



High efficient removal of mercury from aqueous solution by polyaniline/humic acid nanocomposite

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ABSTRACT

A composite sorbent PANI/HA was prepared by adding humic acid (HA) into chemical oxidation process of polyaniline (PANI). The sorbent was characterized by BET analysis, transmission electron microscopy, and FT-IR spectra. Batch adsorption results showed that the sorbent had high affinity to Hg(II) in aqueous solutions. The adsorption kinetics results of Hg(II) showed that the adsorption reached equilibrium within 200 min and adsorption rates could be described by pseudo-second-order kinetics. Sorption of Hg(II) to PANI/HA agreed well to the Langmuir adsorption model at different ionic strengths with the maximum adsorption capacity of 671 mg g^{-1} ($I = 0.20 \text{ M}$). The experimental results showed solution pH values had a major impact on Hg(II) adsorption and with the help of HA the sorbent can effectively remove Hg(II) in a wide pH range (pH 4–7.5). An adsorption mechanism was proposed based on the XPS results.

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1. Introduction

Mercury is considered as one of the most toxic heavy metals in both atmospheric and aqueous systems because of its bioaccumulation in the food chain [1]. Exposure to mercury leads to different toxic effects in human bodies, such as dyspnoea, chest pain and cell damage [2,3]. Water contamination of mercury arises from various ways including electrical and electronics manufacturing plants, chloro-alkali plants, sulfide ore roasting operations and battery industries [4,5]. Therefore, effective treatment of the wastewater containing mercury is very important.

The conventional methods for treatment of mercury ions include chemical precipitation, ion exchange, solvent extraction and adsorption [6–11]. Relatively, adsorption is considered to be an effective and economical method to removal mercury ions. Different types of adsorbents have been proposed including active carbon [12,13], ferromagnetic materials [14–16], polymer [17] and biosorbents [18–20].

Conducting polymers such as polyaniline have been used in many fields including corrosion protection, secondary rechargeable batteries, sensors and controlled drug delivery [21–24]. Polyaniline is a promising conducting polymer because of its good combination of properties, stability, price, ease of synthesis and treatment, etc. Recently, PANI has been used as base material for the adsorption of mercury. Gupta et al. reported that the polyaniline/polystyrene composite can remove mercury ions from aqueous solutions [25].

Karunasagar et al. reported the preconcentration and speciation of organic and methyl mercury in waters using polyaniline and gold trap-CVAAS [17]. However, bare PANI particles are easily aggregated in aqueous solutions. The adsorption of natural organic matters such as humic and fulvic acids (HA and FA), and their effects on the surface charge and the colloidal stability of iron oxide particles have been examined in several papers [26–29]. Considering the high complex capacity with heavy metal ions, HA was applied to remove heavy metal ions from water.

The primary aim of this work is to present the results of a laboratory study focused on efforts to remove mercury ions in aqueous solutions via HA modified PANI nanocomposite. The physical and chemical characterization of the synthesized PANI/HA nanocomposite was conducted. The applicability of PANI/HA in mercury ions adsorption was evaluated in view of the sorption kinetic and isotherm, the effects of solution pH and ionic strength, as well as coexisted ions. And a possible adsorption mechanism was proposed.

2. Experimental

2.1. Materials

Mercury nitrate monohydrate ($\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$) of ACS reagent grade was purchased from Sigma–Aldrich Chemical. Other chemicals, such as HNO_3 , NaCl were of analytical reagent grade and used as received (Nanjing Chemical Co., Nanjing, China). Aniline was distilled under reduced pressure before use. All solutions were prepared with deionized water. HNO_3 and NaOH were used to adjust the solution pH.

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2.2. Preparation of PANI/HA nanocomposite

The typical preparation procedure of the PANI/HA nanocomposite is as follows: 2.35 mL aniline monomer and 7.75 mL HCl were dissolved in 250 mL deionized water. Then 7.75 mL HCl, 0.6 g HA and 5.71 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ dissolved in 250 mL of deionized water were dropped into the above solution with stirring at room temperature. After having been stirred for about 10 h, the resulting product was separated by filtration and finally washed with deionized water until the filtrate was colorless. The resulting product was dried under dynamic vacuum at 65 °C for 24 h.

2.3. Characterization of the PANI/HA nanocomposite

The pH values of the solutions were determined by using a PB-10 pH meter (Sartorius). The FT-IR spectra of the samples were measured on a pressed pellet with KBr using a Nicolet NEXUS870 FTIR spectrometer (USA). BET surface area of PANI/HA composite was calculated from the N_2 adsorption/desorption isotherms with a Micromeritics ASAP 2010 analyzer (US). The morphology of the PANI/HA composite was observed by using a JEOL JEM-200CX Transmission electron microscopy (TEM) at an accelerating voltage of 200 kV. The spectrum of the X-ray photoelectron spectroscopy (XPS) of the sample was measured on a Thermo ESCALAB 250 spectrometer with an Al $K\alpha$ X-ray source (1486.6 eV). All binding energies were referred to C1s neutral carbon peak at 284.6 eV.

