorbent are readily reusable, and have potential for heavy metal removal from wastewater. The adsorption behavior in multi-metal systems was shown to be complex, including surface complexation, antagonistic competition and displacement reactions. The diversity and selectivity in metal ion adsorption onto the micro/nanofibers relate mainly to the stability constants, and the microscopic coupling mechanism between the heavy metal ions and the functional groups on the fiber surface. This interaction mechanism between the favorable component and other metal ions could contribute significantly to the direct displacement impact illustrated schematically.

Key words: adsorption behavior, adsorption capacity, APAN micro/nanofibers, competitive adsorption, hexahydroxy metallic system, mechanism

HIGHLIGHTS

- Amidoxime-functionalized polyacrylonitrile micro/nanofibers were prepared.
- Competitive adsorption behavior of hexahydroxy metallic system was investigated.
- APAN micro/nanofibers had a better selective adsorption for Pb(II) and Cr(III).
- The mechanisms included surface complexation, antagonistic competition and displacement reaction.
INTRODUCTION

Heavy metals are among the most important pollutants in source and treated waters, and are becoming a severe public health problem. Industrial and municipal wastewaters frequently contain metal ions. Special attention should be given to heavy metal pollution – such as Cd, Cr, Pb, Ni, Zn and Cu – which are not only the commonest in industrial wastewater but also pose serious threats to ecological systems and public health, because of their high toxicity, and 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; Ihsanullah et al. 2016).

Adsorption has long been perceived as a simple, economical, and widely used environmental remediation process for the removal of toxic metals from wastewater. Various adsorbents have currently been synthesized and modified in an effort to enhance the affinity to metal ions and bring fast and high adsorption capacity. Among the modified adsorbents, chelating polymer fibers, with one or more reactive functional groups containing O, N, S and P donor atoms and extensive structural diversity, are capable of forming stable complexes with metal ions, and thus induce large adsorption capacity, high selectivity, and excellent mechanical properties as well as easy recovery.

Recently, polyacrylonitrile (PAN) nano fibers obtained by electrospinning or solution-blowing were used as the base material of an adsorbent, because of their small diameter and easy preparation. This kind of adsorbent has a high surface area because of the nano-scale diameter of the polymer nanofibers, and surface groups can be changed by choosing different polymers or modification. It can satisfy the criterion of a material used for adsorption (Saeed et al. 2008; Kampalanonwat & Supaphol 2010; Neghlani et al. 2011; Huang et al. 2013; Deb et al. 2020a, 2020b). There has been substantial interest in surface modifying PAN micro/nanofibers, with several advantages associated with their characteristic large surface area, chemical resistance, thermal stability, low flammability and good mechanical properties, and they have performed well in heavy metal and dye adsorption (Deng & Bai 2003; Saeed et al. 2008; Neghlani et al. 2011; Deb et al. 2020a, 2020b). Modified PAN micro/nanofibers can be regenerated and reused in other cycles after adsorption (Neghlani et al. 2011; Horzum et al. 2012). Hong et al. (2015) successfully fabricated aminated PAN nanofibers, which had a maximum uptake capacity 1,520 mg/g for Pb(II), and retained over 90% of their extraction capacity after six adsorption-desorption cycles. Ndayambaje et al. (2016) used PAN imidazole ligand nanofibers to adsorb Ni(II) in aqueous solution, and equilibrium uptake of Ni(II) at pH 5 and pH 5 was 0.3 and 0.7 mol/kg respectively, at a Ni(II) concentration of 0.0025 mol/L.
Supaphol 2014; Ndayambaje et al. 2011; Hossain et al. 2011; Koong et al. 2013; Hizal et al. 2016; Fan et al. 2017; Berber-Mendoza et al. 2018). Therefore, it is more crucial to evaluate the simultaneous adsorption behavior and interactions involving two or more metal species to better simulate the actual wastewater. Heavy metal adsorption depends not only on the characteristics of adsorbents but also the nature of the different metals involved because of their competitive behavior for adsorption sites. Many studies have been focused on competitive and selective adsorption of heavy metals using various sorbents (Li et al. 2011; Koong et al. 2013; Yang et al. 2015). However, as of much significance, involved in the combined impact of the different metal ions and various adsorbents, the conclusion of interactive effect between metal species is not quite consistent with each other (Scibain et al. 2007; Laus & Fävere 2011; Hossain et al. 2014; Tan et al. 2016). Furthermore, a few of studies have been dedicated to the competitive adsorption of heavy metals by PAN or modified PAN micro/nanofibers (Park et al. 2010; Kampalanonwat & Supaphol 2014; Ndayambaje et al. 2016; Bouazzaa et al. 2018). However, competitive adsorption of six metals by modified PAN has rarely been reported previously. So, it is necessary to extensively investigate the competitive adsorption behavior and mechanism of multiple heavy metal ions solutions such as Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) onto modified PAN micro/nanofibers thoroughly.

