



Adsorption of Hg(II) from Aqueous Solutions by Two Aniline Copolymers

HUABIN YIN¹, CHAO WANG^{1,*} and QIAN YAN²

¹College of Environmental Science and Engineering, Hohai University, Nanjing 210098, P.R. China

²State Key Laboratory of Pollution Control and Resource Reuse and School of the Environment, Nanjing University, Nanjing 210093, P.R. China

*Corresponding author: Tel/Fax: +86 025 83786971; E-mail: cwang@hhu.edu.cn

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Two derivative copolymers of polyaniline, poly(aniline-co-2,4-diaminophenol) (PANDAP) and poly(aniline-co-*o*-aminophenol) (PANOA) were synthesized and used for adsorption of Hg(II) from aqueous solutions. The results show that both PANDAP and PANOA have excellent adsorption ability for Hg(II) and the sorption process follows the Langmuir model and the pseudo-second-order kinetic model well. It was found that the solution pH values had a major impact on Hg(II) adsorption by PANDAP with optimal removal observed at pH 5-7 and the maximal adsorption capacity was more than 800 mg g⁻¹ at pH 5.5. Although PANOA has a smaller maximal adsorption capacity (about 200 mg g⁻¹), its adsorption process was independent of pH and the Hg(II) removal efficiencies by PANOA were all over 90 % in a wide pH range of 3-9. The results also proved that these two adsorbents could be effectively desorbed in HCl solution (0.1 mol L⁻¹) with 0.5 % sulfocarbonide for reuse.

Key Words: Poly(aniline-co-2,4-diaminophenol), Poly(aniline-co-*o*-aminophenol), Mercury(II), Adsorption, Waste water.

INTRODUCTION

Mercury is considered as a ubiquitous global pollutant that has long been of great concern due to its persistence, bioaccumulation and toxicity (PBT) in the environment¹⁻⁵. The predominant species of atmospheric mercury is Hg⁰, which has a long residence time in the atmosphere from 0.5 to 2 years and can be transported and deposited to remote areas even 1000 km away from the source⁵. The release of mercury to atmosphere comes from both natural sources and anthropogenic activities. The major natural sources are volcanoes and geothermal activities, evasion from surface soils, water bodies, vegetation surfaces, wild fires, as well as reemission of deposited mercury⁵. However, the anthropogenic activities, such as metal mining, wastewater discharging, oil and coal combustion, refining and manufacturing, chlor-alkali production and waste incineration⁵⁻⁷, are believed to be responsible for the elevated mercury levels in the environment^{1,2}.

It is known that mercury can be converted to monomethylmercury (MMHg), one of the most toxic methylated mercury forms and biomagnified in aquatic food chain, *e.g.* fish and marine products, to high levels from very low concentrations^{1,5,8}. Approximately, mercury is concentrated a million times between water and piscivorous fish, most of which is methylmercury⁹. These mercury-accumulated fish may ultimately be consumed by human beings, leading to serious and even fatal diseases such as Minamata⁸. The main threats of mercury

poisoning to human health are known as neurological disease and renal disturbance, because mercury can easily pass the blood-brain barrier and affect the foetal brain⁷. In addition, high concentrations of Hg(II) give rise to impairment of pulmonary function, kidney and chest pains, as well as dyspnoea⁷. Accordingly, the prescribed limit for Hg(II) discharge into inland surface waters is 10 µg L⁻¹ and that for mercury in drinking water is 1 µg L⁻¹, which is the lowest among all heavy metal ions¹⁰⁻¹².

Adsorption has been widely studied among the conventional technologies for treatment of aqueous mercury including precipitation, coagulation, reduction, membrane separation or ion exchange⁸. As one of the most important conducting polymers, polyaniline (PANI) carries large amounts of nitrogen-containing groups of amine and imine types and it may have interactions with some nitrogen-affinitive metal ions¹³⁻¹⁵. The effective use of polyaniline for preconcentration and separation of mercury from waters for instrumental analysis has been proven by several researchers^{16,17}.