2.4. Batch experimental systems

All batch reactors were placed on a shaker at 160 rpm under controlled temperature of 24 ± 1 °C. Ionic strength was controlled at 0.20 M by NaNO_3 unless otherwise stated. An equilibrium time of 24 h was adopted in all the adsorption experiments based on a preliminary kinetic test. Batch adsorption experiments were conducted to investigate Hg(II) adsorption as a function of initial mercury concentration, aqueous pH, ionic strength, and coexisted ions. After reaching the sorption equilibrium, the mixture was filtered with a syringe filter of 0.45 μm , and the supernatant was collected and analyzed by atomic fluorescence spectrophotometer (AFS-610, Beijing Rayleigh Analytical Instrument Co., China) for mercury concentration. In all batch experiments, average values were taken from triplicate measurements with the experimental error in the range of 0.5–3%.

2.4.1. Sorption kinetics

Sorption kinetics was conducted to assess both the rate of Hg sorption and the equilibrium time required to obtain the sorption isotherm. The experiments were performed under conditions of variable pH (3–11). In each test, 20.0 mg of sorbent was weighed into a 50 mL glass bottle, followed by the addition of 40.0 mL of Hg(II) solution, resulting in a sorbent loading of 0.5 g L^{-1} . At each predetermined time point, a 5.0 mL solution was collected, filtered and analyzed for Hg(II). Adsorption kinetics was modeled using both pseudo-first-order and pseudo-second-order which is expressed as follows (Eqs. (1) and (2)):

The pseudo-first-order equation:

$$\ln(q_e - q) = \ln q_e - K_1 t \quad (1)$$

The pseudo-second-order equation:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q is the amount adsorbed at time t (min), and q_e denotes the amount adsorbed at equilibrium, both in mg g^{-1} . K_1 (min^{-1}) and

K_2 ($\text{g}(\text{mg min})^{-1}$) are the pseudo-first-order and pseudo-second-order adsorption rate constants, respectively.

2.4.2. Sorption isotherms

The adsorption isotherms were studied by varying the concentration of Hg(II) solutions with a fixed dose of adsorbent (i.e., 20.0 mg). Adsorption isotherms were modeled using both the Langmuir and the Freundlich equations which are expressed as follows (Eqs. (3) and (4)):

Langmuir:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{C_e}{q_m} \quad (3)$$

Freundlich:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where C_e is the equilibrium concentration of Hg(II) (mg L^{-1}), q_e is the amount adsorbed under equilibrium (mg g^{-1}), 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. The initial adsorption rate (h ($\text{mg}(\text{g min})^{-1}$)) can be determined from K_2 and q_e using:

$$h = K_2 q_e^2 \quad (5)$$

2.4.3. Effects of pH and ionic strength

The solution pH was controlled by HNO_3 and/or NaOH and the final pH was recorded as the equilibrium pH. Ionic strength was maintained at desired values (0.02, 0.20, 1.00 M) using NaNO_3 . Initial Hg(II) (50.0 mg L^{-1}), sorbent (20.0 mg), and temperature (24 ± 1 °C) were kept constant.

2.4.4. Coexisted ions

Effects of competing anions were examined. Competing anions included chloride, sulfate, and phosphate at the concentrations of 2.5, 5.0, 10, 20 and 30 mM, while initial Hg(II) concentration was set at 50 mg L^{-1} , ionic strength at 0.20 M, and pH at 5.0 (by 0.01 M acetate buffer).

3. Results and discussion

3.1. Characterization of the PANI/HA nanocomposite

The N_2 adsorption-desorption isotherms of PANI (insert curve) and PANI/HA are shown in Fig. 1A. BET analysis revealed the surface area for PANI/HA is $35.4 \text{ m}^2 \text{ g}^{-1}$, which is similar to that of PANI ($35.7 \text{ m}^2 \text{ g}^{-1}$). This is attributed to the highly narrow microporosity of HA, which adsorbs no N_2 at 77 K. It was reported that the measured surface area of humic substances was $42.5 \text{ m}^2 \text{ g}^{-1}$ with CO_2 at 273 K, but less than $1 \text{ m}^2 \text{ g}^{-1}$ with N_2 at 77 K [30].

The FT-IR spectra of HA (spectrum curve 1), PANI (spectrum curve 2) and PANI/HA (spectrum curve 3) are shown in Fig. 1B. As illustrated in Fig. 1B, the peaks at about 1704, 1598 and 1381 cm^{-1} of spectrum curve 1 are attributed to the C=O stretches in free carboxylic acid [31], the C=C stretching vibrations of quinone ring and the CH_2 scissoring [32], respectively. The peaks observed at about 1568, 1480, 1300, 1240 and 800 cm^{-1} of spectrum curve 2 are attributed to the C=C stretching vibrations of quinone ring and benzene ring vibrations, the C–O stretching vibrations, C–N stretching vibrations and C–H out of plane bending vibration, respectively. Compared with spectrum curve 2, two characteristic peaks in spectrum curve 3 are observed, that is, the peaks at about 1750 and

