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Effective adsorption of sulfate ions with poly(*m*-phenylenediamine) in aqueous solution and its adsorption mechanism

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Abstract: Sulfate adsorption by poly(*m*-phenylenediamine)s (PmPDs) with various oxidation states synthesized through chemically oxidative polymerization was investigated. Series of sorption experiments were conducted, and the adsorption mechanism and the relationship between oxidation state and adsorption performance were studied with the characterization of Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), pH tracking and energy calculation. The results show that the adsorption performance in acidic solution is improved with the decrease of oxidation state of poly(*m*-phenylenediamine) (PmPD). The rate constant is as high as 425.5 mg/(g·min) in the short equilibrium time of 30 min. The estimated highest adsorptivity of sulfate ions is 95.1%. According to the Langmuir equation, the adsorbance is 108.5 mg/g. The sulfate desorption efficiency is about 95% and the accumulative adsorbance is up to 487.95 mg/g in 5 cycles.

Key words: poly(*m*-phenylenediamine); sulfate ions; adsorption; adsorption rate; oxidation state; desorption efficiency

1 Introduction

Polyaniline (PANI) and its derivatives, as conducting polymers, have attracted considerable interest mainly owing to their potential applications in sensors, actuators and electronic devices [1,2]. In recent years, investigations have been intensively conducted to characterize the adsorption ability of these conducting polymers. They exhibited high removal efficiency of metallic cations from wastewater. The adsorption of Pb^{2+} with poly(*m*-phenylenediamine) (PmPD) was more than 99% and the accumulated adsorbance reached 720.4 mg/g in 5 cycles [3]. Polyaniline was used to adsorb Hg^{2+} with a maximal adsorptivity of 95% [4]. A 100% reduction in 60 mg/L Cr^{6+} solution with polypyrrole as adsorbent has been reported by RODRIGUEZ et al [5]. Ag^{+} could be removed effectively by poly(1,8-diaminonaphthalene) with a high adsorbance of 1920 mg/g [6]. These adsorption mechanisms have been studied broadly in previous reports. The metal-complexation with amine and imine nitrogen along the polymer backbones is certainly regarded as adsorption driving force, such as the adsorption of Pb^{2+} [3,7]. Another possible mechanism is cationic exchange, through which metallic ions, such as Hg^{2+}, can dope in the polymer molecules replacing H^{+} [6]. More importantly, the reduction reaction of amine groups was found to be a crucial factor for the adsorption of Ag^{+} and Cr^{6+} [5,6,8], which significantly enhanced the polymers adsorption capability compared with ordinary adsorbents [9].

Of course, some researchers reported that through the fabrication of polyaniline/alumina composites, fluoride ions in aqueous solution can be removed with a maximal adsorbance of 8.0 mg/g [10]. This indicates that polyaniline and its derivatives could also be used to treat anion-containing wastewater. However, up to now, less attention has been paid to this area. Moreover, the interaction between these conducting polymers and anion ions in aqueous media has not been studied in depth and the mechanism is still unclear.

Acidic sulfate wastewater, from electroplating, steel pickling, mining, nonferrous smelting, and so on, has become one main source of industrial environmental pollution [11]. Several methods have been employed to treat sulfate-containing wastewater, including chemical precipitation [12], crystallization [13], ion exchange [14],

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biological treatment [11], electro-dialysis [15], nano-filtration [16], reverse osmosis [17] and adsorption. Among them, adsorption is commonly considered to be the more attractive and mostly-used technique due to the effectiveness and low cost [18,19]. Activated carbon [20], hydrous iron oxide [21], γ-Al_2O_3 [22], chitin [23], etc, were used as adsorbents. However, the used materials still suffer from the low adsorption capacity and high-price for the sulfate wastewater treatment. Great interest has been directed toward the development of new types of adsorbents.

In this work, poly(*m*-phenylenediamine)s (PmPDs) with various oxidation states were synthesized through chemical oxidation method by adjusting the initial polymerization pH and oxidant/monomer mole ratio. The PmPD particle was explored to treat sulfate-containing wastewater. PmPD adsorption behavior of sulfate ions was investigated under various factors, such as initial sulfate solution pH, adsorbent dosage, sorption duration and initial sulfate concentration. The multi-cycle adsorption capability of PmPD was also examined. More importantly, the sulfate adsorption mechanism of PmPD in aqueous solution was discussed based on XPS, FTIR and energy calculation.

2 Experimental

2.1 Materials

The *m*-phenylenediamine, ammonium persulfate, ethanol, ammonia and sodium sulfate of analytical reagent grade were purchased from Sinopharm Chemical Reagent Co., Ltd., and used as received.

2.2 Preparation of uniform PmPD micro-particles

Uniform PmPD micro-particles were synthesized at 25 °C using ammonium persulfate (APS) as oxidant [3]. Briefly, 10.0 g mPD was dissolved in 175 mL distilled water and stirred for 30 min to form monomer solution. 55 mL APS aqueous solution (oxidant/monomer molar ratio is 1) was added dropwise to the monomer solution at a rate of one drop per second in ~20 min. The solution was further stirred for 5 h, then filtrated and rinsed with distilled water. Ammonium solution (1:1 in volume ratio) and ethanol were used to remove the soluble residuals and oligomers. The end product was dried in vacuum at 60 °C for 12 h and designated as sample 1.

To investigate the effect of polymerization factors, 6 samples were prepared at initial solution pH from 1.5 to 13.2 and the oxidant/monomer mole ratio range of 0.5−1.5. The results are shown in Table 1.

2.3 Adsorption experiments

Adsorption experiments were carried out to examine the effects of initial sulfate solution pH, dosage, adsorption time and initial sulfate concentration on the adsorption behaviors of PmPD, multi-cycle adsorption performance and the adsorption capability of PmPD. The adsorption experiments were conducted in an 150 mL flask in a water bath at 30 °C. A certain amount of PmPD particle sample was added into 15 mL of aqueous solution which contains a given concentration of sulfate ions prepared by sodium sulfate. HCl or NaOH was used to adjust the initial pH value of the sulfate solution. After adsorption, PmPD micro-particles were separated from the solution and washed with distilled water twice for further characterization.

The concentration of filtrate was determined by barium chromate spectrophotometry with a detection range of 8−200 mg/L. The sulfate concentration after adsorption in experiment exceeded 8 mg/L and the filtrate was diluted when the concentration was more than 200 mg/L. The adsorptivity and adsorbance of sulfate ions on PmPD were calculated by

$$q = \frac{\rho_i - \rho_a}{\rho_i} \times 100\% \quad (1)$$

$$Q = \frac{\rho_i - \rho_a}{m} \times V \quad (2)$$

where q is the adsorptivity; Q is the adsorbance; ρ_i and ρ_a are the sulfate concentrations before and after adsorption, respectively; V is the volume of sulfate solution; m is the dosage of PmPD.

