



Polyaniline nanofibers assembled on alginate microsphere for Cu^{2+} and Pb^{2+} uptake

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ARTICLE INFO

Article history:

Received 5 August 2011

Received in revised form 7 February 2012

Accepted 8 February 2012

Available online 28 February 2012

Keywords:

Polyaniline nanofibers

Calcium alginate

Adsorption

Pb^{2+}

Cu^{2+}

ABSTRACT

Polyaniline (PANI) nanofibers were assembled on the micro- or millimeter-scale calcium alginate (CA) beads by “competitive adsorption-restricted polymerization” approach. The CA beads made the dimensional expansion of PANI nanofibers evident, which overcame the serious aggregation of PANI nanofibers and benefited the practical operation of PANI nanofibers. Batch adsorption results showed that the millimeter-scale CA beads decorated by PANI nanofibers had high affinity to Cu^{2+} and Pb^{2+} in aqueous solutions. The removal percentages of Cu^{2+} and Pb^{2+} in aqueous solutions by this PANI/CA composite with milli/nano hierarchical structure surpassed 90% in a wide pH range from 3 to 7. Sorption of the two kinds of ions to PANI/CA composite sorbent agreed well with the Freundlich adsorption model. The adsorption kinetic results of Cu^{2+} and Pb^{2+} showed that the adsorption reached equilibrium within 120 min and 40 min, respectively. And their adsorption rates could be described by pseudo-second-order kinetics. The desorption percentages of Pb^{2+} and Cu^{2+} from this PANI/CA composite are 62% and 75%, respectively. The Pb^{2+} and Cu^{2+} removal capacity of the sorbent could be further reinforced when the diameter of CA beads turned from millimeter to micrometer.

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1. Introduction

As a typical conductive polymer, polyaniline (PANI) has been attracting great research interests in recent years because of its low cost, ease of synthesis, environmental stability, etc. [1–3]. In addition, it possesses a large amount of amine and imine functional groups, which can interact with some metal ions due to the strong affinity of nitrogen. Based on this characteristic, some investigators have directed their research toward the application of PANI for determination of metal ions and removal of heavy metal ions from aqueous solutions [4–6]. Moreover, it is well known that the nano-scale adsorbents with large specific surface areas have higher efficient removal than the regular scale ones. Recently, Zhang et al. [7] has investigated the PANI/humic acid nanocomposite for mercury ions removal. However, it is worthwhile pointing out that the macroscopic morphology of the PANI nanomaterial is powder form, which will make the separation of the adsorbent from the solution so complicated in practice. And the aggregation of the nano-scale adsorbents is also a headache for the researchers. Consequently, the PANI nanoadsorbent may only have value in a laboratory-scale study.

In the last several months we have successfully constructed uniform PANI nanofibers on the micro-scale surface via a novel and effective one-pot synthesis method, “competitive adsorption-restricted polymerization” [8]. This work naturally gives us a new idea about fabricating PANI nanofibers on a substrate with milli- or micrometer scale for the heavy metal ions uptake. The nano/micro or nano/milli hierarchical structure actually realizes the shape control of PANI nanofiber on a large scale, which will simplify the separation of the nanoadsorbent and avoid the second micro-pollution caused by its residue to water after the adsorption. Meanwhile, if the milli- or micro-scale substrate also can adsorb metal ions, the practical value of the composite adsorbent will be further increased.

Herein, we chose calcium alginate as the milli- or micro-scale substrate for the growth of PANI nanofibers. Alginate is a linear polysaccharide biopolymer composed of (1 → 4)-linked residues of α -L-guluronic acid (G) and β -D-mannuronic acid (M). It can form stable biodegradable gels in the presence of divalent cations such as Ca^{2+} . Calcium alginate (CA) has shown a high affinity for metal ions [9–12]. But due to its tendency to swell in water and mechanical weakness, its application in wastewater treatment is limited [13,14]. To overcome the drawbacks and further increase its absorptive capacity, some researchers have engaged in the study of alginate composite gel in recent years [12–16]. Li et al. [16] simply mixed carbon nanotubes (CNTs) with CA gels, and found that the composite gels have a higher biosorption capacity for

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Cu²⁺ compared with the pure alginate gels. Chitosan was another good candidate to improve the mechanical and absorptive property of alginate owing to the strong electrostatic interaction between the amino groups of chitosan and the carboxyl groups of alginate [13–15]. PANI nanofibers not only possess the same nano dimensional effect as CNTs, but also have plenty of amino groups. Given this point, we expect that PANI nanofiber and CA gel will be an ideal match for the metal ions uptake. In this study we prepared PANI nanofibers on the surface of CA beads via “competitive adsorption-restricted polymerization”. The Cu(II) and Pb(II) ions removal properties of the PANI/CA hierarchical adsorbent were evaluated in terms of the sorption kinetics and sorption isotherm, the effects of solution pH and the CA particle size. Desorption studies of pre-adsorbed samples in Cu(NO₃)₂ or Pb(NO₃)₂ bulk solutions (10 mg/L) were also discussed.

2. Materials and methods

2.1. Materials

All reagents were of analytical grade and were used as received except styrene and aniline (AR, Shanghai Chemical Reagent Co.), which were distilled before use. All solutions for the metal sorption experiments were prepared using Cu(NO₃)₂ and Pb(NO₃)₂ purchased from Merck. HNO₃ and NH₃·H₂O were used to adjust the solution pH throughout the experiments.