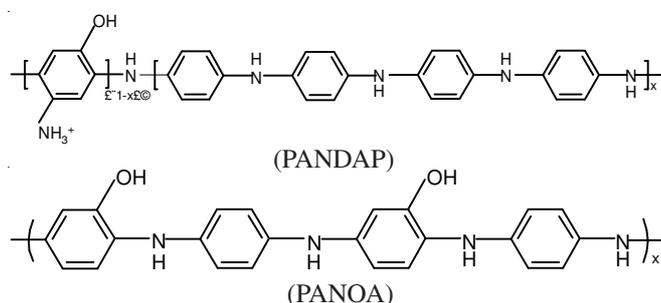
In this study, two derivatives of polyaniline, poly(aniline-co-2,4-diaminophenol) (PANDAP) and poly(aniline-co-*o*-aminophenol) (PANOA) were synthesized by chemically oxidative polymerization. The removal efficacy of aqueous Hg(II) ions was determined by batch experiments and the adsorptive kinetics as well as equilibrium isotherm modeling were carried out. And the adsorption capacity of Hg(II) onto these copolymers

was investigated as a function of pH value, ionic strength, as well as coexisted ions.

EXPERIMENTAL

2,4-Diaminophenol and *o*-aminophenol of analytical grade were purchased from Aldrich. Aniline was distilled under reduced pressure prior to use. Ammonium peroxodisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ (> 98 %)) was purchased from Fluka. Mercury nitrate monohydrate [$\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$] of ACS reagent grade was purchased from Sigma-Aldrich. All solutions were prepared with ultrapure water (18.25 M Ω cm). All other chemicals used in this study were of analytical grade.

Chemical synthesis of PANDAP and PANOA: Poly(aniline-co-2,4-diaminophenol) (PANDAP) and poly(aniline-co-*o*-aminophenol) (PANOA) were synthesized through a chemical oxidation process. Detailed processes can be represented as the following steps: (1) 0.001 mol 2,4-diaminophenol (or 0.001 mol *o*-aminophenol) and 0.02 mol freshly distilled aniline were dissolved in 100 mL of 2 mol L⁻¹ H₂SO₄. (2) 100 mL of 0.4 mol L⁻¹ (NH_4)₂S₂O₈ solution was slowly added to the mixture under vigorous stirring over a period of 5 h at room temperature. (3) After being filtered, the precipitated polymer was washed thoroughly with ultrapure water and vacuum-dried at 333 K until reaching constant weight. The resultant copolymer was powdered in a mortar and stored before used as adsorbent. SEM analyses of the samples were done by a Philips XL30 FEG scanning electron microscope. The chemical structural formula of PANDAP and PANOA are shown as follow:



Batch adsorption experiments: Each adsorption experiment was conducted in batch mode using 10 mL polyethylene bottles. 0.005 g sample was mixed with 10 mL of Hg(II) solution with the desired concentration and appropriate pH₀. HCl and NaOH were used as pH controls. For determination of the adsorption isotherm the adsorbent was added to solutions at fixed NaCl concentration. Other competing ions including Cl⁻, H₂PO₄⁻ and SO₄²⁻ were added when necessary. The mixture was shaken in an incubator shaker and vibrated at 150 rpm for 24 h to ensure the equilibrium adsorption. Preliminary experiments showed that adsorption equilibrium was completely achieved within approximately 24 h under the experimental conditions. Batch kinetic experiments were carried out at 298 K for predetermined time intervals and the concentration of 1000 mg L⁻¹ was selected as the initial concentration of Hg(II) solution.

After adsorption, the mixture was filtered with a syringe filter of 0.22 μm . The initial and the final concentration of Hg(II) in the aqueous salt solution were measured with an

atomic fluorescence spectrophotometer (AFS-610, Beijing Rayleigh Analytical Instrument Co., China). The amount of Hg(II) adsorbed by the material can be calculated using Eq. (1).

$$Q = V[(C_0 - C)]/m \quad (1)$$

where, Q is the amount of Hg(II) adsorbed (mg g⁻¹), C₀ is the initial concentration of Hg(II) solution (mg L⁻¹), C is the liquid-phase Hg(II) concentration (mg L⁻¹), m is the mass of adsorbent used (g) and V is the volume of Hg(II) solution used (L).