The main objective of this study is to determine the competitive adsorption behaviors through isotherm modeling for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) in a multi-metal system onto APAN micro/nanofibers at an optimal initial concentration and contact time. Furthermore, the interactive process and adsorption mechanism are also systematically illustrated.

**MATERIALS AND METHODS**

**Materials and apparatus**

Sodium carbonate (Na$_2$CO$_3$), hydroxylamine hydrochloride (NH$_2$OH-HCl), cadmium nitrate [Cd(NO$_3$)$_2$$\cdot$$4$H$_2$O], chromic nitrate [Cr(NO$_3$)$_3$$\cdot$$9$H$_2$O], copper nitrate [Cu(NO$_3$)$_2$$\cdot$$3$H$_2$O], nickel nitrate [Ni(NO$_3$)$_2$$\cdot$$6$H$_2$O], lead nitrate [Pb(NO$_3$)$_2$], and zinc nitrate [Zn(NO$_3$)$_2$$\cdot$$6$H$_2$O] 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 microscopy (SEM; Hitachi TM-3,000, Tokyo, Japan). A Nicolet 8,700 Fourier transform infrared spectroscope (FT-IR), operating at a wavenumber range of 4,000–400 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 fiber diameters of micro/nanofibers were analyzed by Image J processing software (National Institutes of Health, Bethesda, MD, USA).

**Functionalization of solution-blown PAN micro/nanofibers**

Solution-blown PAN fibers were prepared according to our previous studies (Lou et al. 2013, 2014). 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 into a sealed chamber containing 5.5 g of Na$_2$CO$_3$, 3.5 g of NH$_2$OH-HCl, and 100 mL of Milli-Q water. The reaction temperature and time were fixed at 70 ± 2 °C and 2–8 hours. Then the obtained micro/nanofibers were washed several times with deionized water to remove the remaining salts, and then dried in a vacuum oven at 50 °C.

**Competitive adsorption experiments**

The batch technique was used with a mixed-metal solution containing equal concentrations of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) – thus ‘100 mg/L mixed solution’ means that the concentration of each metal...
ion was 100 mg/L. The metal ion concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Thermo iCAP 6,000, Thermo Fisher Co., MA, USA), which was calibrated with 0.1, 1, and 10 mg/L standard solutions prepared by diluting a 1,000 mg/L standard solution with 2% HNO₃.

The competitive adsorption experiments were conducted in multi-metal systems (Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II)) with the metal concentrations of 20-200 mg/L. The pH value of each solution was adjusted to 6.0 ± 0.2 using 0.1 M HNO₃ and 0.1 M NaOH. 0.1 g of APAN adsorbents were firstly added in 100 mL above solutions in 250 mL flasks and then shaken at 125 rpm at room temperature (25°C). After reaching adsorption equilibrium, the adsorption capacity (qₑ) of APAN micro/nano fibers in a single-metal system and multi-metal system for each metal ion was calculated, respectively.

Effects of initial concentration and contact time

The multi-metal system and single-metal system solution were formulated according to the above-mentioned methods. Samples were withdrawn at predetermined time intervals to analyze the remaining metal concentrations in the aqueous solution, and adsorption amount (qₜ) for each metal ion was calculated with different initial concentration.