2.2. Preparation of calcium alginate particles with 2.5 mm diameter

2 g sodium alginate (AIBI, Shanghai, China) was dissolved in 98 mL deionized water by stirring for 24 h. In order to degas, the solution was left undisturbed for 12 h in the refrigerators, and then added dropwise into 0.1 mol/L CaCl₂ solution. The gel beads were kept in the calcium solution with gentle agitation for approximately 12 h until complete gelation. The product was the particle with a diameter of 2.5 mm.

2.3. Preparation of micro-scale calcium alginate/polystyrene core-shell particles

25 mL of distilled water, 0.25 g of polystyrene (PS) microspheres (prepared by dispersion polymerization [8]) and 0.035 g of polysorbate 80 (Tween 80) were added into a 150 mL round-bottom flask. Following the attainment of a uniform dispersion, 0.02 g of sodium alginate was added. The mixed solution was stirred for 1 h and then centrifugally separated. Another 25 mL of distilled water was used to suspend the sediment. And then 0.045 g of sorbitan oleate (Span 80) and 35 mL of hexane were added. Under stirring, 6 mL 0.1 mol/L calcium chloride solution was added dropwise. The cross-linking reaction proceeded for 2 h at the room temperature. Finally, the resulting product was obtained by filtering and washing several times with deionized water.

2.4. Preparation of polyaniline/alginate sorbents with hierarchical structure

Polyaniline/alginate sorbents with hierarchical structure were synthesized by a simple and effective route, according to our previous study [8]. The surface of alginate particles possesses lots of negative electrons that can strongly attract cationic surfactant and anilinium cations. So the anilinium cations self-assemble and polymerize on the alginate particles to form nanofiber morphology in the presence of cationic surfactant.

In a typical procedure for the synthesis of PANI/CA composite with milli/nano hierarchical structure, cationic surfactant solution was prepared by dissolving 0.0111 g of didecyldimethylammonium bromide (C₁₀DAB) in 2 M HCl (10 mL) aqueous solution. 0.5 g of CA particles with 2.5 mm diameter and the above surfactant solution were added to a 50 mL two-necked round flask. The flask was purged with nitrogen before the addition of 2.5 mL 10 g/L aniline *n*-hexane solution under magnetic stirring. On stirring, 5 mL ammonium peroxydisulfate aqueous solution (APS, 0.5 mmol) was added in 0.05 mL aliquots at 10 s intervals. During the above process, the temperature was maintained at room temperature (RT). The resulting product was rinsed off with deionized water and ethanol several times, consecutively. Finally, the product was dried under vacuum for 48 h at room temperature before characterization.

In order to investigate the effect of CA size on the sorption capacity, we adopted the PS/CA core-shell microspheres as the micro-scale substrate for the growth of PANI nanofibers. The synthesis process of this PANI/CA composite with micro/nano hierarchical structure was similar to that with milli/nano hierarchical structure except three points: 1 g core-shell PS/CA microspheres replaced the 0.5 g of CA particles with 2.5 mm diameter, and the dosages of aniline monomer and APS were 0.025 g and 0.057 g, respectively.

2.5. Characterization

SEM images of the samples were obtained from a LEO 1530VP SEM instrument. Samples for the SEM experiment were made on a conducting stage and observed after gold coating. FT-IR spectra of the samples were recorded using a Nicolet Avatar 360 Fourier Infrared spectrophotometer (FTIR) with the KBr pellet technique. CHN elemental microanalyses of the samples were performed by using Vario EL III.

2.6. Batch adsorption experiments

Stock solutions (1000 ppm) of Cu²⁺ and Pb²⁺ ions were prepared by using analytical-grade reagent, respectively. The two kinds of single metal stock solutions were then diluted to give standard solutions of appropriate concentrations. Batch sorption experiments were conducted in 250 mL beakers and equilibrated using a magnetic stirrer. 0.01 g of the polyaniline/alginate sorbents with hierarchical structure were added into these single metallic solutions. After removing the polyaniline/alginate sorbents from the solution, the metal concentration was measured by atomic absorption spectroscopy (AAS), performed in a Varian Spectral spectrometer.

The effect of initial pH on the sorption of Pb(II) and Cu(II) was studied in pH range of 2–7. The pH of Cu(NO₃)₂ and Pb(NO₃)₂ solutions with the concentration of 10 mg/L were respectively adjusted to the required pH value using either 0.1 mol/L HNO₃ or 0.1 mol/L NH₃·H₂O.

The batch kinetics studies were carried out by using 0.01 g of the sorbents in a 80 mL of 10 mg/L Cu(NO₃)₂ or Pb(NO₃)₂ solution. After a certain period of time, aliquots of the solution were taken from the system and measured by atomic absorption spectrometer (Varian Spectral).