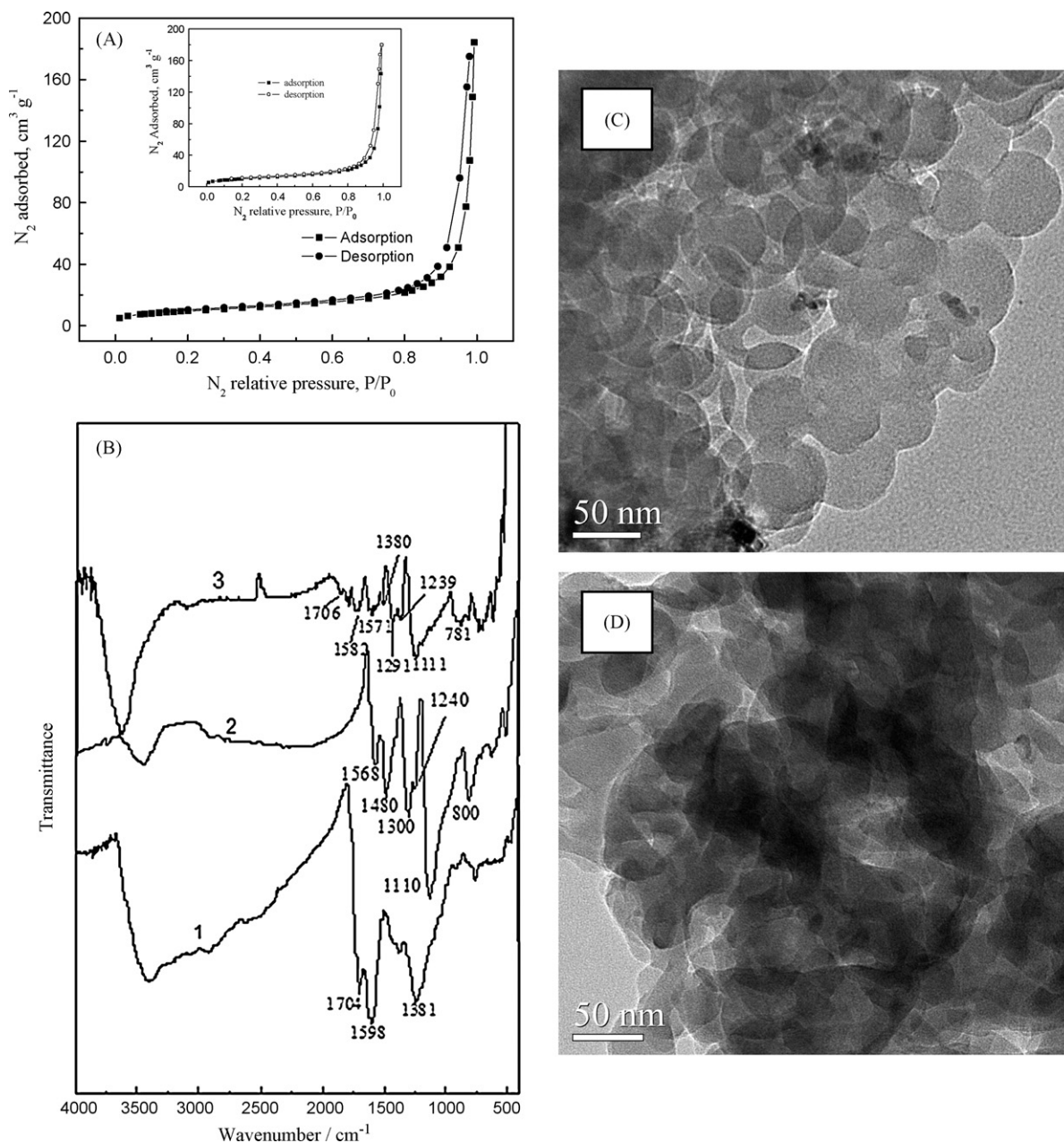


Fig. 1. (A) N_2 adsorption-desorption isotherms of PANI (insert curve) and PANI/HA. (B) FT-IR spectra of the samples, spectra curves: (1) HA, (2) PANI, (3) PANI/HA. (C and D) TEM images of PANI and the PANI/HA nanocomposite.

1380 cm^{-1} , which are attributed to the HA. This result indicates that the HA has successfully composite with PANI.

Fig. 1C shows the TEM image of the as prepared PANI/HA composite. As shown in Fig. 1C, the PANI/HA particles display morphologies of spherical particles with average size of 50–60 nm, which is similar to that of PANI reported in the literature [33]. However, the morphologies of PANI/HA show a less particle aggregation than that of PANI (Fig. 1D), which means HA added in the PANI/HA composite has effectively improved the particles morphology.

3.2. Sorption kinetics

Fig. 2 shows the kinetics of the adsorption of $Hg(II)$ by PANI/HA nanocomposite. The kinetic curve for $Hg(II)$ ions showed that the adsorption was initially rapid, and reached equilibrium after approximately 200 min. In order to evaluate the kinetic mechanism that controls the adsorption process, pseudo-first-order and

pseudo-second-order models were used. The kinetics parameters are shown in Table 1. The experimental q_e value (98.3 mg g^{-1}) is close to the calculated values (101.4 mg g^{-1}) using pseudo-second-order kinetics.

Table 1
Kinetic parameters for Hg^{2+} adsorption by PANI/HA.

