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Removal of Humic Acid Using PEI-Modified Fungal Biomass

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Abstract: A modified fungal biomass was prepared through the adsorption of polyethylenimine (PEI) and subsequent crosslinking with glutaraldehyde on the biomass surface. FTIR result verified that the amine groups were introduced on the biomass surface. As a large number of amine groups are present on the biomass surface and can be protonated in solution, the modified biomass was positively charged at $\text{pH} < 10.3$. The modified biomass was used as an adsorbent to remove humic acid in a series of batch adsorption experiments. The amount of humic acid adsorbed on the biosorbent decreased with increasing solution pH, and the electrostatic interaction between the positive protonated amine groups on the biomass surface and the negative carboxyl groups in the humic acid molecules played an important role in humic acid adsorption. The time-dependent sorption of humic acid on the biomass can be described well by the Fickian diffusion model at the initial stage and the pseudo-second-order equation over 10 h. Using the Langmuir adsorption isotherm, the maximum sorption capacity of the modified biomass for humic acid at pH 5 was 96.5 mg/g. The desorption experiments showed that the humic acid loaded biomass could be easily regenerated in a 0.1 M NaOH solution, and the regenerated biomass possessed good adsorption capacity up to the

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fifth cycle. The PEI-modified biomass with polyamine chains shows the potential for application in water treatment for the removal of humic substances.

Keywords: PEI-modified biomass, zeta potential, adsorption behavior, humic acid, FTIR analysis

INTRODUCTION

Humic substances, a kind of flexible macromolecular polyelectrolyte, are commonly present in natural water. They not only cause undesirable color and taste problems, but also are very active in binding metal ions and organic substances, which increases their transportation in water (1, 2). In addition, humic substances can serve as food for bacterial growth and can react with chlorine in water treatment to produce carcinogens and suspected carcinogens. Recent studies also show that membrane fouling by humic substances in water is a critical issue in the successful application of membrane; long-term flux decline occurs which cannot be fully recovered by hydraulically cleaning the membrane (3–5). Hence, it is desirable to minimize the presence of humic substances in natural water.

Adsorption technology is an effective method for humic acid removal from aqueous solution. Biosorption, which involves the use of inactivated biomass, including algae, bacteria, fungi, and yeasts for passive sorption in pollutant removal, has attracted considerable attention in recent years (6). As the biomass employed is often the byproducts of food, beverage, or pharmaceutical production, it is a viable alternative for the development of inexpensive biosorbents (7). However, the sorption capacity for pollutants is generally low due to the low density of effective functional groups on the pristine biomass.

Functional groups such as carboxylate, hydroxyl, sulfate, phosphate, amide, and amino groups on the biosorbents have been reported to be responsible for adsorbate sorption (8), and the sorption mechanisms including ion exchange, electrostatic interaction, and surface complexation have been elucidated in the sorption process (9, 10). For anionic humic substances, the surface electrostatic interaction between the positively charged adsorbents and the negatively charged humic acid has been found to play an important role in the adsorption process (11–13). Adsorbents such as metal oxides, polypyrrole-coated granules, and chitosan have been found to be effective in adsorbing humic acid from aqueous solutions as they all possessed high zero point of zeta potential (11, 14). Our previous study showed that the polyacrylonitrile fibers modified with diethylenetriamine had a zero point of zeta potential at pH 8.1 and enhanced the sorption capacity for humic acid (13).

In this study, polyethylenimine (PEI) was chemically bonded to the fungal biomass of *Penicillium chrysogenum* through a simple crosslinking reaction. As PEI is a macromolecular polymer with long chains of polyamine, it may increase the density of amine groups on the biomass surface and thus increase the sorption capacity for anionic adsorbates. Many conventional microporous adsorbents were found to be ineffective in removing humic acid due to the unaccessible inner micropores for macromolecular humic substances (15, 16). The fungal biomass with long chains of polyamines can overcome this disadvantage and increase sorption capacity for humic acid. The novel PEI-modified biomass was found to possess positive zeta potentials over a wide range of pH values, and thus is favorable for humic acid removal. The adsorption performances of humic acid on the modified bioamss including effect of pH, sorption kinetics and isotherm were investigated, and desorption kinetics and the reuse of the biomass were also studied.