Adsorption isotherms of Cu(II) were studied at room temperature by adding 0.01 g of the adsorbents into 50 mL Cu(NO₃)₂ or Pb(NO₃)₂ solution with initial pH value of 5.0. The Cu²⁺ concentrations ranged from 5 to 40 mg/L. But for the study of Pb(II), the Pb²⁺ concentration varied between 5 and 100 mg/L. After the suspensions were shaken for 2 h, the Cu²⁺ or Pb²⁺ concentration in the

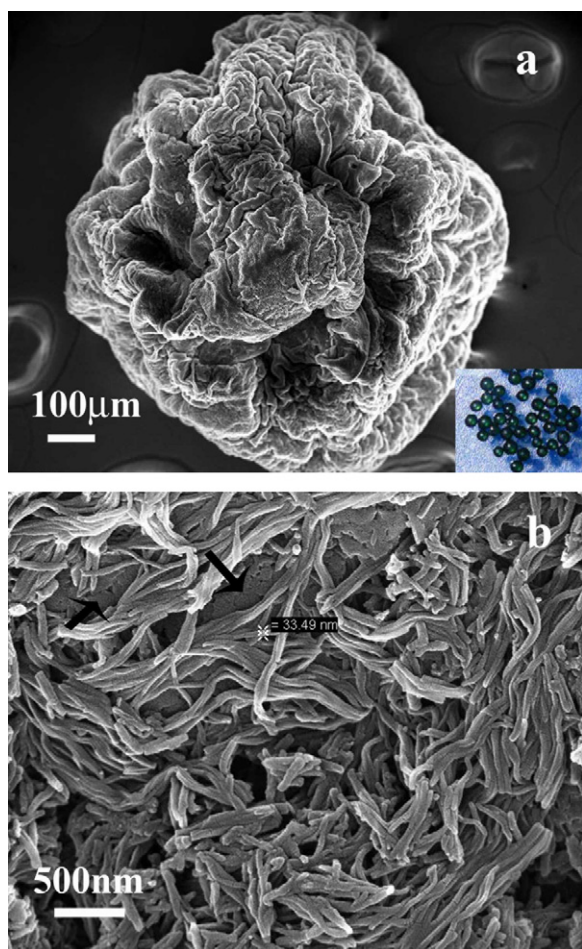


Fig. 1. (a) SEM image of PANI/CA sorbent with milli/nano hierarchical structure, inset: a photograph of the sorbent. (b) Magnified view of the PANI/CA sorbent with milli/nano hierarchical structure.

solution was measured. The amounts of Cu^{2+} or Pb^{2+} ion adsorbed at equilibrium (q_e) were calculated using the following equation.

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where C_0 and C_e were initial and equilibrium concentrations of metal ion, respectively, m was the mass of adsorbent and V was volume of the solution.

3. Results and discussion

3.1. Characterization of PANI/CA sorbent with milli/nano hierarchical structure

Upon decorating the PANI nanofibers, the color of the CA beads with a diameter of 2.5 mm intermediately turned green as shown in the inset of Fig. 1a. Magnified SEM image showed PANI formed lots of nanofibers with an average diameter of about 30 nm on the surface of CA particles (Fig. 1b). The length of these nanofibers ranged from about 500 nm to several micrometers. Because the dried PANI/CA sorbents shrank and caved in, some PANI nanofibers appeared to stack together and covered densely on CA surface. However, it still can be found that the PANI nanofibers do not cover the CA beads completely as indicated by the arrows (Fig. 1b), which is the ideal distribution for us since the heterogeneous surface can contribute to the permeation and adsorption of the metal ions.

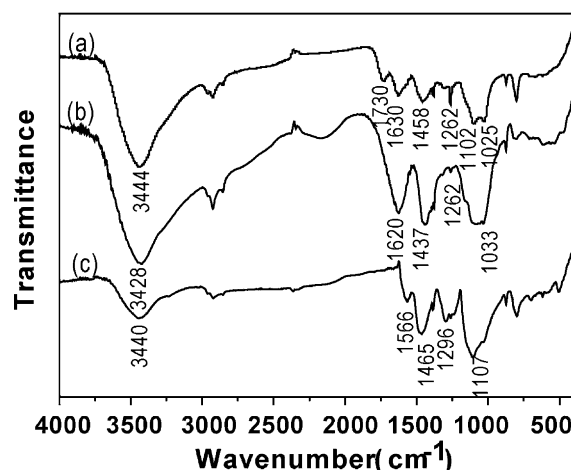


Fig. 2. The FTIR spectra of (a) PANI/CA sorbent, (b) CA, (c) PANI nanofiber.

The result of the element analysis of the PANI/CA sorbent indicated that the sorbent had 0.0145 wt% of nitrogen element. According to the Eq. (2), the actual PANI loading amount (W) was calculated to be 0.096 wt%.

$$W(\text{wt}\%) = \frac{N(\text{wt}\%)}{M(\text{nitrogen})} \times M(\text{aniline}) \quad (2)$$

where $W(\text{wt}\%)$ is the actual PANI loading in the PS/PANI composite, $N(\text{wt}\%)$ is the loading percentage of nitrogen element, $M(\text{aniline})$ is the molecular weight of aniline, and $M(\text{nitrogen})$ is the relative atomic mass of nitrogen.