Type	Parameters			
First-order model	k_1 (min^{-1})	q_1 (mg g^{-1})	R^2	
	29.61	56.39	0.9175	
Second-order model	Parameters			
	k_2 ($\text{g}(\text{mg min})^{-1}$)	q_2 (mg g^{-1})	R^2	h ($\text{mg}(\text{g min})^{-1}$)
	3.08×10^{-4}	101.42	0.9989	3.17

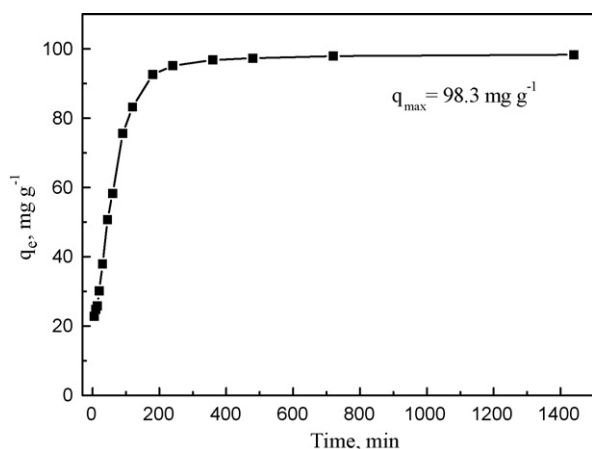


Fig. 2. Effect of contact time on the removal of Hg(II) by PANI/HA nanocomposite. Hg(II) initial concentration = 50 mg L^{-1} ; PANI/HA = 0.5 g L^{-1} ; pH 5.0 buffered by 2 mM NaAc/HAc solution; shaking rate 160 rpm , $24 \pm 1^\circ \text{C}$.

Based on the obtained correlation coefficients, the pseudo-second-order equation was the model that furthered the best fit for the experimental kinetic data, suggesting chemical sorption as the rate-limiting step of the adsorption mechanism and no involvement of a mass transfer in solution [34,35]. The adsorption of the Hg(II) by PANI/HA nanocomposite may be considered to consist of two processes with initial adsorption rate of $3.17 \text{ mg (g min)}^{-1}$.

3.3. Sorption isotherms

Adsorption isotherms of Hg(II) by PANI/HA nanocomposite was studied at pH 5.0 covering a wide range of ionic strengths (0.02, 0.20 and 1.00 M) and Hg(II) concentrations (Fig. 3). As illustrated in Fig. 3, the maximum uptake capacities for mercury (q_m) at 0.02, 0.20 and 1.00 M ionic strengths are about 320, 610 and 450 mg g^{-1} , respectively.

Both the Langmuir and the Freundlich equations (Eqs. (3) and (4)) were used to describe the adsorption isotherms. The parameters obtained from adsorption isotherms for different ionic strengths by PANI/HA nanocomposites are shown in Table 2. As illustrated in Table 2, the Langmuir isotherm correlated better than the Freundlich isotherm with the experimental data from adsorption equilibrium of Hg(II) by PANI/HA nanocomposite, which means the adsorption of Hg(II) by PANI/HA nanocomposite is a monolayer adsorption. The theoretical maximum adsorption capacities

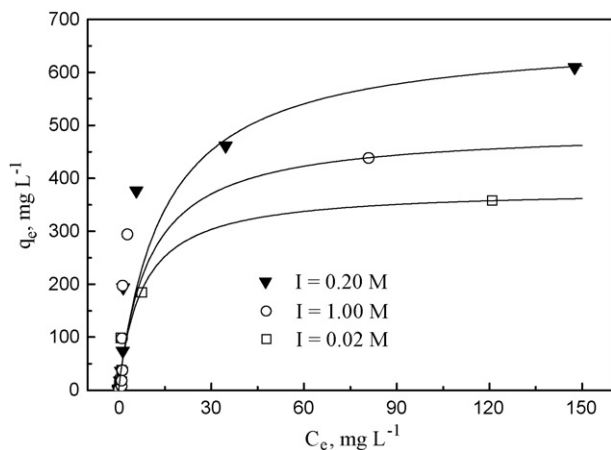


Fig. 3. Sorption isotherms of Hg(II) by PANI/HA at three levels of ionic strength, 0.02 M (\square), 0.20 M (\blacktriangledown), and 1.00 M (\circ) NaNO₃; pH 5.0 buffered by 2 mM NaAc/HAc solution, PANI/HA = 0.5 g L^{-1} .

Table 2
Parameters of adsorption isotherms at different ionic strengths.

