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Adsorption behavior of humic acid onto polypyrrole-coated nylon 6,6 granules

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One of the challenges in water supply is the removal of humic substances as the unit treatment processes in a conventional water treatment plant are usually not effective for this purpose. In this study, nylon 6,6 granules were surface-modified by chemical polymerization of pyrrole and were used as a granular adsorbent for removing humic acid from water. Zeta potential study showed that the coated granules have positive surface charges over a wide range of pH values. X-Ray photoelectron spectroscopy (XPS) indicated that the positive surface charges of the coated granules are attributed to the protonated nitrogen atoms (*i.e.* N^+) in the polypyrrole (PPy) coating. Batch adsorption experiments were conducted under various conditions to examine the removal efficiency and mechanisms. PPy-coated nylon 6,6 granules were found to have much better removal of humic acid, as compared to the uncoated nylon 6,6 granules, suggesting the importance of electrostatic interactions between the positively charged granules and the negatively charged humic acid in the process. Evidence showed that although most adsorption may take place through non-specific electrostatic attraction, some adsorption occurred at specific sites and resulted in charge neutralization. It was found that low pH and high ionic concentration favored the adsorption performance and the adsorption kinetics involved both diffusion-controlled and attachment-controlled mechanisms.

Introduction

Humic substances are ubiquitous in the natural environment, including in soils, sediments, and various surface and ground waters.[1] The presence of humic substances in water resources is of major concern in the water supply, due to humic substances facilitating the transport of many organic and inorganic pollutants through the water treatment facilities, and also by reacting with chlorine during water treatment to produce trihalomethanes, which are known human carcinogens.[2] The unit treatment processes in a water treatment plant usually include coagulation, followed by sedimentation, filtration, and disinfection. It is desirable that the concentration of humic substances is minimized before the disinfection process. Although coagulation using alum has been widely used to enhance the removal of humic substances, the process incurs a high operational cost and generates extra volumes of sludge that are difficult to handle. In addition, aluminium exposure has been suspected to develop or accelerate the onset of Alzheimer's diseases.[3] The conventional filtration process, which uses sand as the filter media, has however long been found to be ineffective in removing humic substances. There has been considerable interest in the use of granular media that can enhance the removal of humic substances in water filtration.[4] One option is to replace the sand with activated carbon as the filter media. Because humic substances exhibit macromolecular features which exclude the small pores of activated carbon from playing a role in adsorbing humic substances, the application of activated carbon in a filter is not always technically advantageous for humic removal, due to the high regeneration cost involved.[5] Since the poor performance of a conventional filter in removing humic substances may be attributed to the unfavorable surface interactions (electrostatically repulsive) between the media grains and the humic substances to be removed, a simple remedy to the problem is to employ granules possessing positive surface charges as humic substances in water usually carry negative charges. A number of attempts have been made in this direction by coating sand with metallic compounds to develop positively charged surfaces.[6-8]

Polypyrrole (PPy), since it was first electrochemically synthesized more than two decades ago,[9] has attracted great interest in its potential applications in preparing actuators, chemical sensors and biosensors, electrodes, and electronic devices,[10–14] because of its environmental stability to oxygen and water, ease of synthesis, and high conductivity at room temperature.[15] More recently, we extended the application of PPy to surface-modification of glass beads as filter media or adsorbents. It was found that PPy-coated glass beads have high positive zeta potentials and greatly enhance the removal of negatively charged colloids, such as clay particles and humic acid.[16,17] These results suggest the significance of surface interactions in colloidal removal by granular media in systems such as deep bed filtration and fixed bed adsorption processes.

In this paper, we report the synthesis of granular media with positive surface charges, obtained by oxidative polymerization of pyrrole on the surface of nylon 6,6 granules. The surface morphology and composition of PPy-coated granules were studied through scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. The adsorption behavior of humic acid onto PPy-coated nylon 6,6 granules was investigated under various humic acid concentrations, salt concentrations and pH values. The results are presented below.

Experimental

Materials

Humic acid (defined as sodium salt) and pyrrole (99%) were purchased from Aldrich Chemical Company (USA). Pyrrole was distilled before use. $(NH_4)_2S_2O_8$ (98%) supplied by Merck (Darmstadt, Germany) was used as the oxidant in the polymerization of pyrrole. Nylon 6,6 granules, with a diameter of

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3.0 mm and a density of 1.12 g cm^{-3}, were obtained from Solutia Inc. (Missouri, USA). Before the experiments, the nylon 6,6 granules were thoroughly washed with deionized (DI) water followed by methanol, then dried under reduced pressure. All other chemicals used in the study were of analytical grade. DI water was used to prepare all the solutions.

