Novel Tetrazole-Functionalized Absorbent from Polyacrylonitrile Fiber for Heavy-Metal Ion Adsorption

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ABSTRACT: A novel functional absorbent, polyvinyl-tetrazole fiber (PVT), was made from polyacrylonitrile fiber through [3+2] azide-nitrile cycloaddition reaction of cross-linked polyacrylonitrile with sodium azide. The obtained PVT showed strong adsorption ability to the investigated heavy-metal ions, Cu(II), Cd(II), Ni(II), and Zn(II), with the maximum adsorption capacities of 323, 278, 200, and 175 mg g^{-1}, respectively. The adsorption process was described as an ion exchange mechanism. The adsorption isotherms were better fitted for Langmuir model, while adsorption kinetics was better described by the pseudo-second order equation. In addition, the tested heavy-metal ions could be desorbed efficiently from PVT at pH below 2.0, and the adsorption capacity of the regenerated PVT had no loss until seven cycles. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 382–389, 2012

Key words: polyacrylonitrile fiber; modification; polyvinyltetrazole; heavy-metal ions; surface adsorption

INTRODUCTION

Polyacrylonitrile fiber is known as acrylic fibers, which has strong mechanical strength, excellent weather ability and antibiotic property, chemical stability, and thermostability, so it has being applied broadly in manufacture of textile product and in industrial development of sunshade, thermal insulation material, filtration materials, etc. In addition, polyacrylonitrile fiber often acts as a raw material for the preparation of various functional materials.

Through translation of cyano- into other function group, various kinds of functional materials have been prepared from polyacrylonitrile fiber, to which adsorbent fiber belongs. For examples, the reaction of polyacrylonitrile with phenylhydrazine or para-toluene sulfamide has been used to synthesize chelating ion exchange fiber containing N,N and N,O ligands for the enrichment of Au(III), Pt(IV), Pd(IV), Ru(III), Rh(III), V(V), Ti(IV), Ga(III), In(III), and Bi(III) etc.[1–3] Another two chelating ion exchange fibers, which contained S and P polydentate ligand, were prepared by modifying polyacrylonitrile initially with hydrazine hydrate, then with diethylenetriamine, followed by treatment with sodium sulfide[4] and metaphosphoric acid.[5] These two fibers possess high selectivity and efficiency to the adsorption of Cu(II), Zn(II), Cd(II), and Hg(II). Anion exchange fibers were obtained by translating cyano into amino group,[6] and they had been successfully applied in air purification from acid gases.[6–8] The cation exchange fibers were prepared by hydrolysis of polyacrylonitrile fiber in solution of sodium hydroxide and hydrazine sulfate and were used for heavy metal waste treatment.[9,10] Anyway, highly efficient adsorbent are always required in the removal and enrichment of metal ions from polluted water, therefore it is of value for exploiting new, versatile function materials through chemical modification of polyacrylonitrile fiber.

Tetrazoles are heterocyclic compounds with five-membered ring constructed by one carbon atom and four nitrogen atoms. Tetrazolyl group has similar structural requirement and aqueous pKa value as carboxylic acid, and thus has become a widely known alternative to a carboxylate moiety.[11–13] In previous work, we have prepared a tetrazole-functionalized ion exchanger and a metal-chelator for the successful adsorption and separation of proteins by introducing tetrazolyl group onto the surface of silica.[14,15] As well known, ion exchange fibers mainly include amino-, carboxyl-, sulfo-, and

phosphate-type. In this work, we made a novel tetrazole-functionalized fiber, which is different from the current ion exchange fibers in the structure, by translation of cyano into tetrazolyl group using the [3+2] cyclization reaction of nitrile with triazo group, and further tested its adsorption property for heavy-metal ions.

EXPERIMENTS

Materials and instruments

Polyacrylonitrile fiber was gifted by Beijing Luojian Technology (Beijing, China). Hydrazine hydrate (80%) was purchased from Tianjin Reagent Chemicals (Tianjin, China). Other chemicals used were of analytical reagent grade.

The stock solutions of 1.0 mg mL^{-1} were prepared by dissolving Cu, Zn, and Cd in concentrated HNO_3 or $Ni(NO_3)_2 6H_2O$ in 2% HNO_3, and then diluted with 2% HNO_3, respectively.

Z-2000 atomic absorption spectrophotometer (Hitach, Xi'an MTian Techcomp) was used to determine the concentration of each metal ion.