MATERIALS AND METHODS

Materials

The strain *P. chrysogenum* (No. 3.3890) was purchased from China General Microbiological Culture Center, Beijing, China. Polyethylenimine (molecular weight of 25,000, branched polymer, $(\text{-NHCH}_2\text{CH}_2\text{-})_x[\text{-N}(\text{CH}_2\text{CH}_2\text{NH}_2)\text{CH}_2\text{CH}_2\text{-}]_y$), glutaraldehyde ($\text{OHC}(\text{CH}_2)_3\text{CHO}$) and humic acid (as a sodium salt) used in this study were purchased from Sigma-Aldrich Company. Other chemicals were of reagent grade.

Growth and Preparation of Biomass

P. chrysogenum was cultivated on 3.9% (w/v) potato dextrose agar in Petri dishes and incubated for 7 days at 30°C. The spores on the Petri dish were added to 100 mL of sterilized liquid medium in a 250 mL conical flask. The composition of the liquid medium was as follows: 30 g glucose, 2 g NH_4NO_3, 2 g yeast extract, 1 g KH_2PO_4, 0.5 g $MgSO_4 \cdot 7H_2O$, and 0.5 g KCl in 1 L deionized water with the initial pH of 5.5. The fungus was cultured on a rotary shaker at 140 rpm and 30°C for 3 days, after which the biomass with a uniform diameter of about 3 mm was obtained and autoclaved at 121°C for 15 min, and then filtered and washed with deionized water.

Surface Modification

The freeze-dried biomass was modified as follows: a 5 g amount of the biomass was added in 10% (w/v) PEI in methanol solution for 24 h at 25°C, and then transferred to a 500 mL solution of glutaraldehyde at various concentrations for a desired time at 25°C. The modified biomass was thoroughly rinsed with deionized water, after which it was freeze-dried and kept in a desiccator before use.

FTIR Spectroscopy

The samples of the biomass before and after chemical modification were analyzed with a Bio-Rad FTS-3500 ARX FTIR spectrophotometer under ambient conditions. Before the analysis, the wet samples were freeze-dried, and each sample was placed on a gold film and determined in reflection mode over the wavenumber range of 400–4000 cm^{-1}.

ζ-Potential Measurement

A 0.2 g of freeze-dried biomass was cut into small pieces and placed into 100 mL of deionized water and stirred for 2 h. The pH of the solution was adjusted with 0.1 M NaOH or 0.1 M HCl. After 1 h of stabilization, the final solution pH was recorded, and the supernatant with small fragments was then decanted and used to conduct ζ potential measurements with a Zeta-Plus 4 instrument (Brookhaven Corp., USA). All data were determined five times, and the average value was adopted. The ζ potentials of humic acid were also determined in a similar procedure as described above.

Adsorption and Desorption Experiments

50 mL of humic acid solution was added to a 100 mL flask, before 0.05 g of biomass was added to the solution in the batch experiments. The flask was shaken at 120 rpm for 10 h at 25°. The final biomass was separated by filtration and the humic acid concentrations in the filtrate were measured using an UV-visible spectrometer (Agilent 8453, Germany) at 254 nm. In the experiment on pH effect, the humic acid concentration was 100 mg/L. During the studies of adsorption kinetics, a 0.05 g amount of the modified biomass was added to 50 mL of 100 mg/L or 50 mg/L humic acid solution at pH 5. The investigation on the sorption isotherm of the pristine and modified biomass was conducted at pH 5, with the initial humic acid concentrations varying from 10 to 800 mg/L.

In desorption experiments, the humic-acid adsorbed biomass (after humic acid adsorption at initial pH 5 with 0.05 g of the biomass in 50 mL of 100 mg/L humic acid solution for 10 h) were regenerated in 50 mL of 0.1 M NaOH solution for 2.5 h and then washed with 0.1 M HCl solution, and finally with DI water. The regenerated biomass was used to adsorb humic acid for the next cycle.