$I \text{ (M)}$	Langmuir			Freundlich		
	$q_m \text{ (mg g}^{-1}\text{)}$	K_L	R^2	n	K_F	R^2
0.02 M	380	0.132	0.988	0.62	85.9	0.949
0.20 M	671	0.069	0.987	0.66	76.4	0.941
1.00 M	493	0.101	0.924	0.29	20.0	0.851

for mercury (q_m) at the three ionic strengths (0.02, 0.20 and 1.00 M) are about 380, 671 and 493 mg g^{-1} , respectively, which are in accordance with experimentally obtained values. This result indicates that the ionic strength has a significant effect on the adsorption capacity of mercury. Therefore, the ionic strength was controlled at 0.20 M by NaNO₃ in batch experiments. It is worth noting that the adsorption capacity ($q_m = 671 \text{ mg g}^{-1}$) of Hg(II) by PANI/HA nanocomposite ($I = 0.20 \text{ M}$) is higher than that of polymer/organosmectite composites (157.3 mg g^{-1}) [5], the aniline and sulfophenylenediamine copolymer (497.7 mg g^{-1}) [36] and the PANI (600 mg g^{-1}) [37] reported in literatures. This is because that the HA has the high complex capacity with heavy metal ions and the presence of HA in PANI effectively inhibit the aggregation of blank PANI, which is in agreement with the result of the TEM.

3.4. Effects of pH

Hg(II) removal by PANI/HA nanocomposite was measured in batch systems with equilibrium pH values from 3 to 11 (Fig. 4). As shown in Fig. 4 that the optimal pH ranges for removal of Hg(II) are from 4 to 7.5, alkaline and acidic solutions inhibit the Hg(II) adsorption. Therefore, solution pH was controlled at 5.0 in batch experiment. In comparison, the removal of Hg(II) by virgin PANI was almost 95% from initial pH 3 to 11. However, it is worth noting that the equilibrium pHs varied far away from the initial pHs and finally reached pH 4.0. This result indicates that the PANI/HA nanocomposite is more stable and pH independent than PANI and the presence of HA can reduce the aggregation of PANI and result in the stability of the PANI [29], which is consistent with the result of TEM.

The significant impact of solution pH on Hg(II) uptake could be explained by the changes in both the physicochemical properties of PANI and aqueous Hg(II) speciation. Usually, in acidic solution, Hg^{2+} is the dominant species. Compared with $\text{Hg}(\text{OH})^+$ and $\text{Hg}(\text{OH})_2$ species of relatively smaller hydrated sizes, Hg^{2+} has lower affinity to nitrogen-containing binding sites [38], causing decrease in

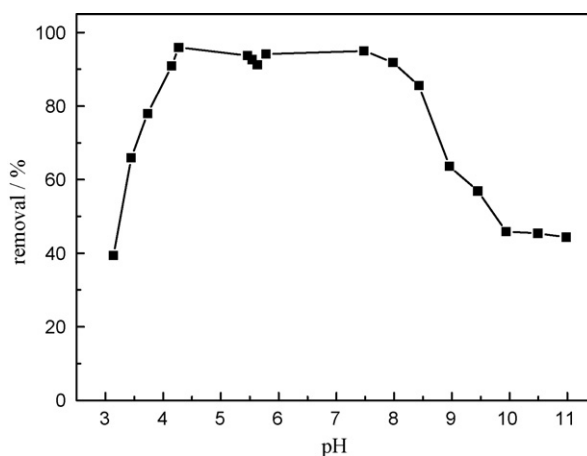


Fig. 4. Effect of solution pH on mercury removal by PANI/HA. Hg(II) initial concentration = 50 mg L^{-1} ; ionic strength = 0.2 M NaNO₃; PANI/HA = 0.5 g L^{-1} .

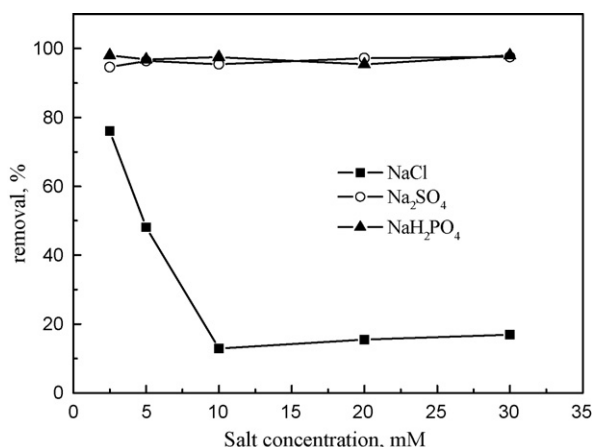


Fig. 5. Effect of coexisted ions on mercury removal by PANI/HA. Hg(II) initial concentration = 50 mg L⁻¹; ionic strength = 0.2 M NaNO₃; pH 5.0 buffered by 2 mM NaAc/HAc solution; PANI/HA = 0.5 g L⁻¹.

mercury adsorption. A possible explanation for the decrease in mercury removal above pH 7.5 could be primarily attributed to the changed physiochemical properties, possibly due to the competitive specific-binding of OH⁻ to the nitrogen-containing functional groups.

3.5. Coexisted ions

The influence of commonly coexisted ions on the removal of Hg(II) is illustrated in Fig. 5. The effects of Cl⁻, SO₄²⁻, and

PO₄³⁻ on Hg(II) sorption were examined at various concentrations (2.5–30 mM) for each anion, where the concentration of NO₃⁻ was 0.20 M. Neither the presence of SO₄²⁻ nor the PO₄³⁻ has any significant influence on the removal of Hg(II), however the effect of Cl⁻ is notable. It can be seen clearly in Fig. 5 that at initial Hg(II) concentration of 50 mg L⁻¹, the removal ratio decreases to less than 20% when the concentration of Cl⁻ is higher than 10 mM. It was reported that at lower chloride ion concentrations HgCl₂ is the predominant species, while at higher chloride ion concentrations HgCl₄²⁻ is predominant [39]. Therefore, Cl⁻ competed favorably with OH⁻ for Hg(II) to form Hg–Cl complexes and these complexes have less affinity to the PANI/HA, causing Hg(II) removal to be substantially decreased. This result is in agreement with the studies of the effect of Cl⁻ on Hg(II) sorption [40].