Preparation of polyvinyltetrazole fiber

Cross-linking of polyacrylonitrile fiber

Totally, 2.0 g of polyacrylonitrile fibers (PAN) and 130 mL of H_2O and 30.0 g of hydrazine hydrate (80%) were added into a 250-mL flask with refluxing for 6 h at 105°C. After the reaction, the fibers were collected, washed with water until the filtration became neutral, and then washed with ethyl alcohol for three times. The resulting fibers were dried at 105°C. The crosslinking degree was calculated by the following equation:

The crosslinking degree
$$= \frac{\text{Crosslinking fiber quality} - \text{The initial fiber quality}}{\text{The initial fiber quality}} \times 100\% \quad (1)$$

Preparation of polyvinyltetrazole fiber

To a 250-mL three-necked flask 2.4 g of cross-linked PAN and 100 mL of DMF were added under stirring for 30 min. The flask was then placed into an oil bath and heated to 120°C, and 2.0 g of NH_4Cl, 2.6 g of NaN_3 were immediately added. The reaction mixture was refluxed under stirring for 16 h. The fibers were filtered, washed with water, 0.5 mol L^{-1} HCl and water in sequence, and was finally left to dry in vacuum oven at 30°C.

Measurement of adsorption isotherm

The adsorption capacities of polyvinyltetrazole (PVT) at different temperatures were investigated as the following procedure. Cu(II) stock solutions were adjusted to pH 5.0, and then diluted with NaAc-HAc solution (pH 5.0) to get a series of operational solutions with different concentrations (5.00 µg mL^{-1} $\sim$ 200.00 µg mL^{-1}). 0.05 g of PVT was added into 100.00 mL of operational solution, and then shaken on a shaker at 25°C for 12 h. PVT was removed by filtration and the filtrates were collected to measure the final Cu(II) concentration by atomic absorption spectrophotometer. The adsorption capacity was evaluated in term of sorption capacity at equilibrium (Q_e), expressed in mg g^{-1}:

$$Q_e = V(C_0 - C_e)/m \quad (2)$$

Where, V is the volume of the solution (mL), C_0 and C_e are the initial and equilibrium concentrations of metal ions (mg mL^{-1}), and m is the weight of the used fiber (g), or in term of metal removal efficiency, namely the enrichment recovery (R), expressed in %:

$$R = (C_0 - C_e)/C_0 \times 100 \quad (3)$$

Adsorption isotherms of Cu(II) as well as Zn(II), Cd(II), Ni(II) were obtained by plot Q_e against C_e, respectively.

Influence of pH on adsorption was investigated by the above procedure with the solutions of 20.00 µg mL^{-1} Cu(II) and Ni(II), 4.00 µg mL^{-1} Cd(II), and 2.00 µg mL^{-1} Zn(II), respectively.

Sorption kinetic experiment

To a series of 0.05 g of PVT, 100.00 mL of 100.00 µg mL^{-1} Cu(II) as well as Zn(II), Cd(II), and Ni(II) operational solutions were parallelly added, and then the solutions were shaken on a shaker at 25°C. The filtrates were collected at different times for the determination of ion concentrations. The kinetic curve was obtained by plot of the concentrations of metal ions vs. adsorption time.

Desorption experiment

The effects of initial pH on desorption of Cu(II) as well as Zn(II), Cd(II) and Ni(II) from PVT fiber were studied at room temperature. Various fibers saturated with the tested ions were weighed, and then immerged into different aqueous solutions with pH values ranged from 1.0 to 12.0 under stirring 12 h. The final concentrations of the tested ions were analyzed to estimate the amount of desorption.
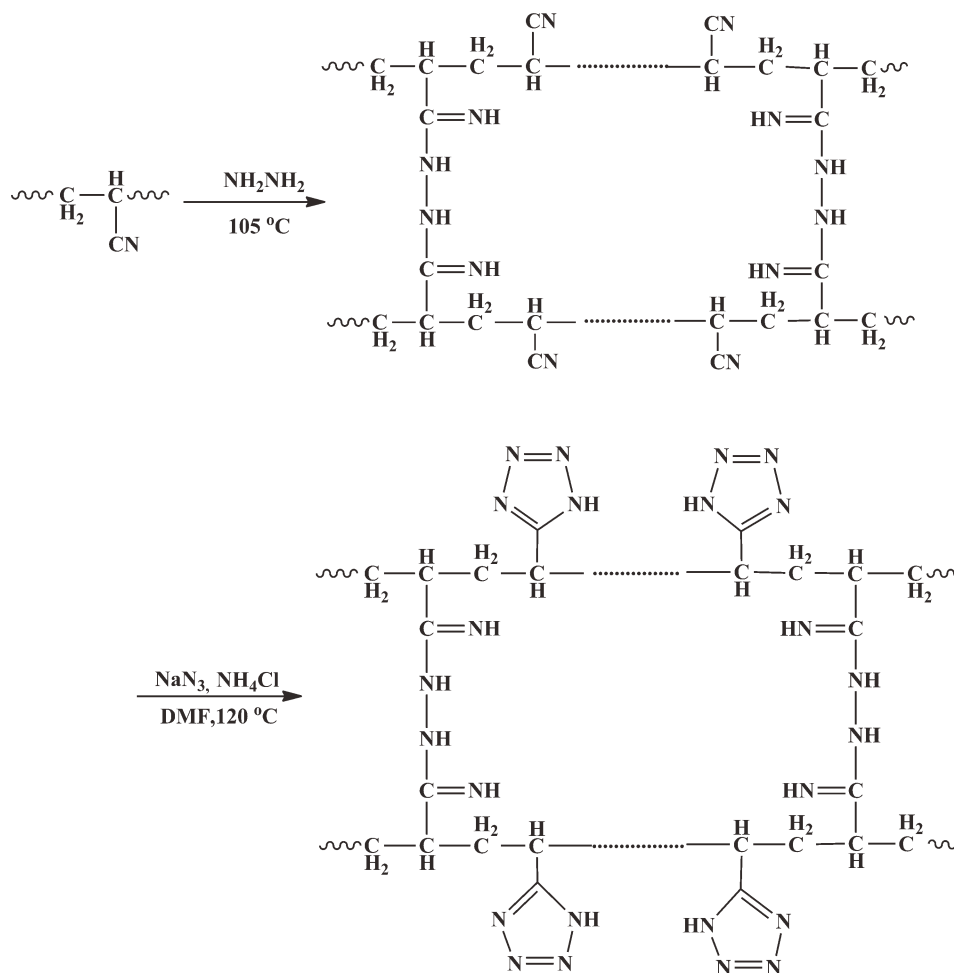
Figure 1 Synthesis route of PVT.