Table 1 Preparation of poly(*m*-phenylenediamine) by chemically oxidative polymerization

Sample No.	Medium	Initial polymerization pH	Oxidant/monomer ratio	Yield[a] /%	q /%	Q/(mg·g^{-1})
1		8.8	1.0	69.0	60.8	91.2
2	H_2O	8.5	0.5	42.1	64.9	97.3
3		8.2	1.5	86.7	52.9	79.4
4	HCl (1.0 mol/L)	1.5	1.0	50.6	44.8	67.2
5	HCl (0.3 mol/L)	2.9	1.0	52.5	49.4	74.1
6	NaOH (0.1 mol/L)	13.2	1.0	69.8	60.3	90.5

Yield[a] was calculated as the ratio of the mass of PmPD to the mass of *m*-phenylenediamine

For multi-cycle adsorption tests, PmPD was regenerated by 15 mL of 1:1 ammonium solution and rinsed with distilled water till the filtrate was neutral. The desorption ability was calculated according to equation (3):

$$Q_{\mathrm{D}} = \frac{\rho_{\mathrm{D}} V_{\mathrm{D}}}{(\rho_i - \rho_{\mathrm{a}})V} \tag{3}$$

where ρ_{D} is the sulfate ion concentration in effluent after desorption and V_{D} is the volume of effluent.

2.4 Analysis

The samples before and after adsorption and PmPDs synthesized under various conditions were pressed into disks with KBr for FTIR analysis. Spectra were recorded on a Nicolet S10 spectrophotometer in the range of 500−4000 cm^{-1}. XPS analyses of PmPD before and after adsorption were carried out on an XSAM800 spectrometer with an Al K_α X-ray source (1486.6 eV of photons) run at a reduced power of 180 W to determine the element N on the surface of PmPD. The pressure in the analysis chamber was maintained at about 266.644×10^{-7} Pa. To compensate the surface charging effects, the neutral C ls peak at 284.6 eV was used as reference of all binding energies. Software Xpeak 4.1 was applied to analyzing the spectra. Full width at half-maximum was kept at 1.5.

3 Results

3.1 Synthesis and performance of PmPD

3.1.1 Effect of oxidant/monomer mole ratio

As summarized in Table 1 (samples 1−3), when the oxidant/monomer mole ratio decreases from 1.5 to 0.5, the yield reduces from 86.7% to 42.1% dramatically. This should be due to the less oxidant which causes lack of radicals to initiate the polymerization effectively, and thus results in the restriction of the growth of polymeric chain [24]. As a result, a low yield of product is obtained. In order to examine the macromolecular structure of PmPD synthesized at different oxidant/monomer mole ratios, FTIR was applied to characterize samples 1−3. As shown in Fig. 1, the adsorption peaks at 3350−3200 cm^{-1} are attributed to the N—H stretching vibration. Two sharp peaks at ~1620 and ~1510 cm^{-1} are due to the stretching vibration of quinoid and benzenoid rings, respectively [25]. The adsorptions at 1322 (very weak) and 1260 cm^{-1} are associated with the C—N stretching mode of quinoid and benzenoid units, respectively. It can be concluded that PmPD is composed of quinoid imine and benzenoid amine [26]. The relative content of quinoid imines is generally used to indicate the oxidation states of these polymers. Apparently, the relative intensity of the peaks enhances at ~1620 cm^{-1} (quinoid rings) but drops at ~1500 cm^{-1} (benzenoid rings) when the oxidant/monomer mole ratio increases from 0.5 to 1.5. It is evident that the oxidation state increases under large oxidant/monomer mole ratio, which is consistent with the results in reported researches on poly(*o*-phenylenediamine) [27].

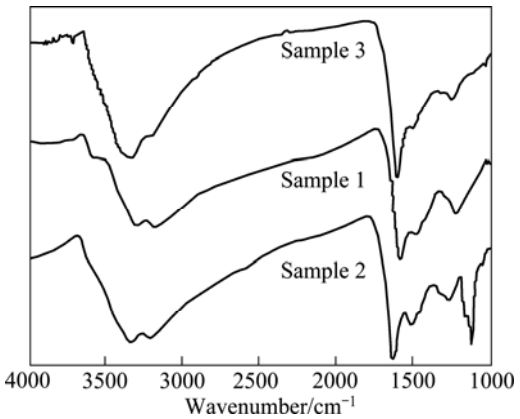

Fig. 1 FTIR spectra of PmPDs synthesized at different oxidant/monomer mole ratios (Samples 1−3 were synthesized at the oxidant/monomer mole ratio of 1.0, 0.5 and 1.5, respectively)

3.1.2 Effect of Initial polymerization pH

As listed in Table 1, when the initial polymerization pH goes from 1.5 to 13.2, the yield increases significantly from 50.6 % to 69.8 %. It indicates that a higher pH tends to enhance the yield of products. This can be attributed to the protonation of amine/imine groups of *m*-phenylenediamines at a lower pH, which inevitably lowers the electron density of mPD monomers and then impairs their oxidation reactivity. The macromolecular structure of PmPDs was also examined with FTIR. As seen in Fig. 2, for the PmPD particles synthesized with the initial polymerization pH higher than 8.0, the relative intensity of quinoid (~1620 cm^{-1})

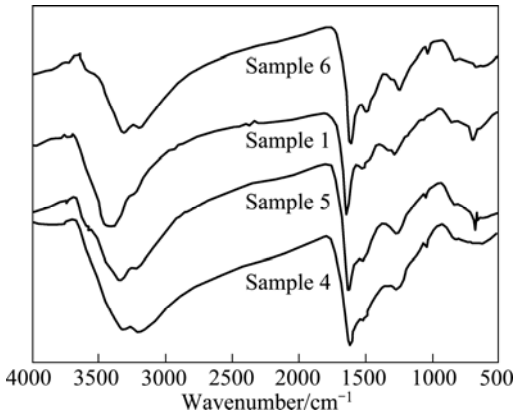

Fig. 2 FTIR spectra of PmPDs synthesized at different initial polymerization pH values (Samples 1 and 4,5,6 were synthesized at the initial polymerization pH values of 8.8, 2.9, 1.5 and 13.2, respectively)

rings and benzenoid (~1500 cm^{-1}) rings have no significant change (Fig. 2, samples 1, 6). However, as the initial polymerization pH is lower than 8.0, the relative intensity of quinoid rings increases clearly in comparison with benzenoid rings (Fig. 2, samples 4, 5). This is strongly indicative that the increased initial polymerization pH can possibly adjust the polymerization to lower the oxidation state and maintain a good yield of PmPD.