Polypyrrole coating

The granular media with positive surface charges were prepared by polymerization of pyrrole onto the nylon 6,6 granules. The preparation process is as follows. A 25 g amount of $(NH_4)_2S_2O_8$ was dissolved in 100 mL of DI water. A 150 g amount of nylon 6,6 granules was then added to the solution. About 5 min later, a solution containing 10 mL of pyrrole dispersed in 10 mL of DI water was added in droplets into the mixture with vigorous stirring. The colour of the mixture rapidly became black. The polymerization of pyrrole on the nylon 6,6 granules was allowed to continue for 3 h and the coated granules were then removed from the mixture, washed with DI water and alcohol, and air-dried for 24 h prior to use.

Batch adsorption experiments

Humic acid solution was prepared by dissolving a certain amount of humic acid in a known volume of DI water. The solution was stirred for 1 h and filtered through a Whatman membrane filter (0.45 μm) before conducting the adsorption tests.

Batch adsorption experiments were conducted by adding a 10 g amount of PPy-coated nylon 6,6 granules to 100 mL of humic acid solution in a glass flask. The flask was slowly shaken at 60 rpm for 48 h at room temperature. Solution samples were taken and analyzed periodically to determine the solution concentration histories. Similar experiments were also conducted using nylon 6,6 granules without PPy-coating. The concentration of humic acid remaining in the solution at different times was determined by an ultraviolet–visible spectrophotometer (Hitachi UV-2000) at 400 nm. The adsorbed amount of humic acid per unit weight of granules at time t, $q(t)$ (mg g^{-1}), was calculated from the mass balance equation, eqn. (1):

$$q(t) = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

where C_0 and C_t (mg L^{-1}) are the initial humic acid concentration and the humic acid concentrations at time t, respectively; V is the volume of the humic acid solution, and m is the mass of the granules.

To study the adsorption kinetics of humic acid onto PPy-coated nylon 6,6 granules, batch adsorption experiments were carried out at different initial humic acid concentrations (C_0 = 5–60 mg L^{-1}), different initial pH values (pH = 2–12), and different ionic concentrations (NaCl = 0–0.3 M) at room temperature. HCl and NaOH were used to adjust the solution pH values as necessary.

Zeta potential measurements

The zeta potentials of humic acid and the nylon 6,6 granules with and without coated PPy were measured with a Zeta Plus4 Instrument (Brookhaven Instruments Corp.). Measurements were made at different pH values and ionic concentrations. For the granules, the zeta potentials of the fragments from the granules' surfaces were taken as an estimation of the zeta potentials of the granules, according to the method described by Bai and Tien.[18] All samples were vibrated in an ultrasonic bath for 1 min before making the measurements and an average value from several measurements was used as a representative value.

SEM measurements

The surface morphologies of coated and uncoated nylon 6,6 granules were examined by a scanning electron microscope (SEM). A JEOL JSM-6400 instrument was used and the images were taken at 10000 × magnifications at 15 kV. The granules were mounted on a metal sample substrate by double-sided adhesive tapes, coated with platinum, degassed and then scanned by the microscope to obtain the images.

XPS measurements

The X-ray photoelectron spectroscopy (XPS) study was made on a VG ESCALAB MKII spectrometer with an Al Kα X-ray source (1486.6 eV photons). All binding energies were referenced to the C 1s neutral carbon peak at 284.6 eV and surface elemental stoichiometries were determined from sensitivity-factor corrected peak area ratios, with the software XPSpeak 4.1 being used to fit the XPS spectra peaks through a pure Gaussian line shape. The line-width (full width at half maximum; FWHM) was maintained constant for all the components in a particular spectrum. The intensities were calculated from the peak areas given by the fitting program.

Results and discussion

Surface morphologies

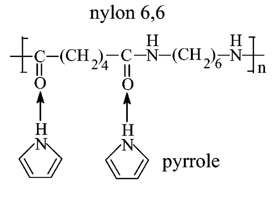
Nylon 6,6 granules were chosen as the substrate because of the possible formation of chemical bonds between the nylon 6,6 surfaces and the polypyrrole molecules.[19] The adsorption of pyrrole at the substrate/liquid interfaces during the polymerization process therefore dictates the resulting structure of PPy coating. The carbonyl groups on the nylon backbones can provide a template for pyrrole monomers *via* hydrogen bonds, then yield a higher ordered and coherent PPy.[20] The structure may be as shown in Scheme 1.[21]

Fig. 1 shows the SEM micrographs of a nylon 6,6 granule and a PPy-coated nylon 6,6 granule. The uncoated granule has a smooth, featureless surface morphology, but a large number of fine PPy particles, of 0.3–0.5 μm or smaller, are present on the surface of PPy-coated granule. The agglomeration of PPy particles leads to a porous and sponge-like morphology, which can be expected to enhance the removal of pollutants from water due to its rough surface and increased surface area.