Recycling experiments

The various Cu(II)-loaded fibers were recovered from 0.1 mol L^{-1} HCl solution, and then collected from the solutions by filtration, washed with distilled water, and then reused in the next cycle of adsorption experiments. The adsorption–desorption experiments were conducted at room temperature for seven cycles.

Stability experiments

The stability of PVT fibers was tested by the dissolution experiment. 1.000 g of the fibers were put in 1000 mL of 0.2 mol L^{-1} HCl and 0.2 mol L^{-1} NaOH solutions for 48 h, respectively, then washed with distilled water and dried for mass and elemental analysis.

RESULTS AND DISCUSSION

Preparation of PVT

In the preparation procedure of PVT (Fig. 1), organic solvent used would dissolve PAN, so it is necessary

to prevent PAN from solubilizing in organic and water solution. Hydrazine hydrate is often chosen as crosslinking agent to cross PAN to keep its fibrous
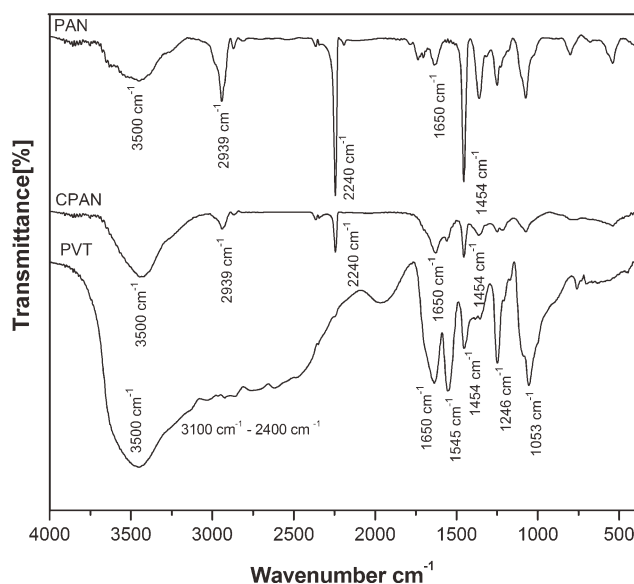

Figure 2 IR spectrums of PAN, CPAN, and PVT.

TABLE I
Elemental Analysis of PAN, CPAN, and PVT

sample	Composition (%)			N(mol)/C(mol)
	N	C	H	
PAN	25.35	66.85	5.305	0.3251
CPAN	26.15	65.01	5.268	0.3448
PVT	44.87	37.83	4.975	1.030