Adsorption isotherm

Adsorption equilibrium studies of the multi-metal system and single-metal system were carried out according to the above-mentioned methods. After reached adsorption equilibrium, 1 mL of the testing solutions was taken and diluted with a proper amount of Milli-Q water for ICP-OES analysis. All the sample solutions were filtered by 0.45 μm filters, and the metal ion concentrations in 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 the walls of the apparatus used.

The Langmuir model is the most popular adsorption isotherm model. It is not only used for prediction of single metal adsorption behavior but also for multi-metal adsorption. By introducing some interaction factors, the Langmuir isotherm can be modified into a multi-metal adsorption isotherm as follows (Srivastava et al. 2008; Padilla-Ortega et al. 2013; Birungi et al. 2017):

\[
qₑ,i = \frac{qₑ,iₖₐₜₖ,i Cₑ,i}{1 + \sum_{j=1}^{j=N} Kₖ,i Cₑ,i}
\]

where \( qₑ,i \) is the equilibrium adsorption capacity for \( i \) metals (mg/g), \( Cₑ,i \) is the equilibrium concentration of \( i \) metal ion (mg/L), \( Kₖ,i \) is the isotherm parameter for \( i \) metal (L/mg), and \( qₑ,iₖₐₜₖ,i \) is the maximum adsorption capacity for \( i \) metals (mg/g), \( j \) is the number of metals of the solution.

In this experiment (\( i = 1-6 \) and \( j = 6 \)), the adsorption system can be formulated by reforming Equation (1) for a hexahydroxy solution of Cd(II)-Cr(III)-Cu(II)-Ni(II)-Pb(II)-Zn(II) system:

For Cd(II):

\[
qₑ,Cd = \frac{qₑ,Cdₖₐₜₖ,Cd Cₑ,Cd}{1 + Kₖ,Cd Cₑ,Cd + Kₖ,Cr,Cₑ,Cr + Kₖ,Cu,Cₑ,Cu + Kₖ,Ni,Cₑ,Ni + Kₖ,Pb,Cₑ,Pb + Kₖ,Zn,Cₑ,Zn}
\]

For Cr(III):

\[
qₑ,Cr = \frac{qₑ,Crₖₐₜₖ,Cr Cₑ,Cr}{1 + Kₖ,Cd,Cₑ,Cd + Kₖ,Cr,Cₑ,Cr + Kₖ,Cu,Cₑ,Cu + Kₖ,Ni,Cₑ,Ni + Kₖ,Pb,Cₑ,Pb + Kₖ,Zn,Cₑ,Zn}
\]

For Cu(II):

\[
qₑ,Cu = \frac{qₑ,Cuₖₐₜₖ,Cu Cₑ,Cu}{1 + Kₖ,Cd,Cₑ,Cd + Kₖ,Cr,Cₑ,Cr + Kₖ,Cu,Cₑ,Cu + Kₖ,Ni,Cₑ,Ni + Kₖ,Pb,Cₑ,Pb + Kₖ,Zn,Cₑ,Zn}
\]
For Ni(II):

$$q_{e,Ni} = \frac{q_{m,Ni}K_{L,Ni}C_{e,Ni}}{1 + K_{L,Cd}C_{e,Cd} + K_{L,Cu}C_{e,Cu} + K_{L,Cu}C_{e,Cu} + K_{L,Ni}C_{e,Ni} + K_{L,Pb}C_{e,Pb} + K_{L,Zn}C_{e,Zn}}$$  \hspace{1cm} (5)

For Pb(II):

$$q_{e,Pb} = \frac{q_{m,Pb}K_{L,Pb}C_{e,Pb}}{1 + K_{L,Cd}C_{e,Cd} + K_{L,Cu}C_{e,Cu} + K_{L,Cu}C_{e,Cu} + K_{L,Ni}C_{e,Ni} + K_{L,Pb}C_{e,Pb} + K_{L,Zn}C_{e,Zn}}$$  \hspace{1cm} (6)