3.1.3 Sulfate adsorption performance of PmPD in different oxidation states

The sulfate adsorption performance of PmPD synthesized under various reaction conditions was explored (Table 1). As the oxidant/monomer mole ratio increases from 0.5 to 1.5, the adsorptivity drops from 64.9% to 52.9%. Moreover, as the initial polymerization pH increases from 1.5 to 13.2, the sulfate adsorptivity enhances from 44.8% to.60.3%. The sulfate adsorbance also shows the same tendency. This implies that the sulfate adsorption performance of PmPD is closely related with its oxidation states. And decreasing the oxidation state is obviously beneficial to improving the sulfate adsorptivity and adsorbance of PmPD. To assure both high yield and good sulfate adsorption performance, an oxidant/monomer mole ratio of 1 and the initial polymerization pH around 9 (distilled water as medium) were chosen for the following adsorption experiments.

3.2 Factors on sulfate ions adsorption

3.2.1 Effect of initial sulfate pH

The effect of initial sulfate solution pH on sulfate adsorption was investigated in the pH range of 1.5−10. As can be seen in Fig. 3, the sulfate adsorption of PmPD keeps relatively constant when pH is more than 3.0. In contrast, when pH declines within 3.0−1.75, the adsorptivity and adsorbance enhance rapidly from 8.6% and 12.9 mg/g (pH 3.0) to 60.8 % and 91.2 mg/g (pH 1.75). Further increase of adsorption performance is observed at pH 1.5. This indicates that the sulfate adsorption onto PmPD particles is more favorable in the acidic solution.

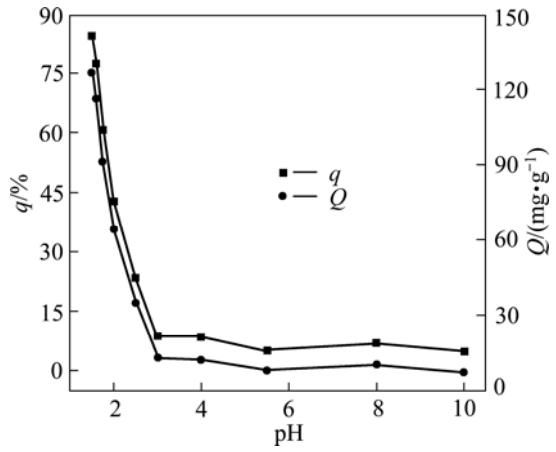

Fig. 3 Effect of initial solution pH value (1.5−10) on SO_4^{2-} adsorption onto PmPD at SO_4^{2-} concentration of 2000 mg/L with 200 mg of adsorbent for 60 min

3.2.2 Optimization of adsorbent dosage

The effect of PmPD dosage on the sulfate adsorption is given in Fig. 4. When the dosage increases from 50 mg to 500 mg, the adsorptivity increases gradually and reaches nearly 80% at a dosage of 500 mg. The adsorbance reaches a maximum of ~170 mg/g at a dosage of 50 mg. Increasing PmPD dosage leads to the decline of adsorbance from 168.6 to 47.7 mg/g. Thus, to keep the high adsorptivity and meet an ideal adsorbance, an optimal dosage of PmPD is around 200 mg in this study.

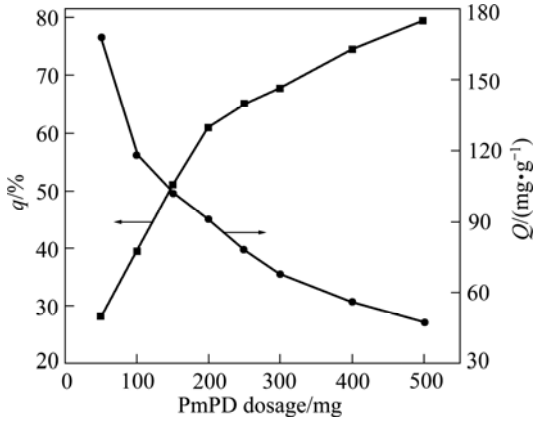

Fig. 4 Effect of PmPD dosage (50−500 mg) on SO_4^{2-} adsorption onto PmPD at initial solution pH of 1.75 and SO_4^{2-} concentration of 2000 mg/L for 60 min

3.2.3 Adsorption kinetics

The data in Fig. 5 show the correlation of adsorptivity and adsorbance with adsorption time for PmPD at an initial solution pH of 1.75. The adsorptivity is 51.3% (adsorbance: 77 mg/g) in 1 min and reaches 59.6% (adsorbance: 89.5 mg/g) in 10 min. Further prolonging the adsorption time to 15 min, the adsorptivity rises slightly to about 60%. Finally, the adsorption stays equilibrium when the sorption time is 30 min. Herein, 10 min of sorption time can be viewed as the watershed to divide the kinetic process into two stages: quick step (<10 min) and slow step (>10 min). At the quick step, the immediate interaction between the surface of PmPD particles and sulfate ions leads to quick adsorption. While at the slow step, the sulfate ions can penetrate into PmPD particles. Thus, in this condition the sorption rate declines.

To determine the sulfate adsorption kinetics of the adsorbent, the classical pseudo first- and second-order kinetic equations were employed. The curves of $\lg(Q_e-Q_t)$ versus t and t/Q_t versus t based on the experimental data

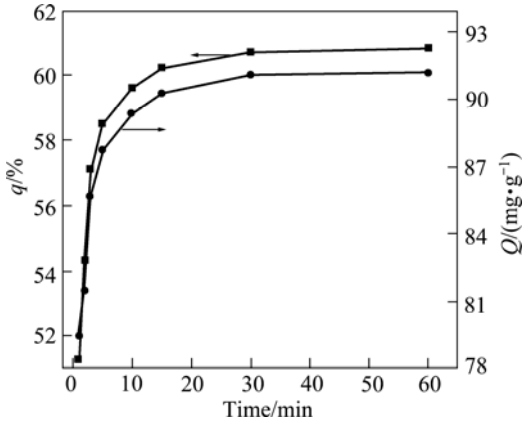

Fig. 5 Effect of adsorption time on SO_4^{2-} adsorption onto PmPD at initial solution at pH 1.75 and sulfate concentration of 2000 mg/L with 200 mg adsorbent

are shown in Figs. 6(a) and (b). And the parameters for the curves are shown in Table 2. Obviously, the pseudo second-order expression rather than the pseudo first-order kinetic model is found to fit the experimental data well. It is generally accepted that the pseudo second-order equation is used to describe the chemical adsorption, suggesting that the adsorption of sulfate onto PmPD might be mainly the chemo-sorption [3]. Evidently, the monitored kinetics of adsorption belongs to multi-step process.