in the first step.[16] The resulting crosslinking degree of crosslinked PAN (CPAN) was calculated to be 5–7% by the weight method. In the second step, CPAN was modified into PVT through [3+2] cycloaddition reaction of nitrile with triazo group. From IR spectra of PAN, CPAN, and PVT (Fig. 2), they all exhibited the absorption at 3500 cm^{-1} and 1650 cm^{-1} assigned to stretching vibration of O—H due to the presence of water and C=N stretching vibration, respectively. For PAN and CPAN, the absorption was observed at 2939 cm^{-1} due to asymmetric CH$_2$ stretching vibration. For PVT, a broad medium band centered at 3100–2400 cm^{-1} suggested the presence of tetrazolyl groups.[17] Through comparing PAN, CPAN, and PVT, it was found that a stronger peak at 2240 cm^{-1}, attributed to the C≡N stretching vibration in PAN, became weaker in CPAN because of crosslinking of PAN, and further disappeared in PVT. Another strong peak at 1454 cm^{-1} for PAN and CPAN due to the characteristic C—H bending vibration became very weak for PVT. However, a medium band appeared at 1545, 1246, 1053 cm^{-1} in PVT, which were due to C—N, C=N, and N—N mixed stretching and bending vibrations of the characteristic tetrazole ring, respectively. These results suggested the translation of C≡N groups and the formation of tetrazolyl groups.

In the whole reaction process as shown in Figure 1, moles of C in polymer chain actually remained constant, while moles of N and H changed with the process of the reaction. To illustrate whether or not the reaction carried out according to the expected route, we suggested a parameter, N/C ratio, which denotes the mole ratio of nitrogen to carbon content, to reflect the change of moles of N in polymer before and after the reaction. Table I listed the results of elemental analysis of PAN, CPAN, and PVT. It was found that N/C ratio of CPAN was slightly higher than that of PAN because of the insert of hydrazine into CPAN, while N/C ratio of PVT was significantly higher than that of CPAN, suggesting that CN group in CPAN was translated into tetrazolyl group leading to the increase of nitrogen content. Therefore, it could be concluded from IR spectrum and elemental analysis that polyacrylonitrile fiber was successfully transformed into PVT.

Theoretically, the content of N, C, and H in PVT are 58.31, 37.50, and 4.19, respectively, and the total

content of three elements should be equal to 100% (in mass ratio). But the measured values were 44.87% for N, 37.83% for C, and 4.98% for H, respectively, and the total accounted to only 87.68%, showing a big discrepancy from theoretical value of 100%. This phenomenon was probably attributed to the reason that tetrazole could easily form tetrazole-hydrate hydrion such that the bound water around tetrazole was difficult to be removed, as reported by Hengxin Ha, etc.[12]

Adsorption isotherms of heavy-metal ions

Adsorption isotherms are useful to determine the amount of adsorbent needed to adsorb a required amount of adsorbate. Figure 3 shows the adsorption isotherms of the tested four ions. Obviously, the prepared adsorbent had strong adsorption ability to the tested metal ions and the adsorption capacities almost remained constant when the equilibrium concentrations of four ions reached ca. 10 μg mL^{-1}, in other words, the saturation adsorption had reached.

The obtained adsorption isotherms were analyzed by three most commonly used model equations, which were Langmuir, Freundlich, and Linear. Table II displays the parameters of the three isotherm equations at 25°C. Langmuir isotherm model were found to best fit the experimental data. From Langmuir isotherm, the adsorption capacities referring to per gram adsorbent were calculated to be 323 mg g^{-1} for Cu(II), 278 mg g^{-1} for Cd(II), 200 mg g^{-1} for Ni(II), 175 mg g^{-1} for Zn(II), respectively. The corresponding value was higher than the value varied from 8.9 to 30.0 mg g^{-1} reported for Cu(II) on polyacrylic acid and polyacrylic acid derivative,[18–22] and higher than 8.2 mg g^{-1} for Cu(II) on semicarbonized polyacrylonitrile,[23] and also higher than 150.6 mg
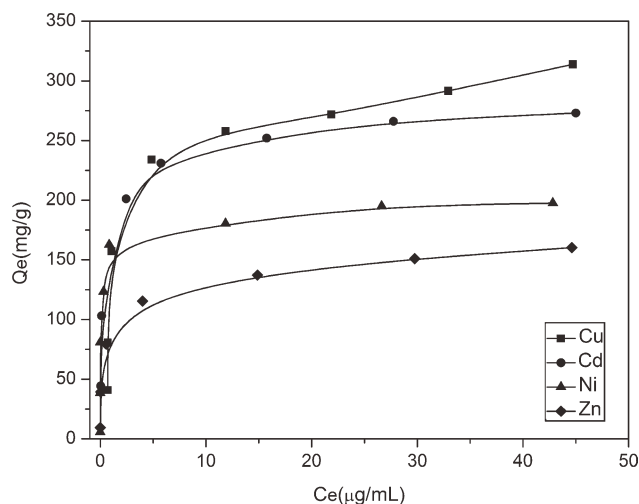

Figure 3 Adsorption isotherms of Cu(II), Cd(II), Ni(II) (II), and Zn(II) on PVT. Conditions: PVT, 0.05 g; temperature, 25°C; time, 12 h; pH of buffer, 5.0.