Desorption experiments: Hg(II)-laden samples were placed in 25 mL of (A) a NaOH solution; (B) a NH₄OH solution and (C) a HCl solution for 24 h. Each kind of eluant was tested for three concentrations (0.2 mol L⁻¹, 1.0 mol L⁻¹ and 2.0 mol L⁻¹). After shaking, the suspension was filtered and the Hg(II) concentration was analyzed as described.

RESULTS AND DISCUSSION

Morphologies of PANDAP and PANOA: The SEM images of poly(aniline-co-2,4-diaminophenol) (PANDAP) and poly(aniline-co-*o*-aminophenol) (PANOA) are presented in Fig. 1a and b, respectively. It can be seen that these two copolymers have similar complex and porous surface texture and porosity. Meanwhile, the SEM micrographs of both copolymers reveal the presence of agglomerated spherical particles. The porous structures may result from the bridging linkage between aniline monomers and *o*-aminophenol (or 2,4-diaminophenol) through copolymerization, which may generate new binding sites in interior walls of the micropores and contribute to homogeneous Hg binding.

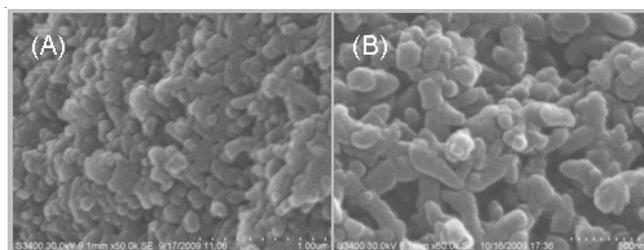


Fig. 1. SEM images of (A) poly(aniline-co-2,4-diaminophenol) (PANDAP); (B) poly(aniline-co-*o*-aminophenol) (PANOA)

Amount of adsorbent: The effect of adsorbent dose on the adsorption efficiency of Hg(II) by these two adsorbents was studied. The amount of adsorbent significantly affected the extent of Hg(II) adsorption as illustrated in Fig. 2. In the case of PANOA, the removal rate of Hg(II) was found to be 46.1 % for 0.1 g L⁻¹ which increased to 86.9 % for 0.25 g L⁻¹. PANDAP presents a higher removal rate compared to PANOA, with 66.7 % of Hg(II) removed at 0.1 g L⁻¹ which increased to 98.6 % at 0.25 g L⁻¹. Further increasing the adsorbent dosage leads to no significant change in the removal rate of Hg(II) adsorption for both adsorbents. Meanwhile, it can be seen that low adsorbent dosage results in a high Q_e value, possibly due to the fact that all adsorbent sites are completely occupied and the surface is saturated. PANDAP shows a much higher Hg(II) uptake capacity (329.8 mg g⁻¹) that PANOA (230.5 mg g⁻¹), indicating it may play a favourite role in Hg(II) removal from aqueous solutions.

Effect of initial pH: The pH of the aqueous solution is an important parameter in the adsorption process as the targeted

ions usually exists as different species at varied pH values. The influence of pH of the equilibrium suspension on adsorption capacity of Hg(II) using both PANDAP and PANOA was therefore studied, within the pH range of 3-10 (Fig. 3). It was obvious that quite different results were obtained for the two adsorbents. The adsorption capacity of PANDAP increased with increasing equilibrium pH and reached maximum adsorption around an equilibrium pH value of 5.5. Adsorption then decreased slowly with further increasing the pH to 10.0. However, in case of PANOA, the Hg(II) adsorption process was independent of solution pH, although the maximum adsorption capacity was much lower (about 160 mg g⁻¹). Such interesting properties are very attractive because it is crucial to wastewater treatment process, where no need of pH adjustment would be favourable. However, further study is still required to clearly reveal the underlying mechanism.