3.6. XPS analysis

To further understand the processes affecting the Hg(II) sorption, the PANI/HA sample after reaction with Hg(II) solution at pH around 5.0 for 24 h was analyzed with X-ray photoelectron spectroscopy (XPS). Fig. 6A shows the XPS spectrum of Hg 4f of PANI/HA after adsorption. As shown in the spectrum in Fig. 6A, the presence of Hg 4f clearly confirmed the adsorption of mercury by PANI/HA. The comparison of the measured binding energy of Hg in the present work with the values available in the literature indicates that the mercury adsorbed in PANI/HA is present as Hg(II) [41]. Fig. 6B shows the high resolution scan of N1s of PANI/HA before (spectrum curve 1) and after (spectrum curve 2) adsorption of Hg(II). Peak fitting illustrated that N1s of curve 1 (Fig. 6B) could

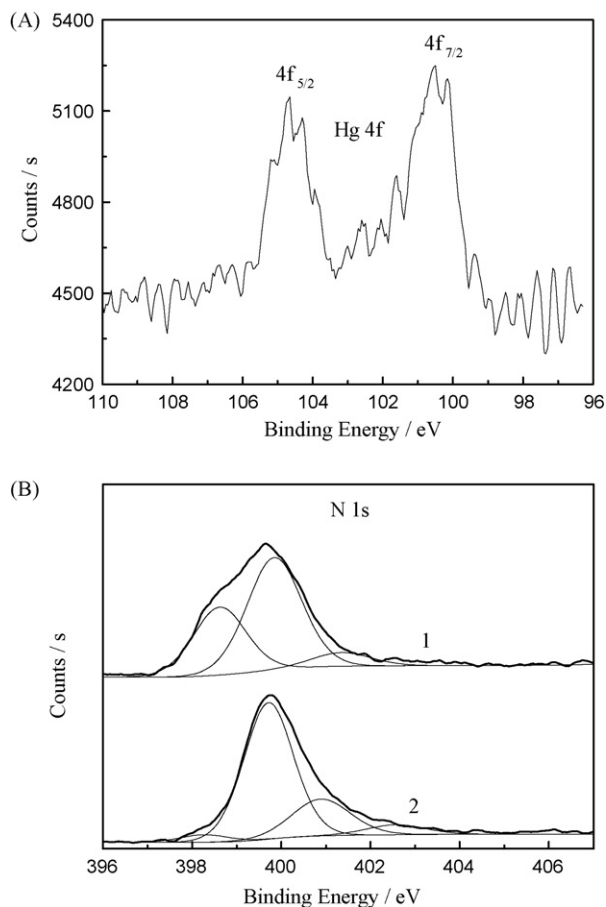


Fig. 6. (A) XPS spectrum of Hg 4f of PANI/HA after adsorption. (B) XPS spectrum of N1s of PANI/HA before and after adsorption.

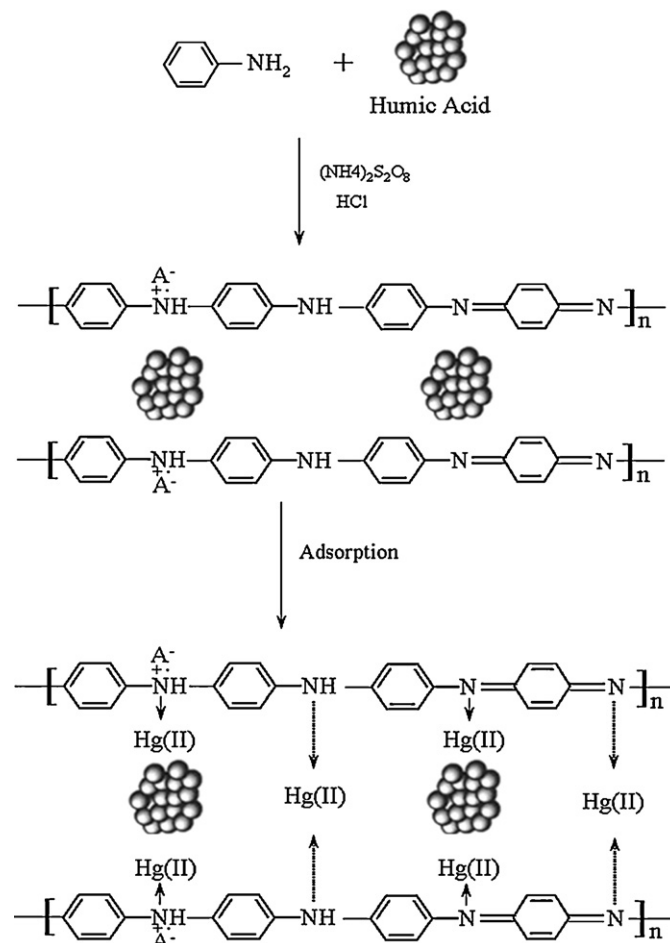


Fig. 7. Schematic mechanism for mercury absorption by PANI/HA.

be grouped into three peaks, corresponding to different nitrogen atoms or functional groups ($-N=$), ($-NH-$) and ($-NH^{*+}$), respectively. It can be seen in curve 2 (Fig. 6B) that N1s could be fitted into four peaks, which is attributed to the four different nitrogen atoms in a PANI unite. On the basis of this study, a possible schematic mechanism for mercury absorption by PANI/HA was proposed (Fig. 7).