TABLE II
Langmuir, Freundlich, and Linear Isotherm Constants and Correlation Coefficients for Four Metal Ions on PVT at 25°C

Ions	Langmuir isotherm			Freundlich isotherm			Linear isotherm	
	q_m (mg g^{-1})	K_c (L mg^{-1})	R^2	K_f	n	R^2	K (L g^{-1})	R^2
Cu(II)	323.4	0.356	0.9935	7.44	2.81	0.7452	4.87	0.6469
Cd(II)	278.5	1.12	0.9994	8.26	4.38	0.8886	3.73	0.5187
Ni(II)	200.7	2.94	0.9993	5.98	3.33	0.2620	3.17	0.4825
Zn(II)	175.1	0.534	0.9951	6.09	3.70	0.9054	2.65	0.6454

g^{-1} for Cd(II) on chelating fibers of polyamino-polycarboxylic acid—functionalized polyacrylonitrile[24] and 52.7 mg g^{-1} for Cu(II) on amidoxime—modified polyacrylonitrile fibers.[25]

The adsorption capacities expressed in moles per gram adsorbent were calculated to be 5.1 mmol g^{-1} for Cu(II), 2.5 mmol g^{-1} for Cd(II), 3.4 mmol g^{-1} for Ni(II), 2.7 mmol g^{-1} for Zn(II), respectively, and they followed the order of Cu(II)> Ni(II) > Zn(II) > Cd(II). This order is exactly consistent with that of the second ionization energy of these metal ions (Cu, 1.96×10^3 kJ mol^{-1}; Ni, 1.75×10^3 kJ mol^{-1}; Zn, 1.73×10^3 kJ mol^{-1}; Cd, 1.63×10^3 kJ mol^{-1}). In PVT absorbent, tetrazole is an electron-donor. Since higher ionization energy implies a greater willingness to accept electrons,[26] the adsorption capacities of four ions showed the order of Cu(II)>Cd(II)>Ni(II)>Zn(II).

Effect of experimental conditions on adsorption property of heavy-metal ions

Effect of pH

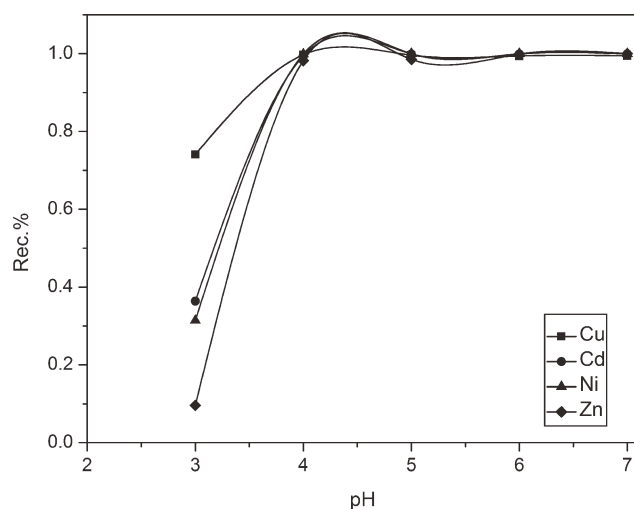pH is an important factor greatly influencing sorption property of PVT because pH of the solution could influence not only on ionic forms, but also on dissociation degree of tetrazole in PVT. Tetrazolyl presented electric neutrality in acid solution of pH < 3, in this case there were no static electricity and chelation interaction between tetrazolyl and metal ions, resulting in the low enrichment recovery (Fig. 4). At pH > 4, tetrazolyl became a negative five-membered ring due to the dissociation of tetrazolyl groups, thus the strong adsorption of PVT to metal ions happened. The maximum enrichment recovery was found for Zn(II), Ni(II), Cu(II), and Cd(II) at pH 4.0 ~ 7.0. To exclude the possibility of the hydrolysis of metal ions, pH 5.0 was selected as the optimum pH value for other adsorption experiments. At pH 5.0, the enrichment recovery of the tested four ions exceeded 98%.

Effect of temperature

The adsorption capacity of Cu(II) on PVT increased with increasing temperature but the increment was not significant for the temperature range investigated (Fig. 5). The similar trends were observed for the adsorption of Zn(II), Cd(II), and Ni(II). This confirmed that the adsorption was endothermic process but it was not sensitive to temperature.