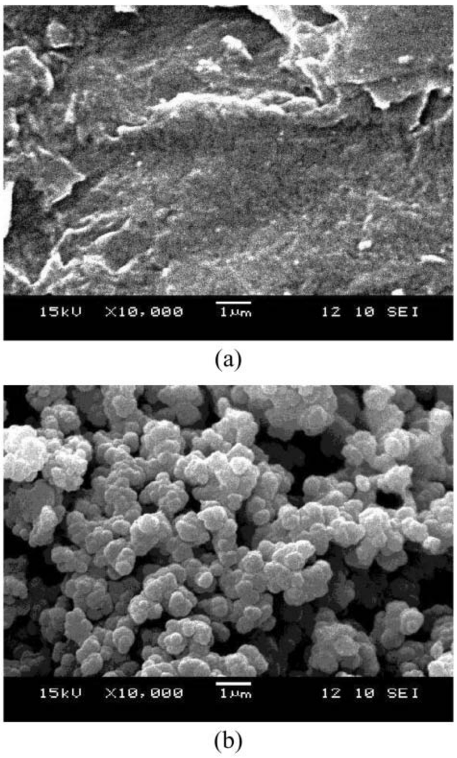
Zeta potentials

The zeta potentials of coated and uncoated nylon 6,6 granules as a function of solution pH values are shown in Fig. 2(a). For PPy-coated nylon 6,6 granules, the zeta potentials are positive for pH below about 10.5, and over the range of pH = 3 to pH = 10, they remain relatively constant (approximately 40 mV). In contrast, the zeta potentials of the uncoated nylon 6,6 granules are only positive at a pH below around 3, and, for the most part of the pH range, are negative. The zeta potentials of humic acid are negative for all pH values greater than about 1.7.

In Fig. 2(b), the variations of the zeta potentials of coated and uncoated nylon 6,6 granules, and humic acid with ionic concentrations are presented. As expected, with the increase of



Scheme 1 Structure of pyrrole momomers bound to a nylon 6,6 granule



(a)

(b)

Fig. 1 SEM images showing the surface morphologies of (a) an uncoated nylon 6,6 granule; and (b) a PPy-coated nylon 6,6 granule.

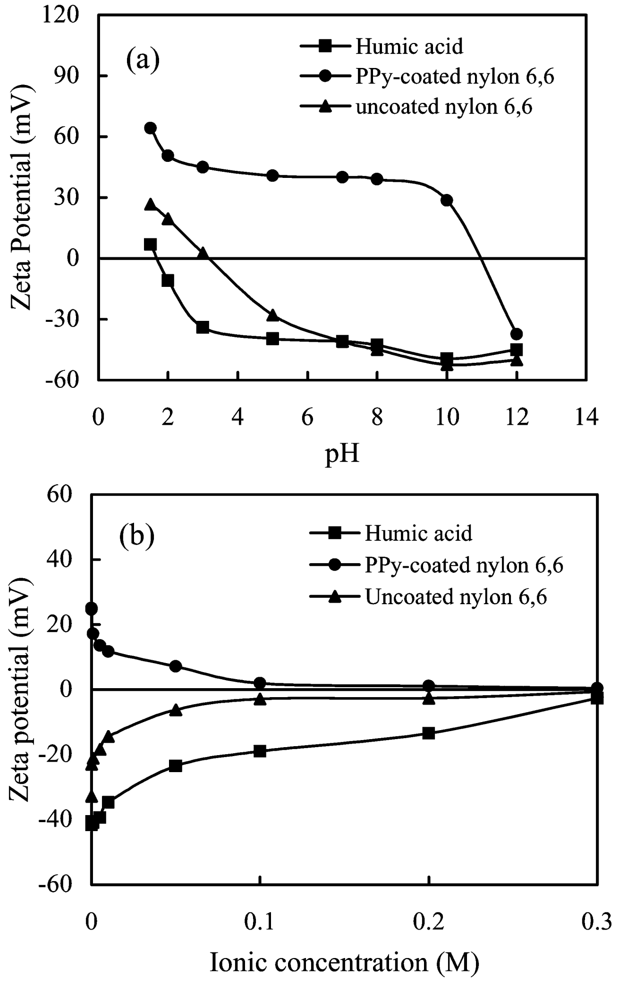


Fig. 2 Zeta potentials of humic acid, nylon 6,6 granules, and PPy-coated nylon 6,6 granules as (a) a function of pH; and (b) a function of ionic concentration (NaCl, M).

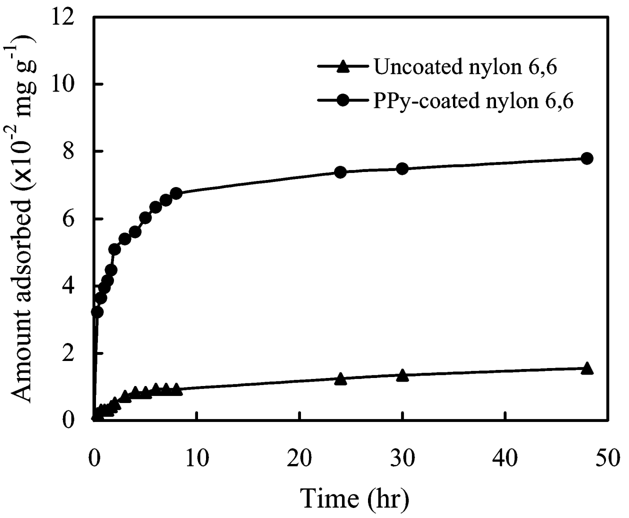


Fig. 3 Typical results showing the amount of humic acid adsorption as a function of time (C_0 = 15 mg L^{-1}, V = 100 mL, quantity of granular media = 10 g, pH = 6.5, no electrolyte added).