Such a low PANI loading makes the FTIR spectrum of the PANI/CA sorbent be very similar to that of pure CA gel (Fig. 2). In the FTIR spectrum of CA (Fig. 2b), the peaks at around 3428, 1627, 1437, 1262 and 1033 cm^{-1} are attributed to the stretching of O–H, –COO– (asymmetric), –CH₂, –C–O– and C–O–C, respectively [17]. Compared with CA spectrum, one new absorption peak in the FTIR spectrum of PANI/CA sorbent (Fig. 2a) can be observed at 1730 cm^{-1} , which is ascribed to the asymmetric stretching of –COO– groups of CA. Apparently, this –COO– stretch peak exhibits a large shift to higher wavenumbers. This peak is specific to ionic binding. As the protonated amino groups (–NH₂⁺–C₆H₄–) in PANI molecular chain are combined with –COO– groups in the alginate blocks. The charge density, the radius, and the atomic weight of the cation are changed, creating a new environment around the carbonyl group. Hence, a peak shift would be expected [18]. Moreover, in the FTIR spectrum of PANI/CA sorbent, other characteristic peaks of the PANI component appeared at 3444 cm^{-1} (N–H stretching vibration), 1458 cm^{-1} (the stretching of benzenoid ring) and 1102 cm^{-1} (C=N stretching vibration) indicating the existence of PANI composite.

3.2. Effect of pH

At pH values higher than 7, precipitations of $\text{Pb}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ occur, which leads to inaccurate interpretation of adsorption. So, Cu^{2+} or Pb^{2+} ion removal of PANI/CA with milli/nano hierarchical structure, CA beads and PANI nanofiber was measured through batch equilibrium experiments with pH values from 2 to 7. The results are shown in Fig. 3a and b, respectively. It is evident that for both CA beads and PANI nanofibers, the removal percentages of Cu^{2+} and Pb^{2+} increased with the increasing of the solution pH value. Previous reports attributed this phenomenon to the change of ionization state of the functional groups (carboxylate, hydroxyl and amino groups) in the two materials [16,19–21]. With the increase of pH, there are more and more carboxylate groups with

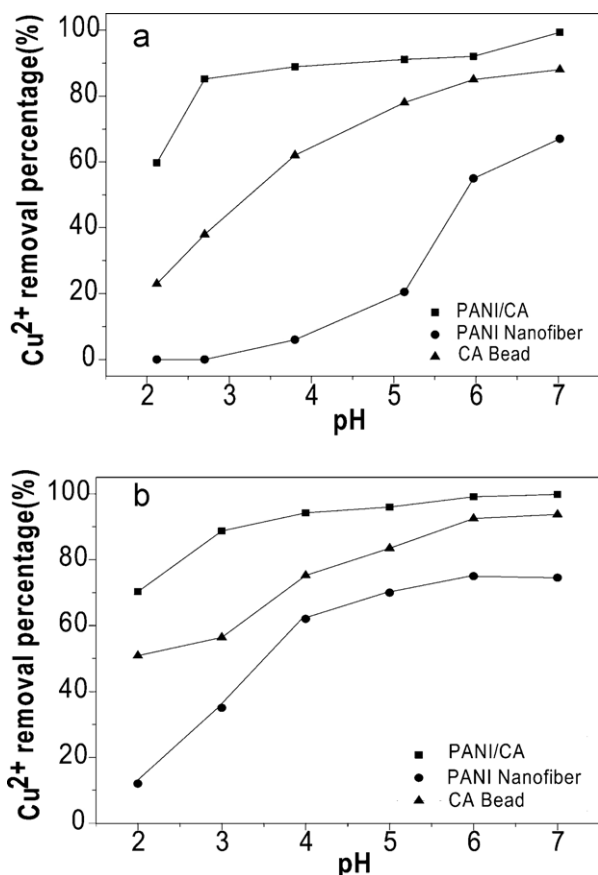


Fig. 3. The initial pH effect on adsorption of metal ions: (a) Cu²⁺; (b) Pb²⁺, by PANI/CA hierarchical structure, CA beads and PANI nanofibers (dosage of adsorbents: 0.01 g, concentration of metal ions: 10 mg/L, T = 25 °C).

negative charges, free hydroxyl groups and free amino or imine groups that become available for the metal ions adsorption. From Fig. 3, it also can be seen that the Cu²⁺ and Pb²⁺ removal percentages of PANI/CA adsorbent with milli/nano hierarchical structure are much higher than that of CA beads and PANI nanofibers, and seems to be insensitive to the variation of pH value from 3 to 7. This result reveals that the combination of PANI nanofibers and CA beads improves the adsorption efficiency of the adsorbent in the mediums at any pH value. The weak pH sensitivity makes the PANI/CA adsorbent suitable for the separation of heavy metal ions in different mediums, which is just as we expected. We believe the possible reason for weak pH sensitivity is the synergistic effect of surface complexation and ion exchange. And the more absorptive sites in PANI/CA may also play an important role in the improvement of adsorption capacity. Furthermore, it is noted that the Cu²⁺ and Pb²⁺ removal percentage of PANI/CA adsorbent with milli/nano hierarchical structure decreases dramatically at the pH value of 2, which can be used for the study of desorption that is discussed in the later part.

We found that if the PANI/CA nanocomposite was immersed in the pH range from 2 to 7 during the equilibrium time, no green precipitation appeared in the solution, which indicated that PANI nanofibers could not be separated from the CA matrix. In fact, as the pH value increased to 7, the PANI/CA composite became steadier and steadier, because there was a much smaller amount of H⁺ to combine the carboxylate groups with negative charges, free hydroxyl groups and free amino or imine groups. We believe the weak acidity and neutrality of the medium is preferred in the practical application of the adsorbent.