For Zn(II):

$$q_{e,Zn} = \frac{q_{m,Zn}K_{L,Zn}C_{e,Zn}}{1 + K_{L,Cd}C_{e,Cd} + K_{L,Cu}C_{e,Cu} + K_{L,Cu}C_{e,Cu} + K_{L,Ni}C_{e,Ni} + K_{L,Pb}C_{e,Pb} + K_{L,Zn}C_{e,Zn}}$$  \hspace{1cm} (7)

Desorption and reusability experiments

The reusability experiments were conducted in multi-metal systems with metal concentrations of 20 mg/L. The metal ion-APAN micro/nanofiber complexes were collected when adsorption reached equilibrium, and washed several times with deionized water to remove any unadsorbed metal ions. Then, the adsorbent samples containing the metals ion were placed in 50 mL of HNO₃ (1 mol/L) solutions and stirred for 2 hours. The amounts of adsorbed and desorbed metal ions were quantified by ICP-OES. After each adsorption-desorption cycle, the APAN micro/nanofibers 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.

RESULTS AND DISCUSSION

Characterization of APAN micro/nanofibers

FT-IR spectra of the neat and amidoxime PAN 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 indicates that the PAN is a copolymer of acrylonitrile and methylacrylate; and the C=O and C–O bands come from methylacrylate comonomer. The spectra of APAN micro/nanofibers (curve b) exhibit correlative characteristic bands of amidoxime at 3,081 cm⁻¹, 1,649 cm⁻¹, 1,580 cm⁻¹,

![Figure 1](http://iwaponline.com/wpt/article-pdf/16/4/1327/943887/wpt0161327.pdf)

**Figure 1** | FT-IR spectra of the (a) neat and (b) amidoxime PAN micro/nanofibers.
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 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 APAN fibers suggests that 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 identified.

The SEM images of PAN and APAN micro/nanofibers are shown in Figure 2. Figure 2(a) indicates the solution blown PAN micro/nanofibers have a main fiber diameter of 500–700 nm. Figure 2(b) shows an SEM image of the APAN micro/nanofibers, and the fiber structure was similar to that of the initial solution-blown fibers, even though the fiber diameters slightly increased due to being modified with hydroxylamine. It was worth mentioning that the APAN micro/nanofibers presented an almost similar morphology with the former state, which did not show any serious surface cracks or degradation.

![Figure 2](image-url) | SEM images of (a) the PAN and (b) the APAN micro/nanofibers.

**Characterization of competitive adsorption behavior**

The equilibrium adsorption capacity \(q_e\) of each metal ion in a single-metal system and multi-metal system onto APAN micro/nanofibers was shown in Figure 3.

Under the same conditions of coexisting with other interfering metal ions, the \(q_e\) of each metal ion in a multi-metal system was 10%–45% lower than that in a single-metal system; especially for Pb(II) and Cr(III), the reduction rates of \(q_e\) were in the range of 10%–15%, while for Cd(II) it is 40%–45%. Besides, the reduction rate increased with increasing initial concentration from 20 to 200 mg/L. The various degree and increasing trend of reduction rates indicated that there was an obvious and intense antagonistic competitive phenomenon between the metal ions in the multi-metal system. The diversity of adsorption reduction rates was attributed to the different physical and chemical properties of metal ions and the different affinity and binding stability between APAN micro/nanofibers and metal ions. Generally, when competitive sorption of metals is compared with their mono-metallic behavior, the adsorption capacity is lower in competitive systems (Hossain et al. 2014; Sellaaoui et al. 2017). Former research results also confirmed that the coexistence of multiple metal ions could affect the adsorption capacity of each metal ion. Ding et al. (2016) found that the adsorption process in the mixture (Cd(II) and Pb(II)) was different from the single solution, and the adsorption capacity both decreased in binary system. Sellaaoui et al. (2017) verified that the adsorption of Cd(II) was affected by the presence of Zn(II) in binary system, and the adsorption capacity of Cd(II) is lower when coexisting with Zn(II) in binary system. Similar experimental results were reported by Jain et al. (2016), Shu et al. (2016) and Du et al. (2016).