ionic concentration, the zeta potentials of the PPy-coated nylon 6,6 granules become less positive, and those of the uncoated nylon 6,6 granules and humic acid become less negative. These results can be attributed to the screening of surface charges and the compression of the double layers due to increased ionic concentrations.

Since PPy-coated granules have positive zeta potentials and humic acid has negative zeta potentials in a wide range of pH values (*e.g.* pH = 2–10), the removal of humic acid by PPy-coated granules can be expected to be enhanced at these pH values, as a result of favorable electrostatic interactions (attractive) between the granules and humic acid. However, in terms of zeta potential, increasing ionic concentration may inversely affect humic acid adsorption as the magnitudes of the opposing zeta potentials (of the coated granules and of the humic acid to be removed) are reduced.

Batch adsorption performance

As shown in Fig. 3, only a small amount of humic acid was adsorbed by uncoated nylon 6,6 granules, but a significant amount of humic acid was adsorbed by the PPy-coated nylon 6,6 granules. The amount of humic acid adsorbed onto the PPy-coated granules is estimated to be up to 7.8×10^{-2} mg g^{-1} in this case (initial humic acid concentration 15 mg L^{-1}, 10 g granules, 100 mL solution, and pH = 6.5), as compared to 1.6×10^{-2} mg g^{-1} for the uncoated granules.

At pH = 6.5, both humic acid and uncoated nylon 6,6 granules have negative zeta potentials. An electrostatic repulsion can occur between the humic acid molecules to be removed and the surfaces of uncoated nylon 6,6 granules. In contrast, PPy-coated nylon 6,6 granules have positive zeta potentials that can result in attractive electrostatic interactions between the humic acid molecules to be removed and the surfaces of the coated nylon 6,6 granules. The results in Fig. 3 therefore show the importance of the electrostatic interactions in the adsorption of humic acid by granular materials.

XPS results

Figs. 4 and 5 show the C 1s and N 1s spectra, respectively, for the uncoated nylon 6,6 granules, the PPy-coated nylon 6,6 granules, and the PPy-coated nylon 6,6 granules with humic acid adsorbed. From Fig. 4a, the C 1s line of the nylon 6,6 granules can be fitted to three peaks at 284.6, 285.6 and 287.7 eV, respectively. The lowest binding energy peak at 284.6 eV is due to the C–C or C–H carbons in the nylon 6,6

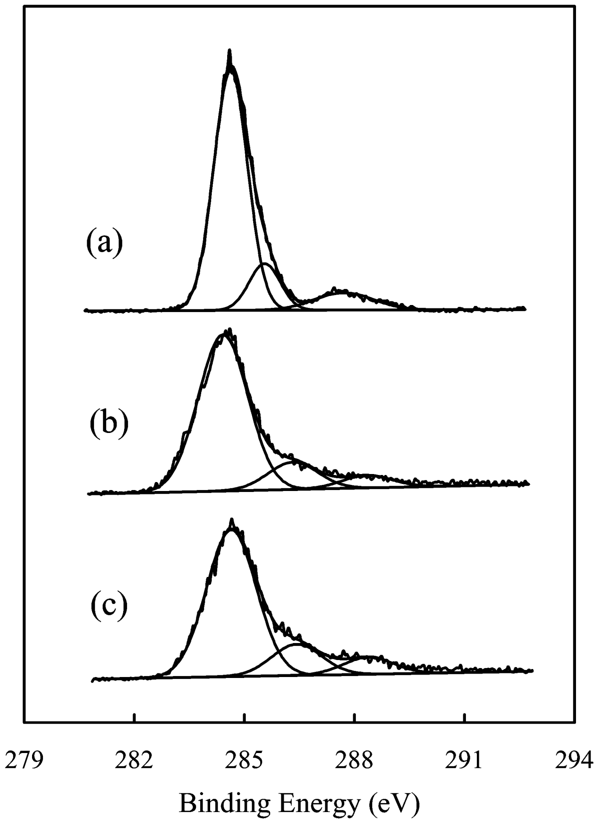


Fig. 4 C 1s XPS spectra for (a) nylon 6,6 granules; (b) PPy-coated nylon 6,6 granules; and (c) PPy-coated nylon 6,6 granules adsorbed with humic acid.