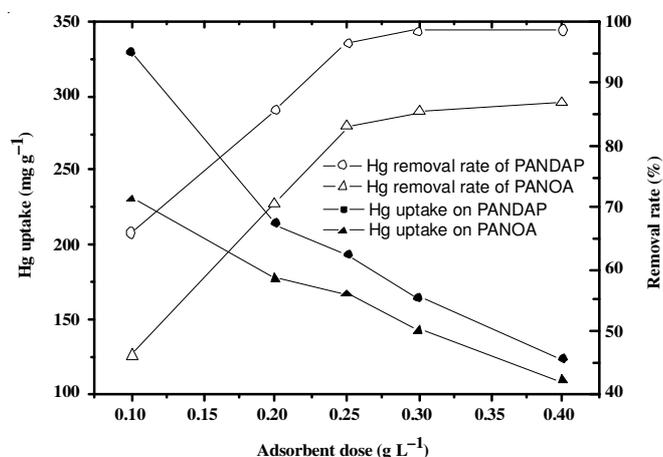


Fig. 2. Adsorption of Hg(II) on PANDAP and PANOA as a function of adsorbent dosage ($C_0 = 50 \text{ mg L}^{-1}$, $I = 0.1 \text{ mol L}^{-1} \text{ NaNO}_3$, $T = 298 \text{ K}$, $\text{pH} = 5.5$, $t = 1440 \text{ min}$)

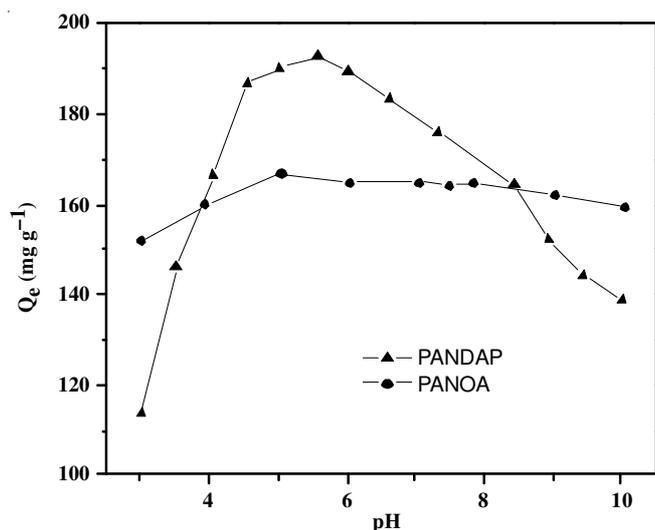


Fig. 3. Effect of initial pH on the adsorption of Hg(II) by both PANDAP and PANOA ($C_0 = 50 \text{ mg L}^{-1}$, $I = 0.1 \text{ mol L}^{-1} \text{ NaNO}_3$, sorbent dosage = 2.5 g L^{-1} , $T = 298 \text{ K}$, $t = 1440 \text{ min}$)

Sorption isotherms and influence of ionic strength: Fig. 4 shows the influence of C_0 on the adsorption capacities of the two adsorbents for Hg(II) at different levels of ionic strengths (0.01, 0.10 and 1.00 mol L⁻¹ NaNO₃). As illustrated in Fig. 4A,

the maximum uptake capacities for PANDAP at 0.01, 0.10 and 1.00 mol L⁻¹ ionic strengths were about 814, 748 and 728 mg g⁻¹, respectively, while that for PANOA (Fig. 4B) were about 224, 188 and 165 mg g⁻¹.