3.3. Adsorption isotherm

The adsorption isotherm is fundamental in explaining the interactive relation between the solute and adsorbent. The batch of adsorption isotherm experiments has been done so as to compare the adsorption characteristics of the CA beads, PANI nanofibers and PANI/CA composite. Two isotherm theories, the Langmuir and Freundlich isotherm, have been adopted to analyze isotherm data. The form of Langmuir equation can be expressed by the following equation:

$$q_e = \frac{bQ_c C_e}{1 + bC_e} \quad (3)$$

where C_e is the equilibrium liquid phase concentration of Cu²⁺ and Pb²⁺ (mg/L); q_e is the lead or copper ions uptake at the equilibrium (mg/g); Q_c (mg/g) is the theoretical maximum adsorption capacity of the adsorbent for Cu²⁺ and Pb²⁺, and b (L/mg) is a Langmuir binding constant related to the energy of adsorption. The model assumes that there are homogeneous binding sites with equivalent sorption energies on the adsorbent surface [22,23].

The Freundlich model considers that the adsorbent is covered by monomolecular layer of solute. It can be of theoretical interest in terms of adsorption onto an energetically heterogeneous surface [24]. Its equation is presented below:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is the Freundlich capacity factor and n is the Freundlich's intensity factor. The value of n in the range of 1–10 denotes favorable adsorption.

Fig. 4 shows the Langmuir and Freundlich plots fitting the Pb²⁺ and Cu²⁺ uptake by the PANI/CA adsorbent, CA beads and PANI nanofibers. The relative Langmuir and Freundlich constants have been calculated from the plots and presented in Table 1. Through comparing the value of correlation coefficient (R^2), we can find that the Freundlich isotherm correlates better than Langmuir isotherm with the experimental data from adsorption equilibrium of Cu(II) and Pb(II) by PANI/CA adsorbent. In contrast, for CA beads and PANI nanofiber, Langmuir model exhibits excellent fit for both Cu²⁺ and Pb²⁺. This result implies that the construction of PANI nanofibers on the surface of CA bead brings about an energetically heterogeneous surface, namely, the basic assumption of Freundlich theory.

In the Freundlich model, the K_F value indicates the relative sorption capacity of the used system. The obtained K_F values for the Pb²⁺ and Cu²⁺ adsorbed by PANI/CA hierarchical structure are 55.94 and 45.83, which are both higher than that for Pb²⁺ and Cu²⁺ uptake by CA beads and PANI nanofibers, as displayed in Table 1. Especially, the K_F value increases by two orders of magnitude when the PANI nanofibers load onto the CA beads. Moreover, the bigger Freundlich's intensity factor n with respect to the PANI/CA hierarchical structure suggests the PANI/CA hierarchical structure has a stronger affinity for Cu²⁺ and Pb²⁺ ions than CA beads and PANI nanofibers. Even comparing all the adsorbents by using the non-linear Langmuir isotherm, the maximum monolayer adsorption capacities of Pb²⁺ and Cu²⁺ obtained from PANI/CA adsorbent are still the highest. And the order of theoretical maximum adsorption capacity for the two metal ions can be put as: Pb²⁺ > Cu²⁺. This order coincides with the results in the previous report about the single alginate gel [25,26].

The Pb²⁺ and Cu²⁺ adsorption capacities of PANI/CA adsorbent (251.25 mg/g, 67.95 mg/g) are comparable with the values reported in the previous studies as shown in Table 2. We consider that the reasons for the high capacity of the PANI/CA adsorbent with milli/nano hierarchical structure can be summarized as follows. Firstly, the milli/nano hierarchical works out the serious aggregation problem of PANI nanofibers, which facilitates interaction of the functional groups on the PANI nanofibers with metal ions. The

Table 1

Langmuir and Freundlich isotherm constants and correlation coefficients for the adsorption of Cu(II) and Pb(II) ions onto CA beads, PANI nanofiber and PANI/CA hierarchical structure.

Adsorbents	Langmuir			Freundlich		
	Q (mg/g)	b (mL/mg)	R^2	n	K_F	R^2
CA bead (Pb ²⁺)	240.46	0.07	0.9526	2.35	34.51	0.9435
PANI nanofiber(Pb ²⁺)	5.67	0.12	0.9511	1.63	0.77	0.9295
PANI/CA (Pb ²⁺)	251.45	0.13	0.9705	2.77	55.94	0.9865
CA bead (Cu ²⁺)	64.75	0.34	0.9861	3.44	23.49	0.9087
PANI nanofiber(Cu ²⁺)	2.27	0.20	0.9720	2.13	0.485	0.9199
PANI/CA (Cu ²⁺)	67.95	2.80	0.8082	7.05	45.83	0.9816