3.2.4 Adsorption isotherm

Figure 7 shows the effect of initial sulfate concentration on the adsorption capability of PmPD. With the increase of initial sulfate concentration, the adsorbance increases significantly. When the initial sulfate concentration rises to 3000 mg/L, the adsorbance reaches 101.7 mg/g. However, the adsorbance increases slightly at a higher concentration. This implies that the adsorption is nearly saturated with an initial sulfate concentration more than 3000 mg/L under our experimental conditions. Nevertheless, the adsorptivity presents a contrary variation. It is noted that at a low sulfate concentration around 500 mg/L, the sulfate adsorptivity can reach more than 95 %. Even when the initial sulfate concentration reaches 1000 mg/L, the residual sulfate concentration after adsorption is just 150 mg/L, which is still far less than the maximum contaminate level of 250 mg/L of sulfate based on the Sanitary Standards for drinking water quality of China (2006).

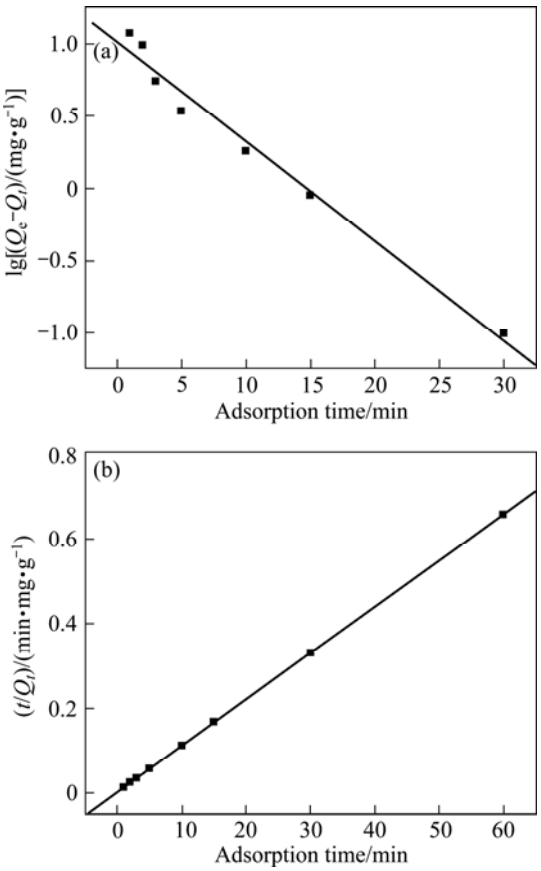

Fig. 6 Kinetics curves: (a) Pseudo first-order kinetic curve; (b) Pseudo second-order kinetic curve

To evaluate the adsorbance, the Langmuir and Freundlich models were used to analyze the sorption data. The results are shown in Figs. 8(a) and (b) and Table 3. It can be found that the Langmuir model well fits the adsorption isotherm behavior with a correlation coefficient of more than 0.999 while the correlation coefficient is just 0.965 when fitting the data with the Freundlich model. This suggests that the adsorption can be expressed better by the Langmuir model, which generally assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. The results indicate the probable monolayer adsorption of sulfate ions onto PmPD.

According to the Langmuir model, the maximum adsorbance (Q_m) of PmPD to sulfate at the initial solution pH of 1.75 is 108.5 mg/g. By comparing with similar researches [28], the adsorption value is apparently superior to most reported adsorbents.

Table 2 Kinetic model equation for sulfate ion adsorption on PmPD

Initial sulfate pH	Mathematical model	Equation	Correlation coefficient	Standard deviation	Rate constant
1.75	Pseudo first-order	$\lg(Q_e-Q_t)=-0.0688t+1.011$	0.9902	0.1096	$k=0.158\ \text{min}^{-1}$
	Pseudo second-order	$t/Q_t=0.0109t+0.00235$	1	0.0004	$h=425.5$ mg/(g·min)

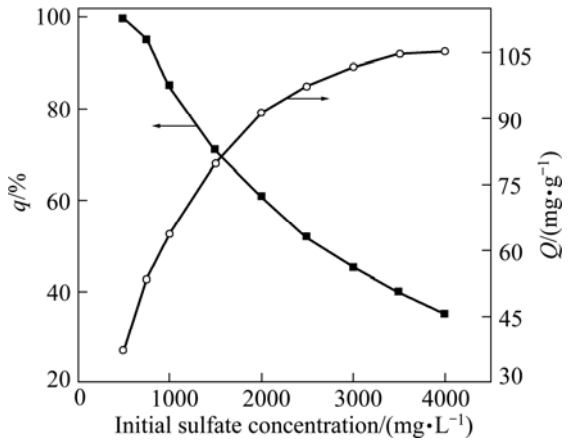

Fig. 7 Effect of initial sulfate ion concentrations on SO_4^{2-} adsorption onto PmPD at initial solution pH 1.75 with 200 mg adsorbent for 60 min

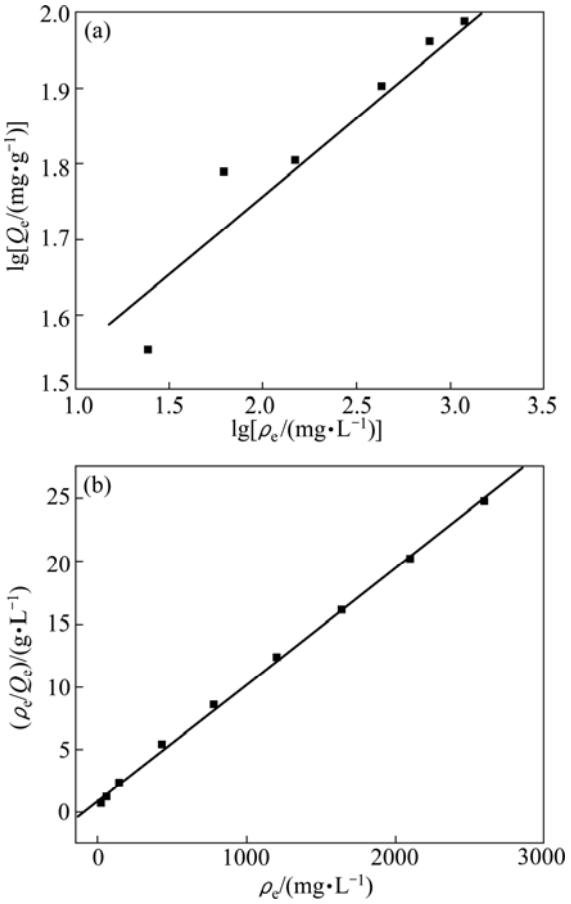

Fig. 8 Adsorption isotherms: (a) Freundlich isotherms; (b) Langmuir isotherms

Table 3 Isothermal model for sulfate ion adsorption

Model	Equation	Correlation coefficient	Standard deviation
Langmuir	$\rho_e/Q_e = 0.00922\rho_e + 0.96432$	0.99923	0.36717
Freundlich	$\lg Q_e = 0.20798\lg\rho_e + 1.34084$	0.96505	0.04350