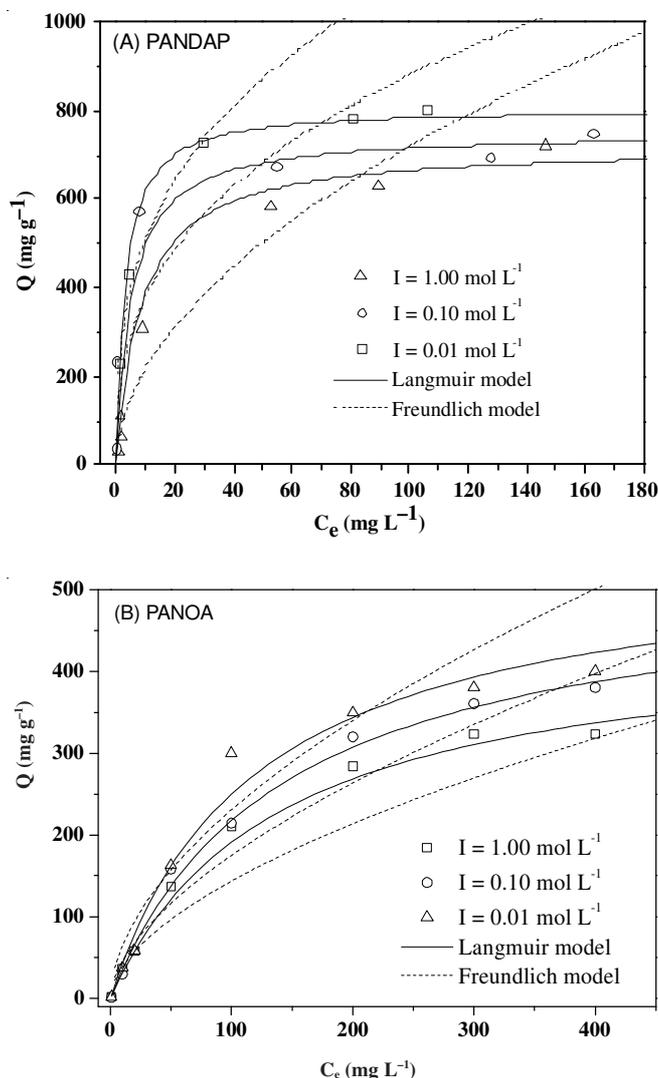


Fig. 4. Sorption isotherms of Hg(II) adsorbed by (A) PANDAP and (B) PANOA at three levels of ionic strength: a 0.01 mol L⁻¹, b 0.10 mol L⁻¹ and c 1.00 mol L⁻¹ NaNO₃ (sorbent dosage = 2.5 g L^{-1} , $T = 298 \text{ K}$, $\text{pH} = 5.5$.)

Both the Langmuir¹⁸ and the Freundlich¹⁹ equations were used to describe the adsorption isotherms of Hg(II) by the adsorbents, which are expressed as follows (Eqs. 2 and 3):

The Langmuir model:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

The Freundlich model:

$$Q_e = K_F C_e^{1/n} \quad (3)$$

where, C_e (mg L⁻¹) is the equilibrium concentration of Hg(II), Q_e (mg g⁻¹) is the amount adsorbed under equilibrium, Q_m (mg g⁻¹) is the theoretical maximum adsorption capacity of the adsorbent for Hg(II) and K_L (L mg⁻¹) is a Langmuir binding constant related to the energy of adsorption, K_F and n are the Freundlich empirical constants.

TABLE-1
COMPARISON OF CORRELATION COEFFICIENTS OF THE LANGMUIR AND FREUNDLICH ISOTHERMS
FOR Hg(II) ADSORPTION ONTO PANDAP AND PANOA AT DIFFERENT IONIC STRENGTH

Samples	Langmuir model				Freundlich model		
	I (mol L ⁻¹)	Q _m (mg g ⁻¹)	K _L (L g ⁻¹)	R ²	K _F	n	R ²
PANDAP	0.01	617.27	0.119	0.971	66.16	1.93	0.943
	0.10	705.32	0.177	0.979	162.94	3.03	0.646
	1.00	806.45	0.329	0.998	237.60	3.01	0.917
PANOA	0.01	245.70	0.0062	0.983	17.62	1.790	0.945
	0.10	212.31	0.0044	0.986	11.47	1.688	0.946
	1.00	167.20	0.0057	0.973	10.17	1.740	0.954

TABLE-2
PARAMETERS AND CORRELATION COEFFICIENTS OF TWO KINETICS MODELS
FOR Hg(II) ADSORPTION ONTO PANDAP AND PANOA

Samples	Q _e (exp ^a) (mg g ⁻¹)	Pseudo-first-order			Pseudo-second-order		
		k ₁ (min ⁻¹)	Q _e (cal ^b) (mg g ⁻¹)	R ²	k ₂ (g mg ⁻¹ min ⁻¹)	Q _e (cal ^b) (mg g ⁻¹)	R ²
PANDAP	192.4	0.012	100.5	0.963	6.76×10 ⁻⁴	196.1	0.998
PANOA	165.5	0.050	40.0	0.913	4.22×10 ⁻⁴	164.2	0.997