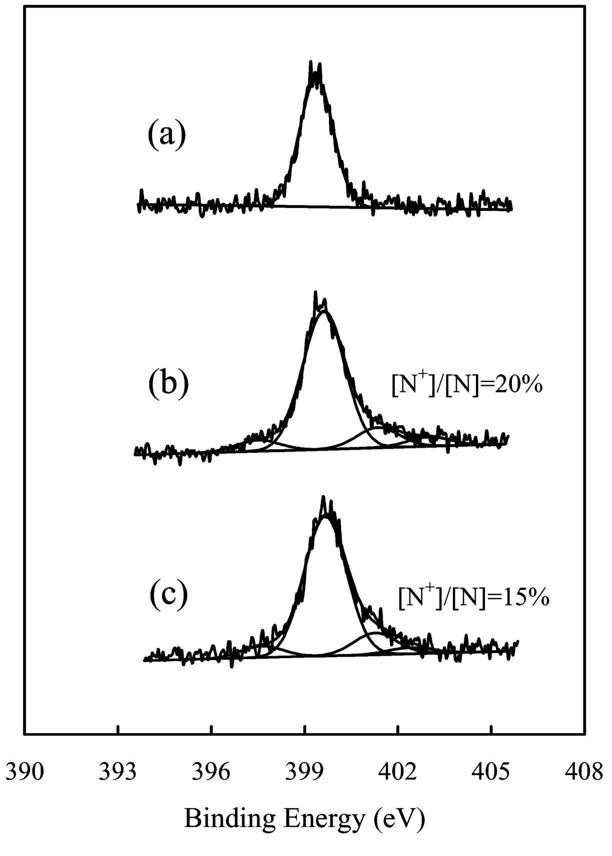


Fig. 5 N 1s XPS for (a) nylon 6,6 granules; (b) PPy-coated nylon 6,6 granules; and (c) PPy-coated nylon 6,6 granules adsorbed with humic acid.

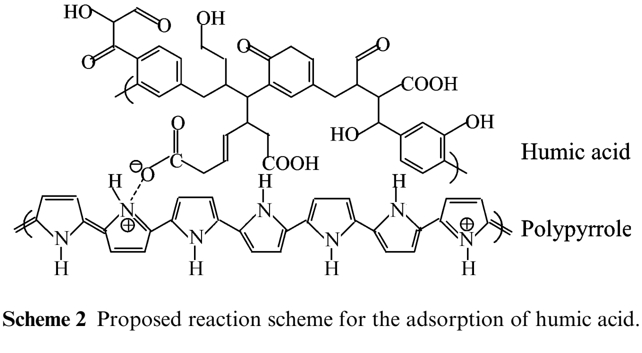
polymer chain while the higher binding energy peaks at 285.6 and 287.7 eV are attributed to the C–N and NH–C=O carbons, respectively. The C 1s spectrum of the PPy-coated nylon 6,6 granules can be fitted to three peaks at 284.6, 286.4 and 288.1 eV; see Fig. 4(b). The shift of binding energies at 285.6 and 287.7 eV in the nylon 6,6 granules to 286.4 and 288.1 eV in the PPy-coated nylon 6,6 granules is a clear indication of the existence of PPy on the surfaces. The lowest binding energy peak at 284.6 eV can be attributed to the β-carbons (C–C), and the intermediate peak at 286.4 eV to the α-carbons (C–N), respectively, in the pyrrole rings. The binding energy peak at 288.1 eV may be due to the C–O and C=O carbons in the polymer chain.[22] The C 1s spectrum of the PPy-coated nylon 6,6 granules with adsorbed humic acid in Fig. 4(c), however, does not show any obvious differences to that in Fig. 4(b). This may be partly due to the complex carbon bonds in the humic acid and partly due to the penetration of the X-rays into the PPy surface. The sizes of the adsorbed humic acid measured by AFM were found to be in a range below 10 nm, while XPS with Al Kα X-ray source can penetrate up to 20 nm in depth.[23]

For the N 1s spectra in Fig. 5, there is only one peak at 399.7 eV for uncoated nylon 6,6 granules; see Fig. 5(a). This peak can be attributed to the amide nitrogen (–CO–NH–) present in the nylon 6,6 polymer.[24] For the PPy-coated nylon 6,6 granules shown in Fig. 5(b), the N 1s spectrum can be fitted with four peaks at 397.6, 399.7, 401.4 and 403.0 eV. These peaks are due to the imine-like nitrogens (=N–), the neutral amine nitrogens (–NH–), and the positively charged nitrogens (=NH$^+$–), respectively, in the PPy coating.[16] It is these protonated nitrogens contributing to the positive zeta potentials of the PPy-coated nylon 6,6 granules. The proportion of positively charged nitrogen atoms ([N$^+$]/[N] ratio) of the PPy-coated nylon 6,6 granules in this study is about 20%, which is lower than the 25–30% for the [N$^+$]/[N] ratio in the PPy when $FeCl_3$ was used as the oxidant,[16,25] possibly due to the lower oxidation potential of $(NH_4)_2S_2O_8$ as compared with that of $FeCl_3$, since the oxidation potential of the solution was reported to strongly affect the polymerization process.[26] After adsorption of humic acid, the results in Fig. 5(c) show that the [N$^+$]/[N] ratio was reduced to about 15%. This indicates that some adsorption occurred at specific sites with N$^+$, and the positively charged nitrogen atoms reacted with the humic acid, resulting in charge neutralization. The process may proceed by the formation of organic complexes, as shown in Scheme 2. The basic structure of humic acid in Scheme 2 is according to the model suggested by Jansen *et al.*[27]