RESULTS AND DISCUSSION

Preparation of Modified Biomass

In the surface modification experiments, the crosslinking agent, glutaraldehyde, can fix the PEI onto the biomass surface so as to avoid desorption of PEI from the biomass during both the sorption and regeneration processes. However, the crosslinked reaction can decrease the sorption capacity for humic acid due to the crosslinking between amine groups in PEI and glutaraldehyde. Hence, it is necessary to determine the optimal reaction conditions including the crosslinking time and glutaraldehyde concentration in the preparation of the modified biomass. It was found that the use of glutaraldehyde at a higher concentration and longer crosslinking time resulted in a more rigid biomass, but the sorption capacity decreased. Our experimental results show that the biomass obtained at 1% glutaraldehyde concentration for 20 min reaction time possessed a better adsorption capacity and good mechanical strength (17). After the crosslinking reaction, the modified biomass became more rigid than the pristine one, which is more amenable for actual sorption application.

Figure 1 shows the FTIR spectra of the pristine biomass and PEI-modified biomass. The spectrum of the pristine biomass is complex due to the numerous and multifarious functional groups on the surface of the biomass. The peaks at 3402, 2936, 1674, 1558, 1161, and 1115 cm^{-1} are observed in the original biomass spectrum shown in Fig. 1a. The broad and strong band ranging from 3200 to 3600 cm^{-1} may be due to the overlapping of OH and NH stretching, which is consistent with the peak at 1115 and 1161 cm^{-1} assigned to alcoholic C-O and C-N stretching vibration (18), thus showing the presence of hydroxyl and amine groups on the biomass surface. The strong peak at 1674 cm^{-1} can be assigned to a C=O stretching in carboxyl or amide

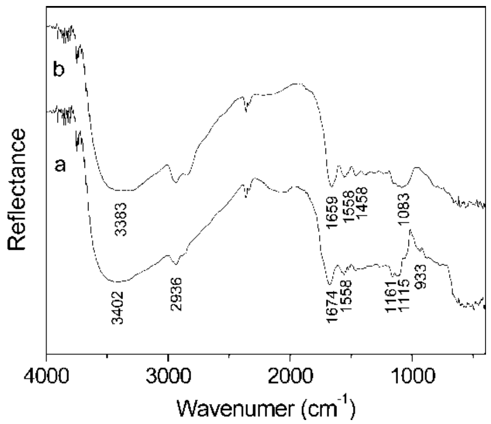

Figure 1. FTIR spectra of (a) the pristine biomass and (b) PEI-modified biomass.

groups. The bands at 2936 cm^{-1} and 1558 cm^{-1} are attributed to CH stretching and N-H bending, respectively. The polysaccharide presence is verified by the weak peak at 933 cm^{-1} attributed to the glycoside bonds in the polysaccharide structure, and the peaks in the range of 1000–1200 cm^{-1} to C-O stretching.

After PEI was crosslinked with the biomass, the spectrum exhibits some changes (see Fig. 1b). The broad overlapping peak shifts to 3383 cm^{-1} because a large number of amine groups in PEI were introduced on the surface and some hydroxyl groups formed during the crosslinking reaction. As the imine group formed in the crosslinking reaction has the characteristic peak at around 1650 cm^{-1}, the peak of C═O stretching at 1674 cm^{-1} shifts to 1659 cm^{-1} due to the overlapping. The new peaks at 1458 and 1083 cm^{-1} are attributed to the C-H bending and C-N stretching, respectively.

During the crosslinking reaction, the amine groups on the pristine biomass surface may be involved in the reaction with glutaraldehyde, thus PEI can be chemically bonded to the biomass surface. Additionally, the crosslinked PEI can also be fixed on the biomass surface around the thin mycelium and form a firm coating on the surface. The PEI-modified biomass had a stable sorption capacity for copper ions over ten successive sorption-desorption cycles, indicating that a firm coating of PEI formed on the fungal biomass surface and almost no release of PEI occurred.

The SEM micrographs show that the diameter of the mycelia is about 2 μm; the biomass surface is rough and uneven, and no micropores are observed. The specific surface area of the modified biomass, measured as 1.92 m^2/g using a BET analyzer, is almost equal to the calculated surface area assuming a biomass density of 1000 kg/m^3 and the diameter of the mycelia (assumed cylindrical) at 2 μm. This indicates that any small pores on the surface of the biomass are negligible, and adsorption may mainly occur on the biomass surface.