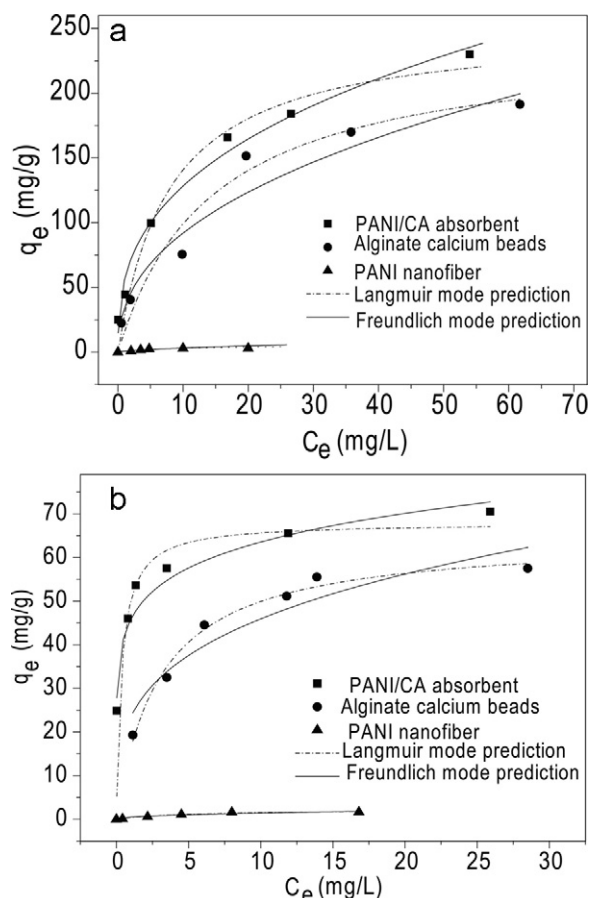


Fig. 4. Adsorption isotherms of Pb²⁺ (b), Cu²⁺ (a) onto PANI/CA hierarchical structure, CA beads and PANI nanofibers (dosage of adsorbents: 0.01 g, pH 5, $T=25^{\circ}\text{C}$).

Table 2

Maximum adsorption capacities for Cu²⁺ and Pb²⁺ by different adsorbents.

Adsorbents	Adsorption capability (mg/g)	Reference
Rhizopus arrhizus (Pb ²⁺)	71.00	[27]
Aureobasidium pollulans (Pb ²⁺)	170.6	[28]
Saccharomyces cerevisiae (Pb ²⁺)	95.3	[28]
Activated sludge (Cu ²⁺)	19.06	[29]
activated carbon (Cu ²⁺)	5.08	[30]
CA encapsulated magnetic sorbent (Cu ²⁺)	60.00	[10]

CA gel as the substrate for the growth of PANI nanofibers also can effectively adsorb the Cu(II) and Pb(II) ions. The synergistic effect of the two components certainly plays a key role in the adsorption. Besides, we believe the amino groups in PANI may improve the coordinate ability of M residue in alginate molecular chain for divalent metal ions. Owing to the undesirable distance determined by the conformation, the carboxylate groups of M residue in two neighbor molecular chains are unable to together coordinate the divalent metal ions. But the amino groups of PANI afford another site for the coordinate of divalent metal ions. Hence, the carboxylate groups of M residue on the CA surface can vigorously bind the Cu(II) and Pb(II) ions in the presence of amino groups.

3.4. Sorption kinetics

Fig. 5 demonstrates the adsorption kinetics of Cu²⁺ and Pb²⁺ by PANI/CA with milli/nano hierarchical structure. There is a sharp increase of lead ion uptake in the first 5 min followed by a slow uptake process that takes about 35 min. And finally the lead

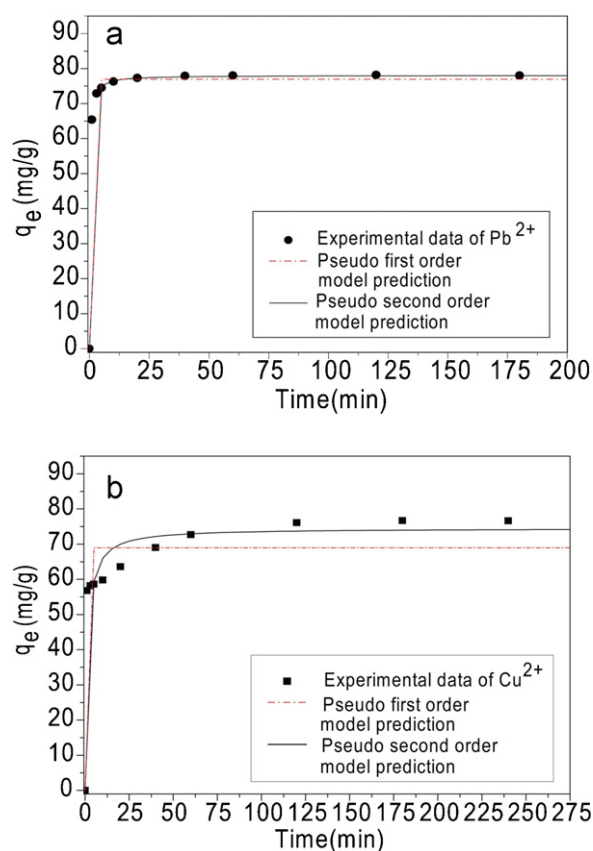


Fig. 5. Adsorption kinetics of metal ions: (a) Cu²⁺; (b) Pb²⁺ by PANI/CA hierarchical structure, CA and PANI nanofiber (dosage of adsorbents: 0.01 g, concentration of metal ions: 10 mg/L, $T=25^{\circ}\text{C}$, pH 5).