XPS analysis also showed that the humic acid used in the study has a C : H : N ratio of 0.455 : 0.044 : 0.0073 and contains no protonated N$^+$. Therefore, a change in the N$^+$/N ratio before and after humic acid adsorption is unlikely due to the composition of the humic acid itself.

Effect of pH and ionic concentration on adsorption

Adsorption of humic acid to solid surfaces is generally a pH-dependent process. In this study, the performance of humic acid adsorption by PPy-coated nylon 6,6 granules was



Scheme 2 Proposed reaction scheme for the adsorption of humic acid.

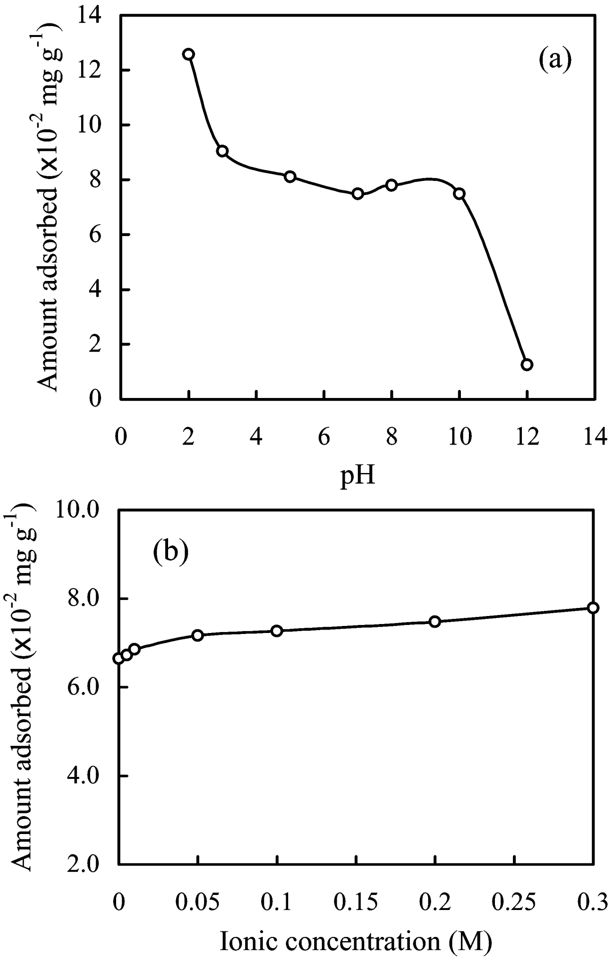


Fig. 6 Amount of humic acid adsorbed at adsorption equilibrium, showing (a) the effect of pH; and (b) the effect of ionic concentration (C_0 = 15 mg L^{-1}, V = 100 mL, quantity of granular media = 10 g, pH = 6.5).

examined at pH values ranging from 2 to 12. From the results shown in Fig. 6(a), the capacity for humic acid adsorption is found to increase in general with decreasing pH, and there was hardly any adsorption of humic acid at pH = 12. Since the zeta potentials of both the PPy-coated nylon granules and the humic acid are negative at pH = 12 (see Fig. 2), the electrostatic repulsion between the humic acid molecules to be adsorbed and the surfaces of the PPy-coated nylon 6,6 granules most probably prevented humic acid from approaching close enough to the surface of the granules for adsorption to take place. From pH = 10 to pH = 3, the zeta potentials of the PPy-coated nylon granules and the humic acid are of opposite sign to each other and are relatively constant. Hence, the interactions between the granules and the humic acid were electrostatically attractive, which led to significant adsorption of the humic acid onto the PPy-coated granules. The large increase of adsorption between pH 3 and 2 may be attributed to a reduction in the size of the humic acid molecules at low pH.[28] Smaller molecular sizes enable more molecules to be adsorbed on the granules' surfaces.

The effect of ionic concentrations on the adsorption performance is shown in Fig. 6(b). Increasing ionic concentrations resulted in slight increases in the amount of humic acid adsorption. The increase in ionic concentration reduced the electrostatic attraction between the negatively charged humic acid molecules and the positively charged granules, and, on the other hand, also reduced the electrostatic repulsion between the humic acid molecules adsorbed and the humic acid molecules to be adsorbed. The first effect may decrease the amount of adsorption, but the second effect can enhance the amount of adsorption. For higher ionic concentrations, the experimental results appear to indicate that the second effect is slightly more significant than the first effect, hence resulting in increased adsorption with the increase of ionic concentrations.