Effect of pH on Zeta Potential and Sorption Amount

Solution pH is an important parameter in the sorption process, which affects both the properties of sorbent surface and adsorbates. The ζ potentials of the pristine and modified biomass in solution at different pHs are shown in Fig. 2. The pristine biomass has a zero point of ζ potential at pH 3.1. In contrast, the zero point of ζ potential for the modified biomass is changed to a much higher value of 10.3 after the modification, which is attributed to the protonation of amine groups on the biomass surface. Thus, the ζ potential of the modified biomass is positive at $pH < 10.3$, while the ζ potential of the pristine biomass is positive at $pH < 3.1$. Tang et al. (19) reported that the zero point charge of nano-zirconia powder shifted from pH 6 to pH 10.5 when PEI was used as a dispersant to stabilize the powder suspension, which is close to our result. Figure 2 also shows that the ζ potential of humic acid

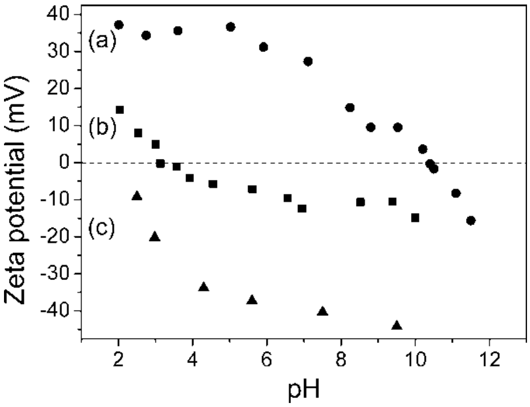

Figure 2. ζ potentials of the (a) PEI-crosslinked biomass, (b) pristine biomass and (c) humic acid at different solution pHs.

is negative at pH > 2.5. From the electrostatic interaction point of view, the PEI-modified biomass can be expected to provide a better adsorption capacity for anionic humic acid than the pristine biomass since the surface attraction between the adsorbent and the adsorbate in the solutions is enhanced.

The effect of initial solution pHs on the sorption amount is shown in Fig. 3. It can be seen that the sorption amount decreased with increasing solution pH. The sorption amount decreased slowly over the pH range of 4–10 and decreased significantly at pH above 10. Almost no sorption took place at pH 12. These results suggested that the electrostatic interaction played a very important role in the humic acid adsorption on the modified biomass. The higher sorption amount achieved at low solution pH are

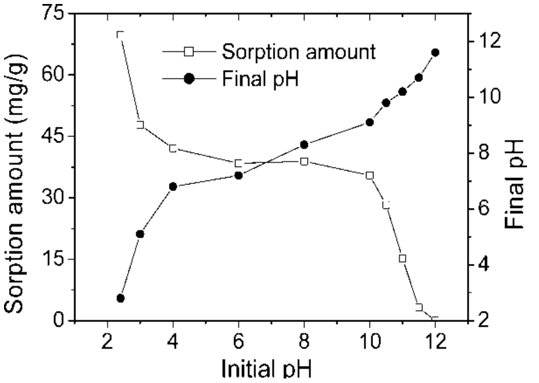

Figure 3. Effect of initial solution pHs on sorption amount of the PEI-modified biomass for humic acid.

attributed to the higher zeta potentials of the biomass and the structure change of humic acid from linear at high pH to coiled configurations at low pH. It is worth nothing that the modified biomass may adsorb the humic acid at initial pH above 10.3 (see Fig. 3), which is unexpected from the viewpoint of electrostatic interaction. The pH values in Fig. 2 are the equilibrated solution pHs, which are different from the initial pHs in Fig. 3. The final solution pH values decreased after humic acid sorption at initial solution pH above 10.3. In Fig. 3, it can be seen that the pH decreased from 11 to 10.2 after humic acid sorption, indicating that the sorption of humic acid may be caused by the electrostatic attraction at initial pH below 11. In addition, other interactions such us hydrogen bonding and van der Waals force may take place in the sorption between the carboxylic/phenolic groups of humic acid and the surface functional groups of the biomass. Our previous paper verified that the surface complexation between the humic acid and the modified fibers also took place during the sorption (13).