Figure 4 Effect of pH on the enrichment recovery of four metal ions. Conditions: PVT, 0.05 g; initial concentrations of ions, 20.00 μg mL^{-1} for Cu(II) and Ni(II), 4.00 μg mL^{-1} for Cd(II), 2.00 μg mL^{-1} for Zn(II); temperature, 25°C.
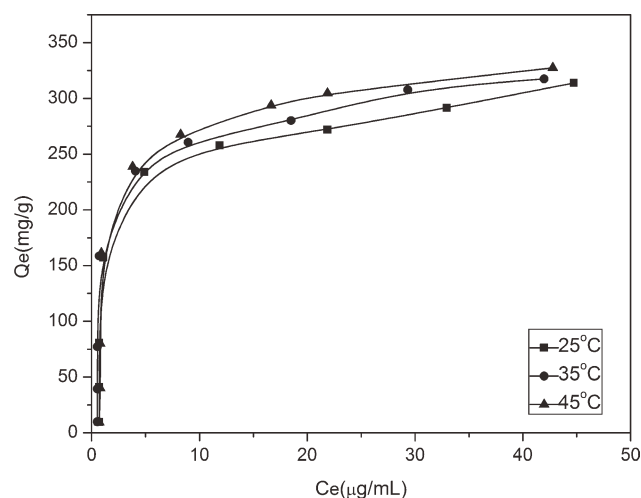

Figure 5 Adsorption isotherms of Cu(II) at different temperatures. Conditions: PVT, 0.05 g; time, 12 h; pH of buffer, 5.0.

TABLE III
Thermodynamic Parameters Estimated for Adsorption of Four Metal Ions onto PVT

metal ions	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})		
			25°C	35°C	45°C
Cu(II)	10.67	62.32	−7.87	−8.61	−9.12
Cd(II)	12.48	56.24	−4.30	−4.89	−5.39
Ni(II)	8.56	39.46	−3.22	−3.58	−4.01
Zn(II)	7.01	27.81	−1.30	−1.51	−1.86

According to Gibbs free energy equation:

$$\Delta G = -RT \ln K_C \qquad (4)$$

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

Where, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T the absolute temperature (K), and K_C the sorption equilibrium constant, which was obtained from Langmuir isotherm at different temperatures.

We could infer van't Hoff equation from eqs. (4) and (5) as follow:

$$\ln K_C = -\Delta H/RT + \Delta S/R \qquad (6)$$

The adsorption enthalpy and entropy of the ions calculated from van't Hoff plots are shown in Table III. The positive values of ΔH and ΔS for the sorption of four ions demonstrated an endothermic nature of this process along with an increased randomness at solid/liquid interface, indicating the temperature to be a beneficial factor on sorption kinetics. According to the stoichiometric displacement model for adsorption (SDM-A),[27] positive values of ΔS were probably attributed to the release of water molecules from the metal ion and/or adsorbent as a result of the adsorption of the solvated metal ion on the surface of the solvated adsorbent. On the other hand, $T\Delta S$ made up a large proportion of the total free energy in the temperature range investigated, suggesting that the increase in entropy which occured during the binding of ion was an important process promoting metal ion-tetrazole interactions.

Adsorption kinetics

To obtain the adsorption rates of metal ions, the relationship between instant ion concentrations and sorption times were investigated (Fig. 6). The adsorption rates of four ions were all fast, and the adsorption equilibrium reached for Ni(II) and Zn(II) in 30 min, for Cu(II) and Cd(II) in 60 min, respectively.

According to the kinetic equation of the pseudo second-order reaction[28]:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{1}{Q_e}t \qquad (7)$$

Where, t is the adsorption time (min); k the adsorption rate constant (min^{-1}); Q_t and Q_e are the adsorption amount at time t and equilibrium, respectively.

The obtained data in Figure 6 could be converted into the plots of t/Q_t vs. t, and good linearity was found with correlation coefficients (R^2) greater than 0.995, indicating that the adsorption kinetics of metal ion on PVT were fitted by the pseudo second-order kinetic model. The adsorption rate constants obtained from the slopes and intercept of the plots are 3.5×10^{-3}, 1.1×10^{-2}, 6.5×10^{-4}, and 1.0×10^{-3} g mg^{-1} min^{-1} for Ni(II), Zn(II), Cd(II), and Cu(II), respectively.