An experimental comparison was conducted for the adsorption performance of polypyrrole powder collected from the polymerization reaction (0.5–1 mm) and activated carbon (0.43–0.85 mm purchased from Aldrich Chemical Company). A 0.1 g amount of polypyrrole powder or activated carbon was put into 25 mL of humic acid solution (15 mg L^{-1} humic acid, pH = 6.5) at room temperature for 24 h with slow shaking. The amounts of humic acid adsorbed onto the PPy powder and activated carbon were determined to be 3.69 mg g^{-1} and 1.82 mg g^{-1}, respectively. The specific surface areas of the PPy powder and the activated carbon were determined to be 7.8 m^2 g^{-1} and 1008 m^2 g^{-1}, respectively. The results therefore indicate that most of the surface area of the activated carbon is not available for humic acid adsorption, due to the large molecular size of the humic acid.

Adsorption kinetics

Recent studies have suggested that the adsorption of humic acid onto solid surfaces can be viewed as two processes: (1) transport from the bulk solution to the subsurface plane adjacent to the surface, and (2) attachment to the surface.[29] During the initial stages, the PPy coating on the coated granules is bare and the kinetics of adsorption may be considered as a transport-controlled process by the diffusion of humic acid molecules from the bulk solution to the subsurface, as all the humic acid molecules that arrive at the subsurface may be assumed to be immediately adsorbed. The mass transport can be interpreted as a Fickian diffusion

$$A(t) = \frac{2}{\sqrt{\pi}} C_0 \sqrt{Dt} \tag{2}$$

where $A(t)$ is the amount adsorbed per unit area surface of the granules at time t, D is the diffusion coefficient of the humic acid molecule in solution and C_0 is the initial bulk concentration.

The plot of $A(t)$ *versus* $t^{0.5}$ according to eqn. (2) in the initial stages of adsorption is shown in Fig. 7. $A(t)$ was calculated from $q(t)$ and the specific surface area, which was measured by a Quantachrome NOVA 1000 analyzer. From Fig. 7(a), a linear dependence of $A(t)$ *versus* $t^{0.5}$ is evident for small values of initial humic acid concentration, but the relationship deviates from a straight line after a very short period of time when the initial humic acid concentrations were high, which is an indication that the adsorption process changed from a transport-controlled to an attachment-controlled process. When the available sites for adsorption on the surface became fewer, not all the humic acid molecules transported to the surface can be immediately adsorbed. In addition, when a layer of humic acid was adsorbed on the surface, the electrostatic repulsion between the adsorbed layer and the incoming humic acid molecules hinders the transport of humic acid from the bulk solution to the subsurface.

Fig. 7(b) shows the effect of solution pH on the adsorption kinetics. A linear relationship between $A(t)$ and $t^{0.5}$ can again be observed. Decreasing pH caused an increase of the adsorption rate (increase of the slope). This can be attributed to a decrease of the hydrodynamic volume (or size) of the humic acid molecules at a decreased pH value,[28] since humic acid molecules of a smaller size can be transported faster by diffusion. At a high pH such as pH = 12, however, both the swelling of the humic acid molecules and the repulsive electrostatic interactions between the PPy-coated nylon 6,6 granules and the humic acid molecules to be adsorbed would