Sorption Kinetics

The adsorption kinetics of humic acid on the modified biomass at the concentrations of 50 and 100 mg/L are presented in Fig. 4a. The sorption amount increased gradually over the period of 10 h, which is different from the rapid sorption of humic acid on the modified polyacrylonitrile fibers at the initial 30 min (13). Compared with the polymer fibers, the biomass in the form of mycelial pellets (of about 3 mm in diameter) used in this study presents a greater mass transfer resistance for macromolecular humic acid to diffuse into the pellets and adsorb onto the biomass surface. Therefore, a longer adsorption time is needed to reach equilibrium on the modified biomass. The sorption amount of humic acid on the modified biomass attained 41.5 mg/g when the modified biomass was used to adsorb 100 mg/L humic acid for 10 h.

As the biomass surface is bare at the initial stage, the adsorption kinetics of humic acid may be mainly controlled by the diffusion of humic acid molecules from bulk solution to the biomass surface if all molecules arriving at the substrate surface can attach instantly to the surface. This mass transport process can be expressed by Fickian diffusion model as:

$$q_t = \frac{2}{\sqrt{\pi}} C_0 S \sqrt{Dt} = kt^{1/2} \tag{1}$$

where q_t is the amount adsorbed per unit weight of the adsorbent at time t; C_0 is the initial bulk concentration; S is the specific surface area; D is the diffusion coefficient of humic acid in solution and k is a constant. The plots of q_t versus $t^{1/2}$ are shown in Fig. 4b. The linear dependence of q_t with $t^{1/2}$ can be clearly observed in the initial 2 h for 100 mg/L and 3 h for 50 mg/L, which supports the existence of the transport-limited adsorption at the beginning of the process. After the initial adsorption of humic acid molecules onto the

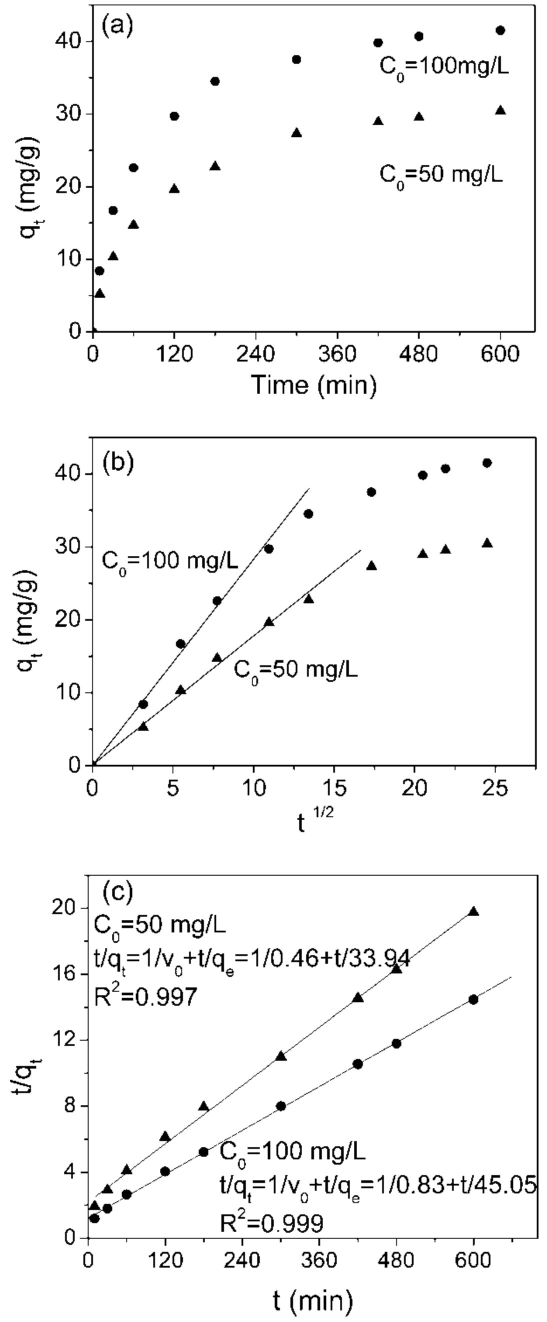

Figure 4. Sorption kinetics of humic acid on the PEI-modified biomass at pH 5. (a) experimental data; (b) modeled result using the Fickian diffusion equation; (c) modeled result using the pseudo-second-order equation.