**Effects of initial concentration and contact time**

As presented in Figure 4, the \(q_t\) increased obviously with the increasing initial concentration, but the increasing trend became slower at higher concentrations, which indicated the initial concentration of metal ions has noticeable influence on the \(q_e\). At lower concentration, the APAN micro/nanofibers were not saturated adsorption, the
initial concentration directly impacted the mass transfer effects in the process of adsorption. Yang et al. (2015) found that the adsorption capacity of Cu(II) and Zn(II) by extracellular polymeric substances increased with increasing initial concentration of metal ions. Similar results were also obtained by Ding et al. (2016). With the increasing of concentration, a higher concentration gradient could produce a larger adsorption driving force, which made the adsorption capacity rise. As most of the active sites of APAN micro/nano fibers were occupied by metal ions, the $q_t$ was close to the maximum adsorption capacity in this condition, so the increasing trend of $q_t$ became slower.

The changing trend of $q_t$ with contact time was different for various metal ions. The $q_t$ of Pb(II) and Cr(III) onto APAN micro/nanofibers were larger than that of other metal ions, which first increased rapidly and then tended to level off, which was similar to the adsorption process of a single-metal system (Kampalanonwat & Supaphol 2014; Lou et al. 2014; Tan et al. 2016). However, the $q_t$ of APAN micro/nanofibers for Cd(II), Cu(II), Ni(II) and Zn(II) firstly increased to the ‘inflection point’, then dropped, and eventually tended to balance gradually with

Figure 3 | The adsorption capacity of APAN micro/nanofibers in a single-metal system and multi-metal system.
Figure 4 | Effects of initial concentration and contact time on adsorption amount ($q_t$).

Table 1 | The isotherm constants of Langmuir model in a multi-metal system and single-metal system

| Metal  | Single-metal system | Multi-metal system |
|--------|----------------------|--------------------|
|        | $q_m$(mg/g) | $K_L$(L/mg) | $R^2$ | $q_m$(mg/g) | $K_L$(L/mg) | $R^2$ |
| Cd(II) | 185.19     | 0.1154     | 0.9989 | 98.04      | 0.0566     | 0.9996 |
| Cr(III)| 204.08     | 0.1234     | 0.9973 | 158.73     | 0.0835     | 0.9997 |
| Cu(II) | 95.26      | 0.1012     | 0.9972 | 80.65      | 0.0519     | 0.9996 |
| Ni(II) | 104.17     | 0.1196     | 0.9982 | 76.34      | 0.0523     | 0.9997 |
| Pb(II) | 344.83     | 0.1593     | 0.9996 | 312.50     | 0.1317     | 1.0000 |
| Zn(II) | 90.91      | 0.1102     | 0.9975 | 58.82      | 0.0526     | 0.9992 |
increasing contact time. This results indicated that Pb(II) and Cr(III) have a stronger affinity to -NH₂ on the surface of APAN micro/nanofibers than Cd(II), Cu(II), Ni(II) and Zn(II), which are easier to react with -NH₂ and form stable complexes, so Pb(II) and Cr(III) are preferably adsorbed on APAN micro/nanofibers. As the adsorption reaction proceeds, the active sites were occupied by different metal ions; however, free Pb(II) and Cr(III) in the solution, which were easier to combine with -NH₂, could adsorb on APAN micro/nanofibers by displacement reaction mechanism, and make Cd(II), Cu(II), Ni(II) and Zn(II) desorption from the adsorbent. Therefore, the $q_t$ of Cd(II), Cu(II), Ni(II) and Zn(II) decreased when the reaction reached a certain degree. In this experiment, the $q_t$ of APAN micro/nanofibers for Cd(II), Cu(II), Ni(II) and Zn(II) appeared to undergo a significant decline at 6–8 hours, and then became equilibrium.