3.3 Multi-cycle adsorption

Desorption and re-adsorption of sulfate ions onto PmPD were conducted in 5 cycles to further assess the feasibility and practicability of the adsorbent. The adsorption and desorption rate and accumulated adsorbance are shown in Fig. 9. Obviously, the adsorptivity of PmPD fluctuates in a small range (61.7%−67.9%) in 5 cycles but does not display an attenuation trend. The accumulated adsorbance after 5 cycles reached remarkably 487.95 mg/g. It should be noted that the desorptivity retained at 94.8% (94.8%, 95.6%, 95.9%, 98.1% and 96.2%, respectively, in 5 cycles) and the desorption time in this study is only 5 min.

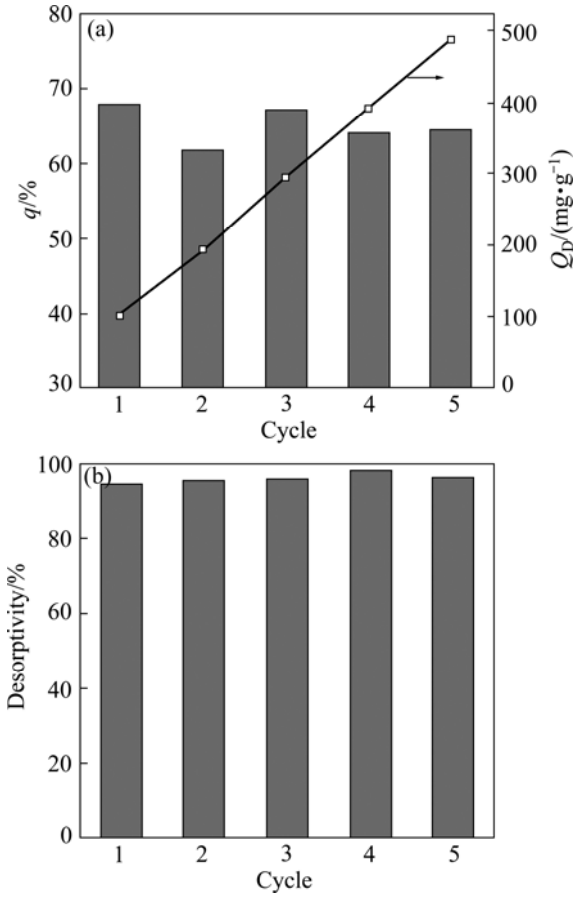

Fig. 9 SO_4^{2-} absorption and desorption in multi-cycle adsorption (sorption time of 60 min; initial SO_4^{2-} concentration of 2000 mg/L, initial solution pH value of 1.63 for every cycle, desorption time of 5 min, PmPD dosage of 200 mg. The data in the figure represent accumulative adsorbance of SO_4^{2-} on the same PmPD micro-particles.)

In sum, the synthesized PmPD particles obviously possess excellent sulfate adsorption performance in aqueous solution. The research topic needs to be investigated further in the future and the relevant research is underway.

4 Discussion

4.1 Sulfate adsorption mechanisms of PmPD

Calculation of H^+ consumption was carried out based on the solution pH variation before and after sorption processes (Fig. 10). When the sorption is conducted in the pH range of 5.5−3.0, H^+ is consumed slightly. However, the H^+ consumption becomes significant when the solution pH is in the range of 3.0−1.5. This tendency is just similar to the variation of adsorptivity and adsorbance of sulfate along the initial solution pH (Fig. 3), demonstrating that H^+ participates in the adsorption processes. It is widely accepted that the N-containing groups in aromatic amine or diamine polymers including PmPD can be protonated in acidic media and then attract the anions [29]. Consequently, the low solution pH benefits the sulfate adsorption of PmPD. Meanwhile, PmPD still possesses relatively weak adsorbability (Fig. 3), especially when the solution pH is higher than 7.0. This might be due to the function of physical adsorption.

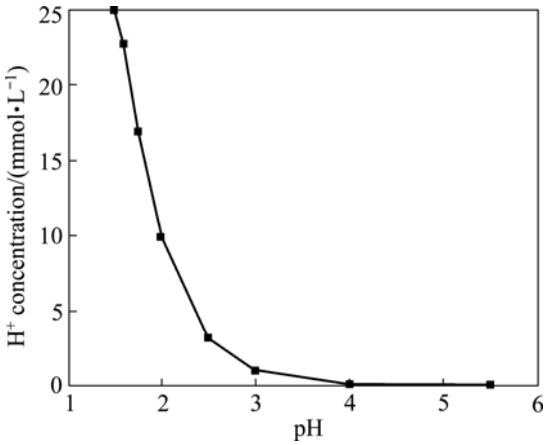

Fig. 10 Decrement values of H^+ concentration before and after adsorption at different initial solution pH values

XPS (Fig. 11) and FTIR (Fig. 12) were further applied to analyzing the adsorption process. As seen in Fig. 11, the XPS N 1s spectrum of PmPD before adsorption can be fitted into two peaks located at 398.9 eV and 399.9 eV. As to aromatic amine and diamine polymers, the N 1s binding energies at <399 eV, 399−400 eV and >400 eV commonly represent the imine, amine and protonated N atom, respectively [30]. Hence, the peak at 398.9 eV suggests the imine while that at 399.9 eV indicates the amine. After adsorbing sulfate ions, a new peak is observed at 401 eV which is related to the protonated imine. But protonated amine cannot be found based on XPS. Meanwhile, the ratio of the peak area for amine to the whole area before and after adsorption is nearly the same (~53 %). As a