biomass surface, the reduction in the number of available binding sites on the surface and the unfavorable interactions from the adsorbed humic acid caused the adsorption to shift from an initial transport-limited to a final attachment-limited process. Thus, the rate of uptake decreased, as shown by the experimental results in Figs. 4a and b.

The pseudo-second-order equation was also adopted to describe the sorption kinetic data. The equation is (20, 21)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t = \frac{1}{v_0} + \frac{1}{q_e} t \tag{2}$$

where k_2 is the rate constant for a pseudo-second-order adsorption (g mg^{-1} min^{-1}), q_e is the adsorption amount at equilibrium, and v_0 represents the initial sorption rate (mg/g min). The parameters of q_e and k_2 can be obtained experimentally from the slope and intercept of the plot of t/q_t versus t. The results using the pseudo-second-order equation for humic acid sorption kinetics are presented in Fig. 4c. The good fit ($R^2 \geq 0.997$) obtained for humic acid at different initial concentrations indicates that the sorption conforms to the pseudo-second-order reaction mechanism, supporting the assumption that the sorption rate is controlled by chemical sorption. The corresponding parameters and regression coefficients for the plot are shown in given in Fig. 4c, with q_e values at 33.94 mg/g at 50 mg/L and 45.05 mg/g at 100 mg/L. The initial sorption rates (v_0) are 0.46 and 0.83 mg/g min at initial concentration of 50 and 100 mg/L, respectively.

Sorption Isotherm

The sorption capacities (q_e, mg/g) of humic acid on the pristine and modified biomass as a function of residual humic acid concentration (C_e, mg/L) at pH 5 are shown in Fig. 5. The sorption capacities increased with increasing humic acid concentrations. To predict the sorption capacity of the biomass for humic acid, Langmuir isotherm ($q_e = q_m C_e/[1/b + C_e]$) was used to fit the experimental data and the corresponding equations are also shown in Fig. 5. It can be seen that the Langmuir equation described the experimental data well ($R^2 \geq 0.97$), and the maximum sorption capacities (q_m) are 96.5 and 12.5 mg/g for the PEI-modified biomass and the pristine biomass, respectively. The maximum sorption capacity of the PEI-modified biomass for humic acid increased by 6.72-fold, which is attributed to the introduction of a large number of amine groups on the biomass surface. Our previous study showed that the maximum sorption capacity for humic acid was 16.22 mg/g according to Langmuir model when the aminated polyacrylonitrile fibers were used to adsorb humic acid at pH 6 (22). Other references also reported the removal of humic substances using the polypyrrole-coated granules (23), chitosan (24) and hematite (25), but the maximum sorption

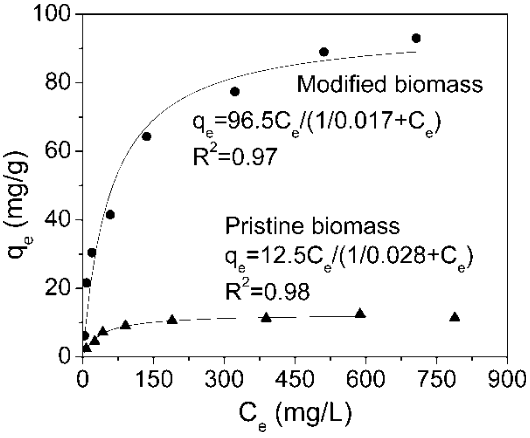

Figure 5. Sorption isotherms of humic acid on the pristine and PEI-modified biomass at pH 5.

capacities were less than 80 mg/g. Obviously, the modified fungal biomass in this study possessed high sorption capacity for humic acid after PEI was introduced on the biomass surface.