4. Conclusion

A PANI/HA nanocomposite was chemically synthesized and characterized in this work. TEM result showed that the presence of HA can enhance the stability of virgin PANI by preventing their aggregation. The PANI/HA was studied for mercury removal from aqueous solutions. Batch adsorption results showed that the PANI/HA nanocomposite exhibits remarkable enhancement of material stability and mercury removal efficiency. Many factors including solution pH, ionic strength and competitive ions had impacts on adsorption. The removal efficiency was highly pH dependent and the optimal removal observed around pH 4–7.5. The maximum adsorption capacity of 671 mg g^{-1} was obtained at ionic strength was 0.20M and pH 5.0, which is much higher than previous studies. The competitive studies showed that the effect from coexisting ions was insignificant except for Cl^- . XPS result showed that mercury could be complexed to different nitrogen atoms, on which an adsorption mechanism was suggested. It is expected that the PANI/HA nanocomposite has wide applicability in the removal of heavy metals from various waters.

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References

- Y. Li, C.Y. Wu, Role of moisture in adsorption, photocatalytic oxidation, and reemission of elemental mercury on a SiO_2-TiO_2 nanocomposite, *Environ. Sci. Technol.* 40 (2006) 6444–6448.
- H.Y. Jeong, B. Klaue, J.D. Blum, K.F. Hayes, Sorption of mercuric ion by synthetic nanocrystalline mackinawite (FeS), *Environ. Sci. Technol.* 41 (2007) 7699–7705.
- D. Mercone, J. Thomson, I.W. Croudace, S.R. Troelstra, A coupled natural immobilisation mechanism for mercury and selenium in deep-sea sediments, *Geochim. Cosmochim. Acta* 63 (1999) 1481–1488.
- R.S. Vieira, M.M. Beppu, Dynamic and static adsorption and desorption of $Hg(II)$ ions on chitosan membranes and spheres, *Water Res.* 40 (2006) 1726–1734.
- R. Say, E. Birlik, Z. Erdemgil, A. Denizli, A. Ersöz, Removal of mercury species with dithiocarbamate-anchored polymer/organosmectite composites, *J. Hazard. Mater.* 150 (2008) 560–564.
- H. Smith, Estimation of mercury in biological material by neutron activation analysis, *Anal. Chem.* 35 (1963) 635–636.
- S. Chiarle, M. Ratto, M. Rovatti, Mercury removal from water by ion exchange resins adsorption, *Water Res.* 34 (2000) 2971–2978.
- U. Wingenfelder, C. Hansen, G. Furrer, R. Schulin, Removal of heavy metals from mine waters by natural zeolites, *Environ. Sci. Technol.* 39 (12) (2005) 4606–4613.
- K.A. Larson, J.M. Wienczek, Liquid ion exchange for mercury removal from water over a wide pH range, *J. Ind. Eng. Chem. Res.* 31 (12) (1992) 2714–2722.
- Z.H. Ai, Y. Cheng, L.Z. Zhang, J.R. Qiu, Efficient removal of $Cr(VI)$ from aqueous solution with $Fe@Fe_2O_3$ core-shell nanowires, *Environ. Sci. Technol.* 42 (2008) 6955–6960.
- A.M. Donia, A.A. Atia, K.Z. Elwakeel, Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde, *J. Hazard. Mater.* 151 (2008) 372–379.
- J. Fang, Z.M. Gu, D.C. Gang, C.X. Liu, E.S. Ilton, B.L. Deng, $Cr(VI)$ removal from aqueous solution by activated carbon coated with quaternized poly(4-vinylpyridine), *Environ. Sci. Technol.* 41 (13) (2007) 4748–4753.
- C. Namasivayam, K. Periasamy, Bicarbonate-treated peanut hull carbon for mercury (II) removal from aqueous solution, *Water Res.* 27 (11) (1993) 1663–1668.
- A.P. Davis, V. Bhatnagar, Adsorption of cadmium and humic acid onto hematite, *Chemosphere* 30 (2) (1995) 243–256.
- J. Hu, G.H. Chen, I.M.C. Lo, Removal and recovery of $Cr(VI)$ from wastewater by maghemite nanoparticles, *Water Res.* 39 (2005) 4528–4536.
- J. Hu, M.C. Lo, G.H. Chen, Adsorption of $Cr(VI)$ by magnetite nanoparticles, *Water Sci. Technol.* 50 (2004) 139–146.
- M.V.B. Krishna, D. Karunasagar, S.V. Rao, J. Arunachalam, Preconcentration and speciation of inorganic and methyl mercury in waters using polyaniline and gold trap-CVAAS, *Talanta* 68 (2005) 329–335.