**Adsorption isotherm**

Adsorption isotherm is established when the remaining concentration of metal ions in solution ($C_e$) is in balance with that being adsorbed onto APAN micro/nanofibers ($q_e$). This level of equilibrium concentration depends significantly on the initial concentration of the metals and the isotherm adsorption results. The isotherm constants ($K_L$) of the Langmuir model along with the correlation coefficients ($R^2$) for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) in a multi-metal system and single-metal system are summarized in Table 1.

For all studied metal ions of multi-metal systems, the modified Langmuir model gives higher regression correlation coefficients ($R^2 > 0.999$); this indicates the modified Langmuir isotherm model successfully fitted the competitive adsorption of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) onto APAN micro/nanofibers. The maximum adsorption capacities ($q_m$, mg/g) of the metal ions determined from the Langmuir isotherms were in the order of Pb(II) (312 mg/g), Cr(III) (158 mg/g), Cd(II) (98 mg/g), Cu(II) (80 mg/g), Ni(II) (76 mg/g) and Zn(II) (58 mg/g) in multi-metal systems, while Pb(II) (344 mg/g), Cr(III) (204 mg/g), Cd(II) (185 mg/g), Ni(II) (104 mg/g), Cu(II) (95 mg/g) and Zn(II) (90) mg/g in single-metal systems. Obviously, the $q_m$ of each metal ion in a multi-metal system were lower than that in a single-metal system. Ding et al. (2016), Park et al. (2016) and Liu & Lian (2019) also confirmed that the adsorption process of metal ions in a multi-metal system fitted the Langmuir model better than the Freundlich model, and the adsorption capacity in a multi-metal system differed from a single-metal system due to the competition behavior.

The non-linear relationships between the adsorption capacities versus the concentration of remaining metal ions in the multi-metal system are depicted in Figure 5. As can be seen from the figure, the calculated adsorption amounts ($q_{e, Langmuir}$) obtained from the Langmuir isotherm are in good accordance with experimental values ($q_{e, exp}$), which further proved that the modified Langmuir isotherm model could accurately estimate the adsorption capacities for all metal ions.

**Distribution coefficient and selectivity coefficient**

The ability for adsorbents to remove a given metal ion from aqueous solution can be expressed in terms of distribution coefficient ($K_d$), which is defined as the ratio of the amount of metal ions adsorbed onto the solid matrix to those in the liquid matrix (Lin et al. 2001; Chen et al. 2015; Wei et al. 2016). $K_d$ is a measurement of the affinity of an adsorbent for a particular ion and an indicator of the selectivity of the adsorbent to the particular ion in the presence of interfering ions. The magnitudes of the distribution coefficient reflect the adsorption selectivity and these values are found to be applicable for multi-component adsorption systems as well, and $K_d$...
can be determined at adsorption equilibrium by Equation (8):

\[
K_d = \frac{(C_0 - C_e)}{C_0} \times \frac{V}{M}
\]  

(8)

where \(K_d\) is the distribution coefficient (mL/g), \(C_0\) and \(C_e\) are the initial and equilibrium concentrations of the metal ions (mg/mL), \(V\) is the volume of the testing solution (mL), and \(M\) is the amount of adsorbent (g).

The \(K_d\) values of APAN micro/nano fibers in multi-metal system of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) are listed in Figure 6. It is clear that the APAN micro/nano fibers showed extremely good selectivity for Pb(II) and...
Cr(III), with $K_d$ values up to 1,786–42,490 and 849–14,709 respectively at initial concentrations ranging from 20 to 200 mg/L. In contrast, the APAN micro/nano fibers had little or no selectivity for Zn(II) and Ni(II) with initial concentrations ranging from 20 to 200 mg/L, and the $K_d$ values were much lower than Pb(II) and Cr(III). Therefore, the aminated on the surface of PAN micro/nano fibers not only provides enhanced adsorption for Pb(II) and Cr(III) but also the possibility of selectively adsorbing or separating Pb(II) and Cr(III) from other ions for the potential benefit of Pb(II) and Cr(III) recovery when they are to be removed from water or wastewater.