Interference of other metal cations

In real water, there coexist many other cations such as Fe(III), Al(III), Mg(II), and Ca(II), which would compete with Cu(II), Ni(II), Zn(II), and Cd(II) for the adsorption sites on the adsorbent surface. Table IV shows the enrichment recoveries of Cu(II), Ni(II), Zn(II), and Cd(II) without and with the competing cations. Obviously, as the analytes coexisted with three competing cations, Al(III), Mg(II), and Ca(II), their enrichment recoveries remained still above 98% even if their concentrations in the mixed solutions (1.0 mg L^{-1}) were much lower than that of Al(III), Mg(II), and Ca(II). However, when the analytes coexisted with Fe(III) ions (20 mg L^{-1}), their enrichment recoveries significantly decreased. This suggests that in practical use for water treatment only the coexisting Fe(III) ion would cause the interference on the enrichment of the heavy-metal ions, thus we can totally ignore the influences of the coexisting Al(III), Mg(II), and Ca(II) on the removal of Cu(II), Ni(II), Zn(II), and Cd(II).
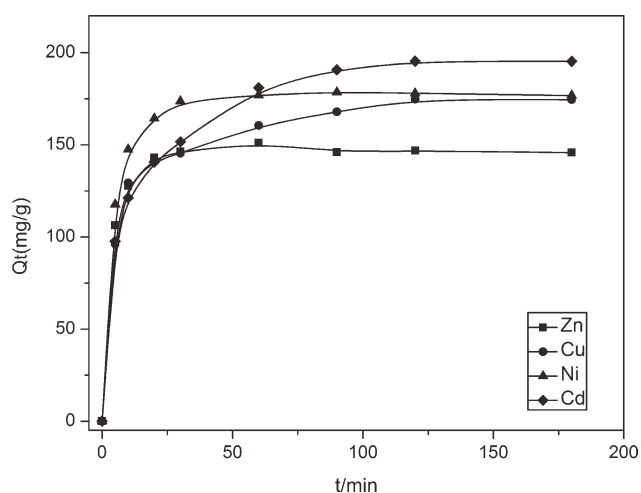

Figure 6 Adsorption dynamic of metal ions onto PVT fiber. Conditions: PVT, 0.05 g; initial concentrations of ions, 100.00 μg mL^{-1} for four metals; temperature, 25°C; pH of buffer, 5.0.

TABLE IV
Enrichment Recovery of Analytes on PVT Fiber with and Without the Competing Cations[a]

Cations	Enrichment recovery (%)		
	Without competing cations	Competing solution[b]	Competing solution[c]
Cu(II)	100.0	99.6	86.7
Cd(II)	99.7	100.00	78.2
Ni(II)	100.00	100.00	75.6
Zn(II)	98.8	98.6	68.2

[a] The concentrations of Cu(II), Cd(II), Ni(II), and Zn(II) are all 1.0 mg L^{-1}.
[b] The competing solution contains Al(III), 20; Mg(II), 30; Ca(II), 30 mg L^{-1}.
[c] The competing solution contains Fe(III), 20; Al(III), 20; Mg(II), 30; Ca(II), 30 mg L^{-1}.

Reusability and stability of PVT fiber

For practical application, desorption experiments were conducted to regenerate Cu(II), Ni(II), Zn(II), and Cd(II)-loaded fibers. It was found that the tested ions started to be released from the fibers at pH below 4.0, and at pH < 2.0, more than 99% of the metal ions was desorbed. However, at high pH (pH > 5.0), the metal ions-load fibers were quite stable. Thus, the desorption process was carried out in 0.1 mol L^{-1} HCl aqueous solution.

The adsorption and desorption processes were repeated to examine the potential of the fibers using Cu(II) ion as an example. Table V showed the amounts of Cu(II) ion adsorbed and the percentages of desorption in seven consecutive adsorption–desorption cycles. It was found that the desorption efficiency was generally high and the adsorption capacity was almost not affected.

In stability experiment, 1.000 g of the sorbents were immerged into strong acid and base solution for 48 h, and no weight loss was found in the treated process, indicating that PVT fiber does not dissolve in aqueous solution. The nitrogen content of the treated fibers was determined to be 45.03 ± 0.58% (n = 3), which is close to 44.87% for the blank PVT fibers. The result showed that tetrazolyl group

TABLE V
Adsorption and Desorption (Recovery) Behaviors of Cu(II) on PVT Fibers

Cycle	Adsorption amount (mg g^{-1})	Recovery (%)
Cycle I	322.7	99.8
Cycle II	323.1	99.9
Cycle III	323.2	99.9
Cycle IV	322.9	99.8
Cycle V	322.3	99.7
Cycle VI	322.4	99.7
Cycle VII	322.8	99.8

in PVT fiber could keep the stability during the process of adsorption. In all, due to the high recycling efficiency and stability, PVT fiber was qualified for practical application.

Adsorption process of electroplating wastewater

In electroplating nickel, Watts bath is often recommended for electrolytic baths. It contains 78 g L^{-1} $NiSO_4$, 11 g L^{-1} $NiCl_2$, 0.02 g L^{-1} sodium dodecyl sulfate, and 35 g L^{-1} boric acid. Watts bath waste was got from Xi'an electroplate factory (Xi'an, China), and the concentrations of Ni(II) and boric acid were determined to be 98 mg L^{-1} and 73 mg L^{-1}, pH 4.35. This electroplating wastewater was let to flow at a rate of 5 mL min^{-1} through a column (5 cm × 25 cm I.D.) filled with 100 g adsorbent, and the concentrations and volumes of the collected eluent were determined at set intervals (Fig. 7). As the concentrations of Ni(II) approached or equal to 1.0 mg L^{-1}, which is imposed by Emission Standard of Pollutants for Electroplating (GB21900-2008, China), the experiment stopped. The collecting volume is the single-pass handling ability for the adsorbent to treat electroplating wastewater. From Figure 7, this value is 93 L/100 g for electroplating wastewater containing 98 mg L^{-1} Ni(II).