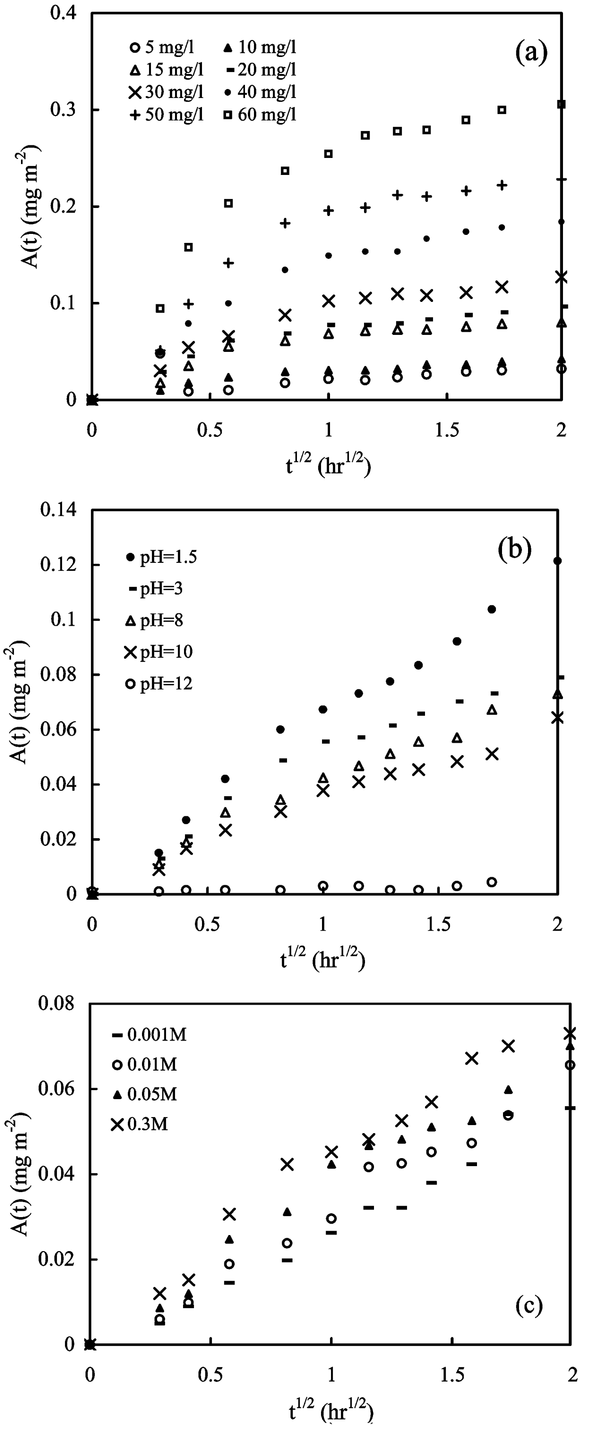


Fig. 7 Adsorption of humic acid as a function of $t^{0.5}$ at (a) different initial concentrations of humic acid C_0 (pH = 6.5, no electrolyte added); (b) different solution pH values (C_0 = 15 mg L^{-1}, no electrolyte added); and (c) different ionic concentrations (pH = 6.5, C_0 = 15 mg L^{-1}).

reduce the rate of adsorption, as the process in this case becomes both transport- and attachment-controlled.

Similarly, a higher ionic concentration resulted in a greater adsorption rate; see Fig. 7(c). As mentioned earlier, a higher ionic concentration could cause the humic acid molecules to form a denser and smaller structure. Due to a faster diffusion rate, the adsorption rate could increase. Furthermore, with a smaller size and a lower zeta potential at a higher ionic concentration, the humic acid molecules can more easily fit their shape and conformed into the adsorbed humic acid layer on the granules' surface and thus enhance the adsorption rate.

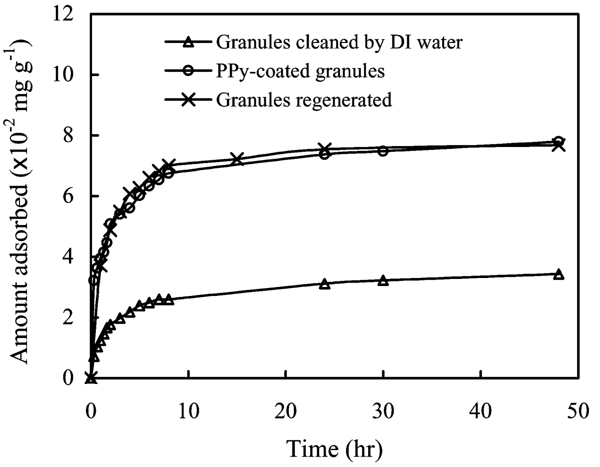


Fig. 8 Effect of cleaning/regeneration of PPy-coated granules on its adsorption capacity (C_0 = 15 mg L^{-1}, V = 100 mL, quantity of granular media = 10 g, pH = 6.5).

Cleaning/regeneration of the PPy-coated granules

As a preliminary study, experiments were conducted to examine the effect of cleaning/regeneration of the coated granules on the adsorption performance. The PPy-coated granules, after adsorption of humic acid, were washed repeatedly with DI water and then used in another batch adsorption experiment. As shown in Fig. 8, the adsorption capacity of the granules after cleaning with DI water decreased to about half their original adsorption capacity. This could be attributed to the strong electrostatic attraction between the granular surfaces and the humic acid adsorbed, which prevented the adsorbed humic acid from being effectively cleaned by the DI water, and therefore caused the lower adsorption capacity for the granules. However, if the granules with adsorbed humic acid were regenerated with NaOH and HCl solution (immersed in 1.0 M NaOH solution and 1.0 M HCl solution, respectively, and then washed with DI water), the results in Fig. 8 indicate a complete recovery of the adsorption capacity. When the used granules were immersed in an NaOH solution, a deprotonation reaction took place and the humic acid molecules bound to the positively charged nitrogen sites were released into the solution. The acid solution then protonated the granules and recovered their adsorption capacity.

Conclusions

Polypyrrole can be coated onto the surface of nylon 6,6 granules through chemical polymerization of the pyrrole using $(NH_4)_2S_2O_8$ as an oxidant. The coated granules possess positive zeta potentials over a wide range of pH values and give enhanced removal of humic acid, due to the favorable (electrostatically attractive) surface interactions between the granules and humic acid to be removed. In general, the amount of humic acid adsorption increases with decreasing pH and increasing ionic concentration. The adsorption kinetics are affected by both transport-controlled and attachment-controlled mechanisms.

Acknowledgements

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