ion uptake reaches an equilibrium state at 40 min. Similarly, the adsorption amount of copper ion grows dramatically in the first 5 min. But then it undergoes a moderate growth during the following 115 min. Moreover, the adsorption of Cu^{2+} needs more than 1 h to reach equilibrium compared with the case of lead ions. In order to evaluate the adsorption kinetics of Cu^{2+} and Pb^{2+} onto the PANI/CA surface, the pseudo-first-order model of Lagergren (Eq. (5)) and pseudo-second-order model (Eq. (6)) are employed to interpret the experimental data.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (6)$$

where q_e (mg/g) and q_t (mg/g) denote the lead or copper ions uptake corresponding to the equilibrium time and the time t , respectively, while k_1 and k_2 are first-order and second-order rate constant, respectively.

The validities of these two kinetic models are checked and depicted in Fig. 4. The corresponding kinetic parameters and the correlation coefficients were calculated from the plots and summarized in Table 3. In light of the good correlation coefficient, it can be found that the pseudo-second-order model better described the sorption of Cu^{2+} and Pb^{2+} ions onto the PANI/CA sorbent with milli/nano hierarchical structure. Besides, the values of equilibrium adsorptive capacities of Cu^{2+} and Pb^{2+} predicted by pseudo-second-order model (74.50 mg/L, 78.50 mg/L) are closer to the experimental results (76.62 mg/L, 78.24 mg/L). In many cases, the first-order equation of Lagergren does not fit well to the whole range of contact time. It would only be applicable over the initial stage of the adsorption process [31]. The pseudo-second-order model is more likely to predict the adsorption behavior over the whole range of adsorption [32]. The pseudo-first-order model is mathematically equivalent to a mass action rate equation for sorption kinetics, while the pseudo-second-order model assumes that the rate limiting step is chemisorption of metal ions onto sorbent binding sites [33]. Thus we can infer that the removal of copper and lead ions by the PANI/CA hierarchical structure is a process that is mainly controlled by the chemical interaction between metal ions and binding sites. Notably, the correlation coefficient (R^2) of the pseudo-first-order model for Pb^{2+} sorption is much higher than that for Cu^{2+} sorption, which means the action of mass transfer becomes greater with the increase of the metal ion diameter.

3.5. Alginate calcium particle size effect

The PS microsphere is readily prepared by dispersion polymerization, and its SEM images are shown in Fig. 6a. After coating with CA, the surface of the PS microsphere become rough as illustrated in Fig. 6b. The PS/CA core-shell microsphere was further decorated with PANI nanofibers via the “competitive adsorption-restricted polymerization” method. From Fig. 6c, it can be seen that PANI nanofibers with the diameter of about 67 nm grow on the surface of PS/CA core-shell microsphere, which results in the micro/nano hierarchical structure. And finally the PS core was dissolved with ethyl acetate. The morphology of the PANI/CA capsules with micro/nano hierarchical structure is depicted in Fig. 6d.

The Cu^{2+} and Pb^{2+} uptake capacities of the PANI/CA capsules with micro/nano structure also have been investigated. The results are shown and compared with the capacity of the PANI/CA adsorbent with milli/nano structure (Table 4). Obviously, the decrease in the CA diameter from milli-scale to micro-scale leads to the higher Cu^{2+} and Pb^{2+} uptake amount of PANI/CA sorbent. The per mass unit of PANI/CA capsules with micro/nano hierarchical structure adsorbs 79 mg of Cu^{2+} and 357 mg of Pb^{2+} . It can be found that replacing CA beads by CA microcapsules increases the