a. exp, experimental data. b. cal, calculation data

Fig. 4A and 4B also present the Langmuir and Freundlich plots for the adsorption of Hg(II) onto the adsorbents at different ionic strength levels. The parameters obtained from adsorption isotherms for different ionic strengths by polyaniline/ATP composite are shown in Table-1. It is obvious that Langmuir isotherm correlated better than the Freundlich isotherm with the experimental data from adsorption equilibrium of Hg(II) for both PANDAP and PANOA. This may be due to a homogeneous distribution of active sites on the adsorbent surface. According to Table-1, the theoretical maximum adsorption capacity of Hg(II) on PANDAP at 0.01, 0.10 and 1.00 mol L⁻¹ ionic strengths were about 617, 705 and 806 mg g⁻¹, respectively, while that for PANDAP were about 246, 212 and 167 mg g⁻¹. These results suggests that the ionic strength has major effect on the adsorption capacity of Hg(II). It is well documented that high Hg(II) adsorptive capacity of nitrogen-rich adsorbents was accomplished by strong Hg-binding to imine (-NH⁺-) functional groups on the adsorbent surface. The imine (-NH⁺-) groups were deprotonated and switched to nitride (-N=) and -N= groups formed a complex with Hg(II) through coordination. When the concentration of sodium nitrate increases in the solution, the deprotonation of imine (-NH⁺-) groups were inhibited because nitrate ions could adsorb onto imine groups through electrostatic adsorption, leading to less active sites for Hg(II).

Kinetic studies: Fig. 5 shows the effect of contact time on the adsorption capacity of PANDAP and PANOA for Hg(II). The adsorption behaviour of the two adsorbents was similar with a rapid initial uptake and a subsequent stable stage. Obviously, the Hg(II) adsorption rates on the adsorbents were fast and the adsorption equilibrium can be reached within about 1 h as shown in the inset. It could also be noted that the equilibrium adsorption capacity of Hg(II) by PANDAP achieved about 250 mg g⁻¹, much higher than that for PANOA and this result is also consistent with the results obtained above.

Several kinetic models can be used to describe the adsorption kinetics. In this study, pseudo-first-order and pseudo-second-order kinetic equations were used to test the

experimental data. The corresponding linear equations are given below.

The pseudo-first order kinetic model:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (4)$$

The pseudo-second order kinetic model:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

where, Q_e and Q_t are the amount of Hg(II) adsorbed at equilibrium and time t (mg g⁻¹), respectively. k₁ is the equilibrium rate constant of the pseudo-first order adsorption (min⁻¹), which is determined from the slope of plot of ln(Q_e-Q_t) versus t (Fig. 6A). k₂ is the equilibrium rate constant of the pseudo-second order adsorption (g mg⁻¹ min⁻¹), which is similarly determined from the slope of plot of t/Q_t versus t (Fig. 6B).

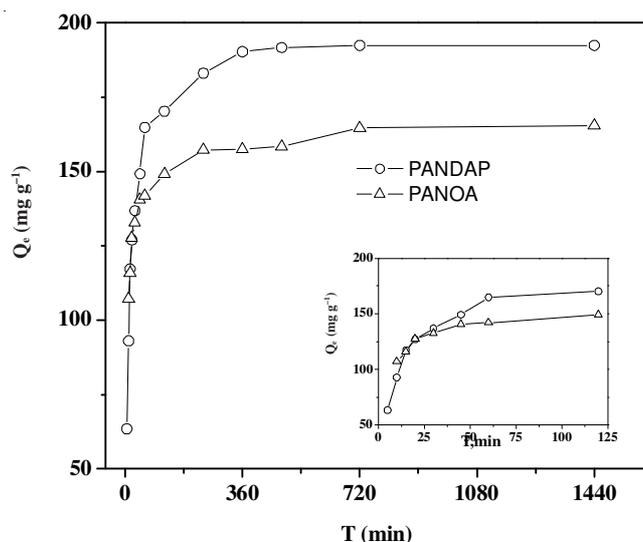


Fig. 5. Adsorption of Hg(II) by both PANDAP and PANOA as a function of contact time. (C₀ = 50 mg L⁻¹, I = 0.1 mol L⁻¹ NaNO₃, sorbent dosage = 2.5 g L⁻¹, T = 298 K, pH = 5.5)

All the corresponding parameters obtained from the linear plots were listed in Table-2. From Table-2, it can be seen