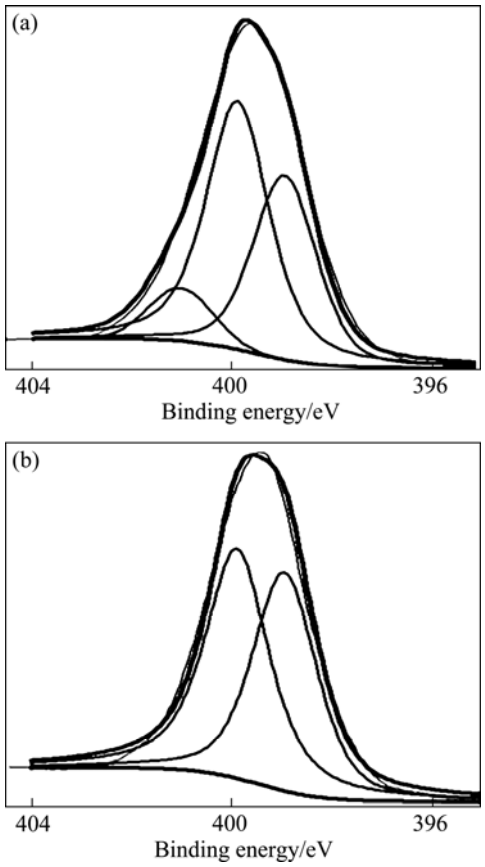

Fig. 11 XPS N 1s core-level spectra of PmPD after (a) and before (b) adsorption

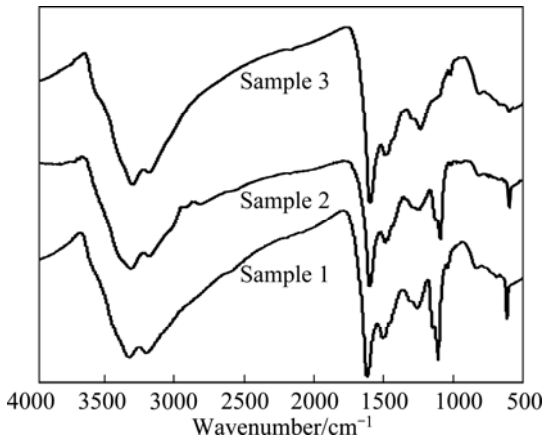

Fig. 12 FTIR spectra of PmPD adsorbed SO_4^{2-} at different initial solution pH values (spectra of samples 1−3 at pH values of 1.5, 1.75, and 5.5, respectively)

consequence, it demonstrated that imine groups may be changed into protonated imines during the adsorption of sulfate ions. What's more, the FTIR spectra were also given to investigate the variation of macromolecular structures of PmPD after adsorption. As shown in Fig. 12 for all spectra, two adsorption peaks at 1110 cm^{-1} and 617 cm^{-1} emerge, demonstrating the existence of sulfate ions on PmPD [31]. With decreasing the sulfate solution

pH, the intensities of these two peaks enhance distinctly. This indicates higher performance of PmPD in stronger acidic conditions. And it can also be observed that the relative intensity of benzenoid rings in comparison with quinoid rings increased obviously with decreasing the adsorption solution pH. This means that the protonation of the imine in acidic conditions possibly turns the quinoid rings into benzenoid rings, which is similar to polyaniline [32].

Based on the analysis of XPS and FTIR, the process can be depicted as follows:

1) As soon as PmPD solid powders were added, H^+ rapidly attacks the electron pair of N atom in imine groups to form the protonated imines;

2) The interaction of H^+ and imine groups induces quinoid rings to change to benzenoid rings while the anions were attracted to neutralize the protonated polymers. The detail is illustrated in Fig. 13.

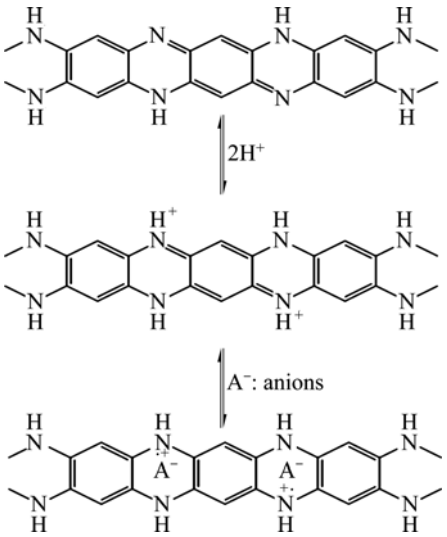

Fig. 13 Protonation and sulfate adsorption process of PmPD

4.2 Oxidation state/adsorption performance relationship studied by energy calculation

Although the imine groups are involved directly in the adsorption process, PmPD in the higher oxidation state which possesses more imine groups has relatively poor adsorption performance. To explain this phenomenon, a minimized energy calculation with the aid of MM2 function (Minimize Energy) of ChemOffice 2010 was employed. Oligomers with identical chain length in two different oxidation states were used as representative to investigate their energy status in protonated and deprotonated states. The structure of *m*-phenylenediamine oligomers is drawn according to report in Ref. [33], but we supposed that the denitrogenation did not happen. Oligomer-A and B have the same chain length. But oligomer-A in low oxidation state contains two quinoid imine units while oligomer-B in high oxidation state contains six quinoid imine units.

The calculation results are given in Fig. 14. The minimized energy values of oligomer-A and -B are 23.657 and 753.269 kJ/mol, respectively. The data indicate that oligomer-B is in a relatively unstable state as compared with oligomer-A. When the two quinoid imine units of oligomer-A are protonated, its minimized energy rapidly rises to 781.029 kJ/mol. However, when oligomer-B undergoes the same protonated level as that of oligomer-A, the energy skyrockets to 1535.562 kJ/mol, suggesting that oligomer-B is transformed into a high-energy, much more unstable form. Generally, the compound in a high energy state tends to transform into a stable state. Thus, compared with oligomer-A, the protonated oligomer-B exists in high unstable state and tends to return to the de-protonated state. It is strongly indicative that PmPD in higher oxidation state is in a relatively low protonation level during the adsorption while the one in low oxidation state can be protonated in a relatively high level. Consequently, PmPD in lower oxidation state in this situation may possess better sulfate adsorption for its decreased protonation energy level. These theoretical findings are in accordance with the experimental results. Further research is deserved to make clear the detailed mechanism for the sulfate adsorption of PmPD.

5 Conclusions

1) PmPD particles in various oxidation states were synthesized facilely through chemical oxidation polymerization. Increasing the oxidant/monomer mole ratio enhances the yields and oxidation states of PmPD. Nevertheless, high initial polymerization pH is beneficial to lower oxidation states of PmPD and maintain a good yield. PmPD particles in lower oxidation state exhibits better sulfate adsorption performance in aqueous solution.