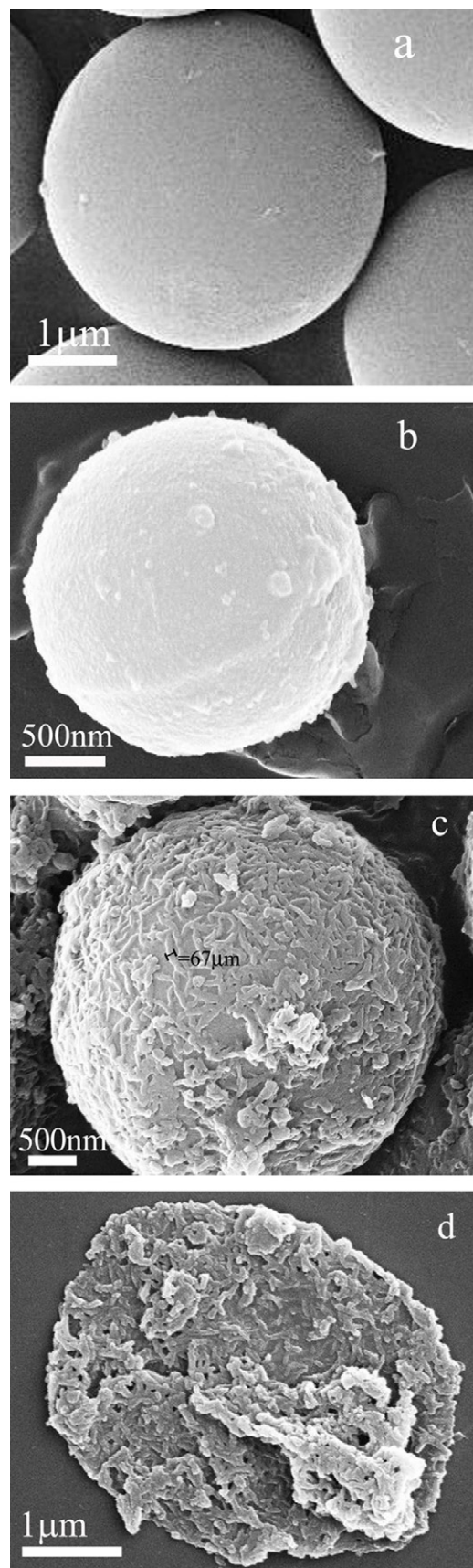


Fig. 6. SEM images of PS microspheres with 3.88 μm in average diameter (a), PS/CA core-shell microspheres (b), PS/CA core-shell microspheres decorated by PANI nanofibers (c) and CA micro-capsules decorated by PANI nanofibers (d).

Table 3
Kinetic model parameters for Cu²⁺ and Pb²⁺ uptake by the PANI/CA sorbent with milli/nano hierarchical structure.

Solution	$q_{e,exp}$	Pseudo-first-order model			Pseudo-second-order model		
		$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2
Cu ²⁺ (10 mg/L)	76.62	68.97	1.64	0.8950	74.50	0.010	0.9509
Pb ²⁺ (10 mg/L)	78.24	76.96	1.87	0.9949	78.05	0.064	0.9998

Table 4
Pb²⁺ and Cu²⁺ binding capacity of the PANI/CA adsorbent with different scale (mg/g).^a

Adsorbents	Time (min)							
	3	10	20	40	60	120	180	240
PANI/CA in milli/nano scale (Cu ²⁺ , mg/g)	58	60	64	69	73	76	76	76
PANI/CA in micro/nano scale (Cu ²⁺ , mg/g)	66	71	76	78	79	79	79	79
PANI/CA in milli/nano scale (Pb ²⁺ , mg/g)	146	202	227	231	235	235	235	235
PANI/CA in micro/nano scale (Pb ²⁺ , mg/g)	201	287	332	357	357	357	357	357

^a 0.01 g of the sorbents in a 80 mL solution of 10 mg/L of Cu(II) or 100 mg/L Pb(II) ions (pH 5, $T=25^\circ\text{C}$). At defined intervals, 5 cm³ of the solution was taken and measured by Varian Spectral spectrometer.

removal capacity of Pb²⁺ by 50%. In the mean time, as the diameter of CA decreases, the equilibrium time of Pb²⁺ and Cu²⁺ adsorption is reduced by about 33% and 50%, respectively. Although the PANI/CA capsule with micro/nano hierarchical structure shows the better adsorption property, its synthesis process and separation from solution is more complicated than that of the milli/nano scale PANI/CA sorbent.

3.6. Desorption and recyclability study

As mentioned in the discussion of the pH effect, the PANI/CA adsorbent with milli/nano hierarchical structure has a low removal efficiency of Cu(II) and Pb(II) at the pH value of 2. The phenomenon reveals that lots of protonated carboxylate and amino groups are unable to bind the metal ions in the strong acid medium. In terms of this, desorption study is performed in 1 mol/L HNO₃ solution. It was found that about 75% of Cu²⁺ and 62% of Pb²⁺ could be desorbed from the pre-adsorbed PANI/CA metal composite. This property is vital for the practical application of the PANI/CA adsorbent with milli/nano hierarchical structure. After treated with desorption, the PANI/CA adsorbent was reused to absorb the 10 mg/L of Cu²⁺ and Pb²⁺ in the solution with pH value of 5. The Cu²⁺ and Pb²⁺ removal percentages were 67% and 58% respectively, which were lower than that of the new absorbent (91%, 95%). However, the re-used absorbent could once again experience the process of desorption for recycling. Furthermore, the sequent nine reuse cycles did not show any significant decrease of adsorption capacity. This result indicates a possibility for extending the useful lifetime of the adsorbents, while further improving its practical application.

4. Conclusion

In summary, a novel PANI/CA sorbent with milli/nano hierarchical structure, which realizes the homogeneous distribution of PANI nanofibers on a large scale, shows high Cu²⁺ and Pb²⁺ removal percentage in a relatively wide pH range (3–7). Based on the results of adsorption isotherm, we found that the PANI/CA composite adsorbent has a higher adsorption capacity of Cu²⁺ and Pb²⁺ than the single-component sorbents. The Pb²⁺ and Cu²⁺ removal capacity of the sorbent could be further reinforced when the CA beads with millimeter scale turned to be CA microcapsules. Through the desorption process, this new type of PANI/CA can be reused to adsorb Cu²⁺ and Pb²⁺. Hence, this PANI/CA adsorbent not only vigorously promotes the practical application of PANI nanofiber, but also possesses great potential in the water treatment processes.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (51173153); the Special Program for Key Research of Chinese National Basic Research Program (2011CB612303); the Scientific and Technical Project of Fujian Province of China (2009J1009, 2010H6021).

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