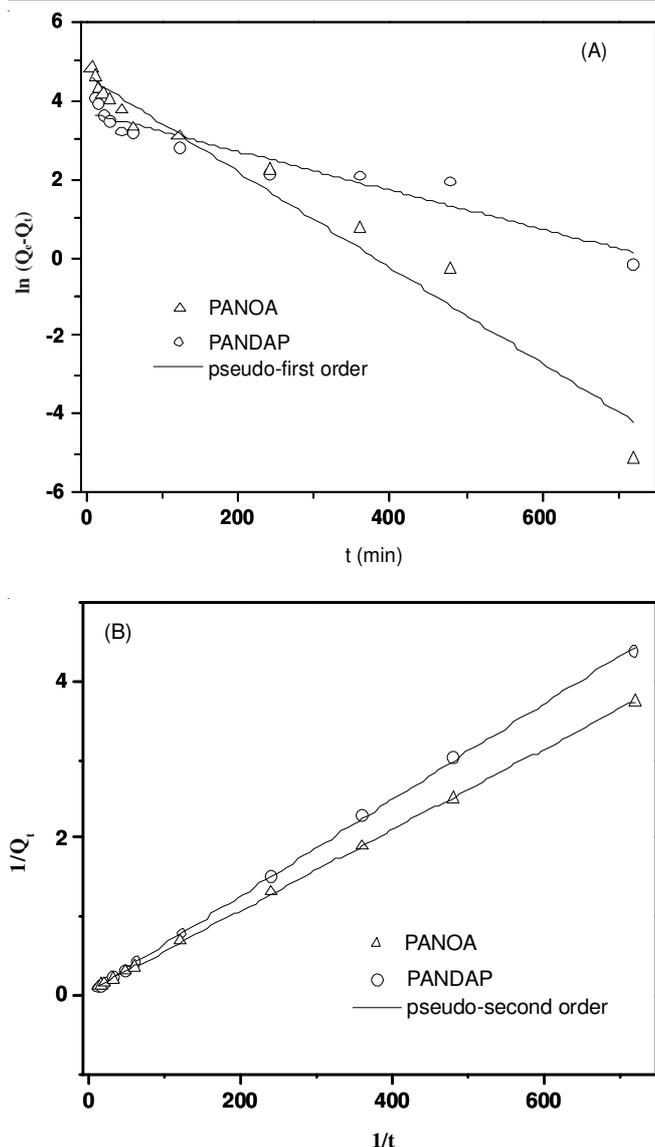


Fig. 6. (A) Pseudo-first-order plots for Hg(II) adsorption by both PANDAP and PANOA and (B) Pseudo-second-order plots for Hg(II) adsorption by both PANDAP and PANOA ($C_0 = 50 \text{ mg L}^{-1}$, $I = 0.1$)

that the linear correlation coefficients (R^2) for the pseudo-first order kinetic model are low and there are large differences between the experimental Q_e values ($Q_{e, \text{exp}}$) and the calculated Q_e values ($Q_{e, \text{cal}}$). However, the R^2 for the pseudo-second order kinetic model are all over 0.99, moreover, the $Q_{e, \text{cal}}$ values for the pseudo-second order kinetic model are all consistent with the $Q_{e, \text{exp}}$ values. These results suggest that for both PANDAP and PANOA, the adsorption processes of Hg(II) can be well described by the pseudo-second order kinetic model and that the chemical adsorption is the rate-controlling step.

Influence of coexisted anions: Generally, the presence of environmental friendly anions such as Cl^- , H_2PO_4^- and SO_4^{2-} have an effect on metal adsorption. They sometimes strongly compete with the toxic metals for active sites of a given adsorbent. In this part, the influence of the coexisted anions was investigated for the adsorption of Hg(II) by PANDAP and PANOA. The results are illustrated in Fig. 7A and B. It can be seen that H_2PO_4^- and SO_4^{2-} do not pose any significant effect

on Hg(II) retention in the test concentration ranges, whereas the Cl^- results in an obvious decrease in Hg(II) adsorption onto both adsorbents. For PANDAP, the capacity approaches to below 25 mg g^{-1} with the increasing concentrations of Cl^- ions. As for PANOA, increasing Cl^- from 5 to 10 mM leads to an obvious drop of its adsorption from 120 to 85-90 mg g^{-1} and further increase in Cl^- concentration does not result in obvious capacity decrease. The possible factor for this phenomenon is the fact that Cl^- could change the species distribution of Hg(II) forming Hg-Cl complexes, which have less affinity to the imine functional groups, causing Hg(II) removal to be substantially decreased.