Adsorption mechanisms

In the developed PVT fibers, it was expected that tetrazolyl groups in PVT acted as adsorption sites for heavy-metal ions. Tetrazolyl group, which served as a surrogate for terminal carboxylic acid residues, shows weak acidic (pKa 5.0) like carboxylic group[18] and can easily dissociate to form a negative five-membered ring in base solution. This electron-rich
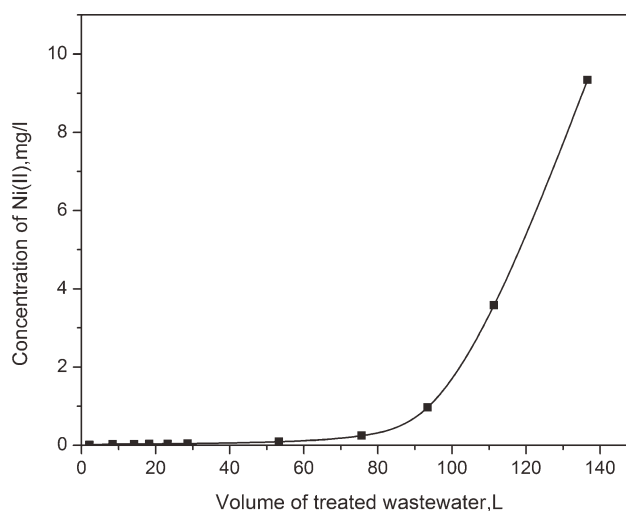

Figure 7 Dynamic adsorption of Ni(II) ions by PVT from electroplating wastewater. Conditions: PVT, 0.05 g; temperature, room temperature.

TABLE VI
Variation of pH for the Mixed Solution with and Before and After Addition of PVT

Num.	pH				
	1	2	3	4	5
Before adsorption	3.01	4.00	5.00	6.01	6.99
After adsorption	2.91	3.94	4.89	5.61	6.06

ring makes it the main binding site and forms stable metal complex. With the above consideration, the chemical reactions in eq. (8) are proposed to account the mechanism of the adsorption and desorption for heavy-metal ion.

The protonation of PVT was established by pH of the initial solution. When this fiber was added into the solution, the adsorption started because the electrostatic interaction between the electron-rich tetrazolyl ring and the heavy-metal ion would be stronger in comparison to the monovalent proton (H^+). This difference in the binding force drives the reaction according to eq. (8) and a competitive adsorption of Cu(II) over H^+ takes place. Such adsorption process can also be termed as an ion exchange mechanism.[29]

$$ \qquad (8) $$
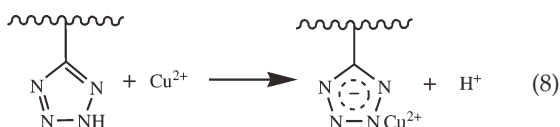
The speculated mechanism was validated by the following facts. (1) In the adsorption experiment, the enrichment recovery of the tested ions was low at lower pH but was high at pH > 4; (2) The adsorbed metal ions were not desorbed even with hot water but could be with dilute acid; (3) After 0.05 g of PVT was added into the mixed solutions containing 20.00 μg mL^{-1} of Cu(II) and Ni(II), 4.00 μg mL^{-1} of Cd(II), and 2.00 μg mL^{-1} of Zn(II), pH values of the solution were found to decrease (Table VI). These three experiments showed that an ion exchange effect took place between metal ion and H^+ in adsorption process.

CONCLUSIONS

A new tetrazole-functionalized absorbent was successfully made from polyacrylonitrile fiber by [3+2] azide-nitrile cycloaddition reaction. The adsorbent showed strong ability to adsorb heavy-metal ions from aqueous solution and the adsorption fitted Langmuir monolayer adsorption model for Cu(II), Cd(II), Ni(II), and Zn(II). The adsorbent also presents better reuse ability and higher stability. In practical application, the adsorbent could efficiently remove Cu(II), Cd(II), Ni(II), and Zn(II) ions in electroplating wastewater. Therefore, the prepared adsorbent was expected to find wide application in the enrichment and removal of heavy-metal ions from waste water, and the established method might become a promising way to recycle waste polyacrylonitrile.

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