To further investigate the selectivity of APAN micro/nano fibers, the selectivity coefficient ($\alpha$) of a specific or targeted metal ion for the binding sites in the presence of other competitive species can be obtained from equilibrium binding data according to Equation (9) (Li et al. 2005; Liu et al. 2010; Monier et al. 2016):

$$\alpha = \frac{K_d(T)}{K_d(I)}$$

where $\alpha$ is the selectivity coefficient, $K_d(T)$ is the $K_d$ value of the targeted metal, and $K_d(I)$ is the $K_d$ value of other metal ions in the multi-metal system. The greater the $\alpha$ value, the better selectivity towards the targeted metal ion.

Figure 7 summarizes the $\alpha$ values of APAN micro/nano fibers towards Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) obtained in the presence of other competitive metal ions. With the concentration ranging from 20 to 200 mg/L for each metal ion, the $\alpha$ value of Pb(II) was greater than 2 towards any other metal ion, and the next is, and the $\alpha$ value of Cr(III) was greater than 1 towards other metal ions except Pb(II). In contrast, the $\alpha$ values of Cd(II), Cu(II), Ni(II) and Zn(II) were lower than those of Cr(III) and Pb(II), respectively. This was consistent with the previous research results of Tripathy et al. (2018) and Li et al. (2011), where the $K_d$ value of Pb(II) and Cr(III) is higher over other competitive metal ions in a binary system and multi-component system. This phenomenon indicated that APAN micro/nanofibers had a better selective adsorption for Pb(II) and Cr(III) than Cd(II), Cu(II), Ni(II) and Zn(II), which was also confirmed with the former-mentioned results of competitive adsorption experiments.

Moreover, the $\alpha$ value changed with different trends with increasing concentration for the better selectively adsorbed metal ions than the relatively weak ones. When the metal ion concentration was increased, the $\alpha$ values for higher selective adsorption ($\alpha > 1$) decreased gradually, while the $\alpha$ values for lower selective adsorption ($\alpha < 1$) had a tendency to increase. This indicated that the antagonistic competition adsorption effect between the metal ions was intense with increasing the metal ion concentration, and the selective adsorption performance of APAN micro/nanofibers was prominent at lower concentration.

Desorption and reusability studies

The results of five cycles of adsorption-desorption in multi-metal systems are graphically displayed in Figure 8. The re-adsorption capacities of the APAN fibers are slightly decreased with increasing adsorption-desorption
cycles, and more than 84.16%, 86.99%, 78.80%, 78.23%, 89.51% and 76.50% 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, which cannot be as high as 100% because of the non-electrostatic forces between the APAN fibers and metal ions (Singh et al. 2007), thus certain binding sites are still occupied; and (2) the loss of some functional groups on the fibers by 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.

Figure 7 | The selectivity coefficient ($\alpha$) of APAN micro/nanofibers towards Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II).
Mechanism of competitive adsorption

In essence, the adsorption of metal ions $M^{n+}$ ($n = 2$ or $3$) is the process to form surface complexes between metal ions and lone pair electrons of the nitrogen atom in the -NH$_2$ functional group on the APAN surface, as shown in Equation (10).

$$\text{RNH}_2 + M^{n+} \rightarrow \text{RNH}_2M^{n+}$$ (10)

It is commonly known that the diversities of adsorption capacity and selectivity of adsorption in the multi-metal system are mainly related to the stability constants and the microscopic coupling mechanism between the heavy metal ions and the functional groups on the fiber surface (Heidari et al. 2013; Chand & Pakade 2015). The stability constant is generally determined by the nature of the interaction between micro-molecular and functional groups, and higher stability constant indicates that the complexing ability between the metal ions and the functional group is stronger. The stability constants between heavy metal ions and -NH$_2$ and -OH functional group on APAN surface are shown in Table 2.