- Z. Reddad, C. Gerente, Y. Andres, P.L. Cloirec, Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies, *Environ. Sci. Technol.* 36 (9) (2002) 2067–2073.
- P.A. Brown, S.A. Gill, S.J. Allen, Metal removal from wastewater using peat, *Water Res.* 34 (2000) 3907–3916.
- Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.* 34 (2000) 735–742.
- L.X. Li, H.H. Song, Q.C. Zhang, J.Y. Yao, X.H. Chen, Effect of compounding process on the structure and electrochemical properties of ordered mesoporous carbon/polyaniline composites as electrodes for supercapacitors, *J. Power Sources* 187 (2009) 268–274.
- S.L. Mu, Catechol sensor using poly(aniline-co-o-aminophenol) as an electron transfer mediator, *Biosens. Bioelectron.* 21 (2006) 1237–1243.
- S.L. Mu, Novel properties of polyaniline nanofibers coated with polycatechol, *Synth. Met.* 156 (2006) 202–208.
- J.X. Huang, R.B. Kaner, The intrinsic nanofibrillar morphology of polyaniline, *Chem. Commun.* 367 (2006) 367–376.
- R.K. Gupta, R.A. Singh, S.S. Dubey, Removal of mercury ions from aqueous solutions by composite of polyaniline with polystyrene, *Sep. Purif. Technol.* 38 (2004) 225–232.
- A.W.P. Vermeer, L.K. Koopal, Adsorption of humic acid to mineral particles. 1. Specific and Electrostatic Interactions, *Langmuir* 14 (1998) 2810–2819.
- J.L. Viota, J. de Vicente, J.D.G. Durán, A.V. Delgado, Stabilization of magnetorheological suspensions by polyacrylic acid polymers, *J. Colloid Interface Sci.* 284 (2005) 527–541.
- E. Illés, E. Tombácz, The role of variable surface charge and surface complexation in the adsorption of humic acid on magnetite, *Colloids Surf. A* 230 (2004) 99–109.
- E. Illés, E. Tombácz, The effect of humic acid adsorption on pH-dependent surface charging and aggregation of magnetite nanoparticles, *J. Colloid Interface Sci.* 295 (2006) 115–123.
- R.A. Alvarez-Puebla, P.J.G. Goulet, J.J. Garrido, Characterization of porous structure of different humic fractions, *Colloids Surf. A* 256 (2005) 129–135.
- W. Yantasee, C.L. Warner, T. Sangvanich, R.S. Addleman, T.G. Carter, R.J. Wiacek, G.E. Fryxell, C. Timchalk, M.G. Warner, Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles, *Environ. Sci. Technol.* 41 (2007) 5114–5119.
- J.F. Liu, Z.S. Zhao, G.B. Jiang, Coating Fe_3O_4 magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water, *Environ. Sci. Technol.* 42 (2008) 6949–6954.
- Y. Zhang, C.X. Zhu, J.Q. Kan, Synthesis and Characterization of ferromagnetic polyaniline with conductivity in an applied magnetic field, *J. Appl. Polym. Sci.* 109 (2008) 3024–3029.
- M. Yurdakoc, Y. Scki, S.K. Yuedakoc, Kinetic and thermodynamic studies of boron removal by Siral 5, Siral 40, and Srial 80, *J. Colloid Interface Sci.* 286 (2005) 440–446.
- F.C. Wu, R.L. Tseng, R.S. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, *Water Res.* 35 (2001) 613–618.
- Q.F. Lu, M.R. Huang, X.G. Li, Synthesis and heavy-metal-ion sorption of pure sulfophenylenediamine copolymer nanoparticles with intrinsic conductivity and stability, *Chem. Eur. J.* 13 (2007) 6009–6018.
- J. Wang, B.L. Deng, H. Chen, X.R. Wang, J.Z. Zheng, Removal of aqueous $Hg(II)$ by polyaniline: sorption characteristics and mechanisms, *Environ. Sci. Technol.* 43 (2009) 5223–5228.
- S.K. Das, A.R. Das, A.K. Guha, A Study on the adsorption mechanism of mercury on *Aspergillus versicolor* biomass, *Environ. Sci. Technol.* 41 (2007) 8281–8287.
- J.E.D. Davies, D.A. Long, The vibrational spectra of the halides and complex halides of the Group IIB elements. Part II. A Raman spectroscopic study of the systems HgX_2-LiX ($X=Cl, Br$) in aqueous and tri-n-butyl phosphate solutions, *J. Chem. Soc. A* (1968) 2564–2568.
- A. Walcarius, C. Delacote, Mercury(II) binding to thiol-functionalized mesoporous silicas, *Anal. Chim. Acta* 547 (2005) 3–13.
- P.S. Remya Devi, S. Kumar, R. Verma, M. Sudersanan, Sorption of mercury on chemically synthesized polyaniline, *J. Radioanal. Nucl. Chem.* 269 (2006) 217–222.