2) The adsorption data of sulfate are well fitted with the Langmuir isotherm with the adsorbance of PmPD 108.5 mg/g. The sorption process follows the pseudo second-order kinetics, and a very rapid initial sorption rate of 425.5 mg/(g·min) is obtained. The loaded micro-particles can be easily regenerated with desorptivity of ~95% and reused without performance degradation. Accumulative adsorbance is up to 487.95 mg/g after 5 sorption-desorption cycles.

3) The sulfate adsorption of PmPD in acid solution must go through the protonation of imine groups and then induces quinoid imine units to change to protonated benzenoid amine. The sulfate anions can be attracted accordingly to neutralize the protonated polymers. While physical surface adsorption dominates when the sulfate solution is mildly acidic or neutral.

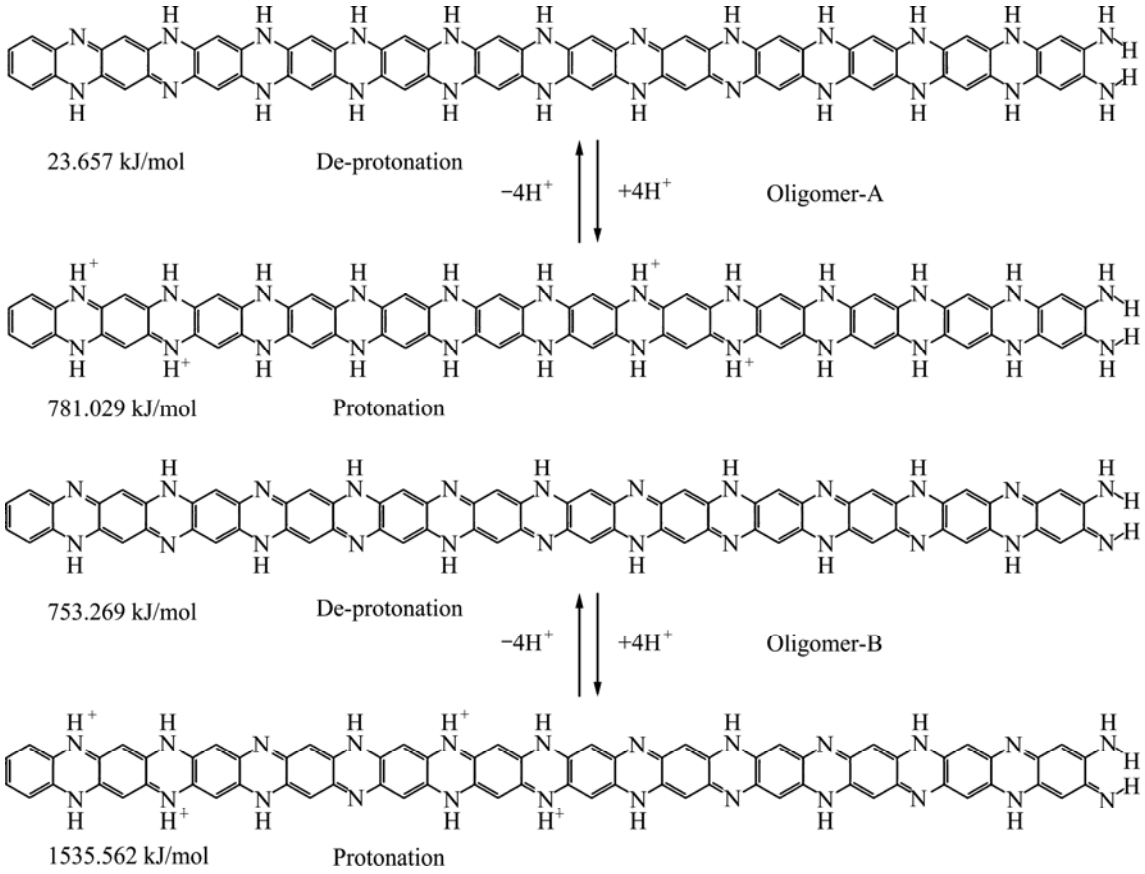

Fig. 14 Minimum energies and protonated energies of amine in molecular structure in different oxidation states

4) The minimum energy calculation proved that protonated PmPD in higher oxidation state tends to be in a higher unstable level. Consequently, PmPD in relatively low oxidation state bearing less imine groups may exhibit a better sulfate adsorption performance.

References

[1] MACDIARMID A G, ZHOU Y, FENG J. Oligomers and isomers: New horizons in poly-anilines [J]. Synthetic Metals, 1999, 100(1): 131−140.

[2] ZHANG L Y, CHAI L Y, LIU J, WANG H Y, YU W T, SANG P L. pH manipulation: A facile method for lowering oxidation state and keeping good yield of poly(*m*-phenylenediamine) and its powerful Ag^+ adsorption ability [J]. Langmuir, 2011, 27(22): 13729−13738.

[3] HUANG M R, LU H J, LI X G. Efficient multicyclic sorption and desorption of lead ions on facilely prepared poly(*m*-phenylenediamine) particles with extremely strong chemoresistance [J]. Journal of Colloid and Interface Science, 2007, 313(1): 72−79.

[4] REMYA DEVI P S, KUMAR S, VERMA R, SUDERSANAN M. Sorption of mercury on chemically synthesized polyaniline [J]. Journal of Radioanalytical and Nuclear Chemistry, 2006, 269(1): 217−222.

[5] RODRIGUEZ F J, RREZ S G, IBANEZ J G, BRAVO J L, BATINA N. The efficiency of toxic chromate reduction by a conducting polymer (polypyrrole): Influence of electropolymerization conditions [J]. Environmental Science and Technology, 2000, 34(10): 2018−2023.

[6] LI X G, HUANG M R, LI S X. Facile synthesis of poly(1,8-diaminonaphthalene) microparticles with a very high silver-ion adsorbability by a chemical oxidative polymerization [J]. Acta Materialia, 2004, 52(18): 5363−5374.

[7] HUANG M R, RAO X W, LI X G. Lead ion-selective electrodes based on polyphenylenediamine as unique solid ionophores [J]. Talanta, 2011, 85: 1575−1584.

[8] LU Q F, HUANG M R, LI X G. Synthesis and heavy-metal-ion sorption of pure sulfophenylenediamine copolymer nanoparticles with intrinsic conductivity and stability [J]. Chemistry A European Journal, 2007, 13(21): 6009−6018.

[9] MOHAN D, PITTMAN C U Jr. Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water [J]. Journal of Hazardous Materials, 2006, 137(2): 762−811.

[10] KARTHIKEYAN M, SATHEESHKUMAR K K, ELANGO K P. Conducting polymer/alumina composites as viable adsorbents for the removal of fluoride ions from aqueous solution [J]. Journal of Fluorine Chemistry, 2009, 130(10): 894−901.