Table 2 | Stability constants between the heavy metal ions and the functional groups

| Metal ions | Stability constants | $q_m$(mg/g) |
|------------|--------------------|-------------|
|            | -NH$_2$            | -OH         |
| Cd(II)     | 2.65               | 4.17        | 98.04       |
| Cr(III)    | 4.15               | 10.1        | 158.73      |
| Cu(II)     | 4.31               | 7.0         | 80.65       |
| Ni(II)     | 2.80               | 4.97        | 76.34       |
| Pb(II)     | 4.92               | 7.82        | 312.50      |
| Zn(II)     | 2.37               | 4.40        | 58.82       |

As can be seen in Table 2, the adsorption capacity of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) is basically consistent with the order of the stability constants between metal ions and -NH$_2$ but different from -OH, which indicated that -NH$_2$ is the main and -OH is the minor functional group in APAN micro/nanofibers. In this experiment, the stability constants of Pb(II) and Cr(III) with -NH$_2$ and -OH were higher than that of other metal ions, which was due to the fact that both -NH$_2$ and -OH can form complexes with Pb(II) and Cr(III), and can even form complex complexes such as -NH$_2$-M-OH. While Pb(II) and Cr(III) have a stronger affinity with the surface functional groups of APAN micro/nanofibers, and it is easier to form stable complexes; therefore, in the multi-metal system, Pb(II) and Cr(III) can reject Cd(II), Cu(II), Ni(II), and Zn(II), which have been adsorbed but have weak affinity with the displacement reaction mechanism (Li et al. 2011).

It may be speculated that Pb(II) and Cr(III) first adhere to the adjacent adsorption sites of Cd(II), Cu(II), Ni(II), and Zn(II) on the APAN micro/nano fibers, then Cd(II), Cu(II), Ni(II), and Zn(II), which have been adsorbed but have weak affinity to -NH$_2$, are repelled by inducing electrostatic repulsion. These results clearly indicate
that the Pb(II) and Cr(III) higher affinity to -NH₂ induce the desorption of the non-dominant heavy metal ions that have been adsorbed through the displacement reaction (Figure 9). It is therefore reasonable to assume that there is a strong competitive adsorption in the process of APAN micro-nano fiber adsorption heavy metal ions in the multi-metal system.

CONCLUSIONS

In this paper, APAN micro/nanofibers were synthesized and utilized to remove Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) in a multi-metal aqueous solution system. Initial concentration and contact time have significant influence on the adsorption amount, and the adsorption capacity in the multi-metal system was lower than that in the single-metal system, while the total adsorption capacity was higher. With each metal ion concentration ranging from 20 to 200 mg/L, the \( q_e \) in the multi-metal system decreased by about 10%-45% compared to that in the single-metal system. Modified Langmuir isotherm model successfully fitted the competitive adsorption of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) onto APAN micro/nanofibers, and the maximal adsorption capacities for Cd(II), Cr(III), Cu(II), Ni(II), Pb(II), and Zn(II) were 98, 158, 80, 76, 312 and 58 mg/g, respectively. The distribution coefficients and selectivity coefficients of Pb(II) and Cr(III) were higher than whose of Cd(II), Cu(II), Ni(II) and Zn(II) at initial concentrations ranging from 20 to 200 mg/L, which indicated that APAN micro/nanofibers had higher selectivity for Pb(II) and Cr(III) in the multi-metal system. Desorption and reusability of APAN micro/nanofibers were determined by five adsorption-desorption cycles, and the re-adsorption capacities were up to 76-90% of initial adsorption values after five succeeding cycle operations. These results show that the APAN micro/nanofibers represent a promising material for treatment of wastewater containing heavy metal ions. The adsorption behavior in the multi-metal system is a complex process including surface complexation, antagonistic competition and displacement reaction, and the diversities and selectivities in adsorption of metal ions onto APAN micro/nanofibers are mainly related to the stability constants and their microscopic coupling mechanism between the heavy metal ions and the functional groups on the fiber surface. This work highlights competitive adsorption behavior of heavy metals by APAN micro/nanofibers, which is helpful for us to gain a deeper understanding of their removing and transport in multi-metal polluted environments.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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