Desorption Study

Figure 6 shows the results of humic acid adsorption on the biomass at pH 5 for 10 h, and then desorption in 0.1 M NaOH solution for 2.5 h. After 10 h sorption, the residual humic acid in solution was 58.5 mg/L (with sorption

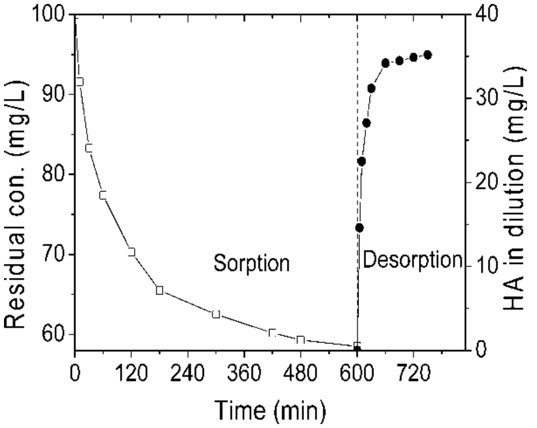

Figure 6. Sequential sorption at pH5 and desorption (50 mL of 0.1 M NaOH) for humic acid on the PEI-modified biomass.

capacity at 41.5 mg/g). The biomass with humic acid was filtered, and then added into 50 mL of 0.1 M NaOH solution. The desorption process was fairly rapid and stabilized after 1 h. After 2.5 h regeneration, the humic acid concentration in the base solution was 35.2 mg/L, indicating that about 85% of the adsorbed humic acid was desorbed from the biomass surface. The humic acid molecules adsorbed on the surface via electrostatic interaction may be easily desorbed from surface to subsurface due to electrostatic repulsion in a basic solution and diffuse quickly into solution. We have previously reported that polymer fibers with adsorbed humic acid were regenerated effectively using 0.1 M NaOH solution (22). After washing with 0.1 M HCl solution, and with DI water, the regenerated biomass was used in the next cycle. Figure 7 shows that the sorption capacities of the biomass for humic acid over five sequential cycles. The uptake capacity of the regenerated biomass in the second cycle (35.7 mg/g) is lower than that of the original PEI-modified biomass in the first cycle (41.5 mg/g), possibly due to the incomplete desorption of humic acid from the biomass surface in the regeneration process. Although the uptake capacity gradually decreased in the subsequent cycles, it stabilized and reached 32.1 mg/g in the fifth cycle. Therefore, the PEI-modified biomass can be used repeatedly for humic acid sorption, and thus show potential for application in humic acid removal in natural water treatment.

CONCLUSIONS

Polyethylenimine was successfully crosslinked onto the biomass surface of *P. chrysogenum* through a simple crosslinking reaction. The modified biomass had stronger mechanical strength than the pristine one. Moreover, the sorption capacity for humic acid increased significantly due to the

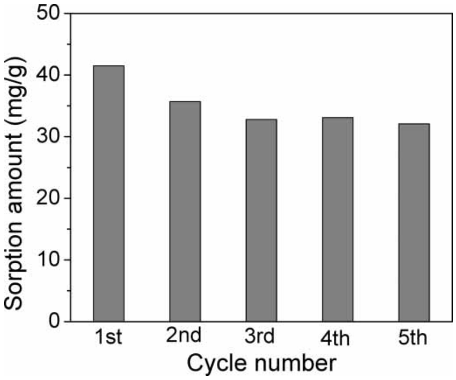

Figure 7. Comparative uptake amount of the modified biomass for humic acid after regeneration.

presence of a large number of amine groups on the biomass surface. According to the Langmuir model, the maximum sorption capacity of the modified biomass for humic acid reached 96.5 mg/L at pH 5. The modified biomass had a zero point of ζ potential at pH 10.3, indicating that electrostatic interaction played an important role in the sorption of anionic humic acid, which was consistent with the decreasing sorption amount of humic acid with increasing solution pH. The humic acid adsorbed biomass could be easily regenerated in a 0.1 M NaOH solution for 2.5 h, and the regenerated biomass possessed good adsorption capacity in the successive five cycles. Our study indicates that the sorption capacity of the biomass can be enhanced through an incomplete crosslinking of polyamine chains on the biomass surface.

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