[11] MAREE J P, GREBEN H A, BEER M. Treatment of acid and sulphate-rich effluents in an integrated biological/chemical process [J]. Water SA, 2004, 30(3): 183−189.

[12] BENATTI C T, TAVARES C R G, LENZI E. Sulfate removal from waste chemicals by precipitation [J]. Journal of Environmental Management, 2009, 90(1): 504−511.

[13] TAIT S, CLARKEB W P, KELLER J, BATSTONEA D J. Removal of sulfate from high-strength wastewater by crystallization [J]. Water Research, 2009, 43(3): 762−772.

[14] BASHA C A, SELVI S J, RAMASAMY E, CHELLAMMAL S. Removal of arsenic and sulphate from the copper smelting industrial effluent [J]. Chemical Engineering Journal, 2008, 141(1−3): 89−98.

[15] LEE H J, OH S J, MOON S H. Recovery of ammonium sulfate from fermentation waste by electrodialysis [J]. Water Research, 2003,

37(5): 1091−1099.
[16] GALIANA-ALEIXANDRE M V, IBORRA-CLAR A, BES-PIFI A, MENDOZA-ROCA J A, CUARTAS-URIBE B, IBORRA-CLAR M I. Nanofiltration for sulfate removal and water reuse of the pickling and tanning processes in a tannery [J]. Desalination, 2005, 179(1−3): 307−313.
[17] BÓDALO A, GÓMEZ J L, GÓMEZ E, LEÓN G, TEJERA M. Reduction of sulphate content in aqueous solutions by reverseosmosis using cellulose acetate membranes [J]. Desalination, 2004, 162: 55−60.
[18] LI E P, MIN X B, SHU Y D, YANG S H, CHAI L Y. Treatment of wastewater containing zinc and sulfate ion in immobilized beads of SRB sludge with inner cohesive carbon source [J]. Journal of Central South University: Science and Technology, 2011, 42(6): 1522−1527. (in Chinese)
[19] ZHANG L Y, CHAI L Y, WANG H Y, LIU Q, TAN X B. Synthesis of polyamine macromolecule PED and its adsorption in sulfate wastewater [J]. Journal of Central South University: Science and Technology, 2010, 41(2): 422−427. (in Chinese)
[20] ZHAO F, RAHUNEN N, VARCOE J R, CHANDRA A, ROSSA C A, THUMSER A E, SLADE R C T. Activated carbon cloth as anode for sulfate removal in a microbial fuel cell [J]. Environmental Science and Technology, 2008, 42(13): 4971−4976.
[21] BOUKHALFA C. Sulfate removal from aqueous solutions by hydrous iron oxide in the presence heavy metals and competitive anions: Macroscopic and spectroscopic analyses [J]. Desalination, 2010, 250(1): 428−432.
[22] KOLICS A, POLKINGHORNE J C, WIECKOWSKI A. Adsorption of sulfate and chloride ions on Aluminum [J]. Electrochimica Acta, 1998, 43(18): 2605−2618.
[23] SAG Y, AKTAY Y. Mass transfer and equilibrium studies for the sorption of chromium ions onto chitin [J]. Process Biochemistry, 2000, 36(1−2): 157−173.
[24] LI X G, DUAN W, HUANG M R, YANG Y L, ZHAO D Y. Preparation and solubility of a partial ladder copolymer from p-phenylenediamine and o-phenetidine [J]. Polymer, 2003, 44(20): 6273−6285.
[25] CHAI L Y, ZHANG L Y, WANG H Y, YU W T, SANG P L. An effective and scale-up self-assembly route to prepare the rigid and smooth oligo(*o*-phenylenediamine) microfibers in acidic solution by $NaClO_2$ [J]. Materials Letters, 2010, 64(21): 2302−2305.
[26] ZHANG L Y, CHAI L Y, WANG H Y, YANG Z H. Facile synthesis of one-dimensional self-assembly oligo(*o*-phenylenediamine) materials by ammonium persulfate in acidic solution [J]. Materials Letters, 2010, 64(10): 1193−1196.
[27] LI X G, HUANG M R, DUAN W. Novel multifunctional polymers from aromatic diamines by oxidative polymerizations [J]. Chemical Reviews, 2002, 102(9): 2925−3030.
[28] NAMASIVAYAM C, SANGEETHA D. Application of coconut coir pith for the removal of sulfate and other anions from water [J]. Desalination, 2008, 219(1−3): 1−13.
[29] MAHANTA D, MADRAS G, VRADHAKRISHNAN S, PATIL S. Adsorption of sulfonated dyes by polyaniline emeraldine salt and its kinetics [J]. The Journal of Physical Chemistry B, 2008, 112(33): 10153−10157.
[30] HAN J, DAI J, GUO R. Highly efficient adsorbents of poly(*o*-phenylenediamine) solid and hollow sub-microspheres towards lead ions: A comparative study [J]. Journal of Colloid and Interface Science, 2011, 356: 749−756.
[31] BLINOVA N V, STEJSKAL J, TRCHOVÁ M, PROKEŠ J, OMASTOVÁ M. Polyaniline and polypyrrole: A comparative study of the preparation [J]. European Polymer Journal, 2007, 43: 2331−2341.
[32] AYAD M M, ZAKI E A. Doping of polyaniline films with organic sulfonic acids in aqueous media and the effect of water on these doped films [J]. European Polymer Journal, 2008, 44: 3741−3747.
[33] HUANG M R, PENG Q Y, LI X G. Rapid and effective adsorption of lead ions on fine poly(phenylenediamine) microparticles [J]. Chemistry A European Journal, 2006, 12: 4341−4350.

聚间苯二胺对硫酸根离子的吸附及其机理

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摘　要：通过化学氧化聚合法合成具有不同氧化态的聚间苯二胺，将其用于吸附硫酸根离子，进行一系列的吸附实验；通过 FTIR、XPS、 pH 跟踪及能量计算，研究了聚间苯二胺吸附硫酸根离子的机理，探讨了聚间苯二胺的氧化态与吸附性能之间的关系。结果表明：聚间苯二胺的氧化态越低，其对硫酸根离子的吸附性能越好。吸附在 30 min 内达到平衡，吸附速率达 425.5 mg/(g·min)；吸附率最高达到 95.1%；通过 Langmuir 等温线拟合计算出吸附量为 108.5 mg/g；解析率在 95%左右，5 次循环吸附实验的累积吸附量达 487.95 mg/g。

关键词：聚间苯二胺；硫酸根；吸附；吸附率；氧化态；解吸率

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