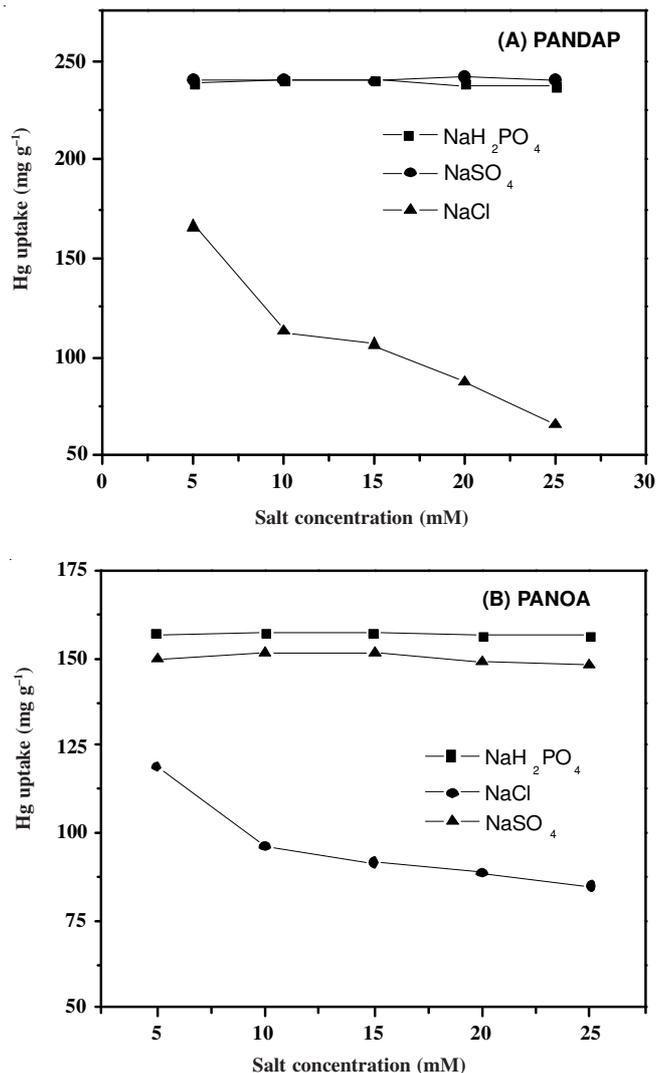


Fig. 7. Effect of coexisted anions (chloride, sulfate, phosphate with the concentration ranges of 5-25 mmol L^{-1}) on Hg(II) removal by (A) PANDAP and (B) PANOA ($C_0 = 50 \text{ mg L}^{-1}$, $I = 0.1 \text{ mol L}^{-1} \text{ NaNO}_3$, sorbent dosage = 2.5 g L^{-1} , $T = 298 \text{ K}$, $\text{pH} = 5.5$)

Conclusion

Two copolymers poly (aniline-co-2,4-diaminophenol) (PANDAP) and poly (aniline-co-*o*-aminophenol) (PANOA) were synthesized, characterized and examined as adsorbents of Hg(II). For both PANDAP and PANOA, the adsorption of Hg(II) is a chemisorption and the imine functional groups on the adsorbent surface was involved in the adsorption processes

through complex formation with Hg(II) in aqueous solutions. Both adsorption processes follow the Langmuir model and the pseudo-second-order kinetic model well, although ionic strength had a significant effect on their adsorption capacity. The PANDAP exhibited higher uptake properties of Hg(II) than those of PANOA, with the maximum adsorption capacity of more than 800 mg g⁻¹ at pH 5.5. However, PANOA presents an efficient Hg(II) removal (>90 %) in a wide pH range of 3-9, while Hg(II) removal efficiencies by PANDAP were relatively pH independent. As far as competing anions are concerned, the adsorption capacities of the adsorbents were affected by Cl⁻ only in all the coexisted anions. These results suggests that PANDAP and PANOA may be used as novel type, fast-responsive and selective adsorbent material for Hg(II). Further work is still required to provide strong evidence for the adsorption mechanism.

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