Enhanced removal of pentachlorophenol and 2,4-D from aqueous solution by an aminated biosorbent

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ARTICLE INFO

ABSTRACT

The fungal biomasses of *Penicillium chrysogenum* were used as raw materials to prepare the aminated adsorbent through chemical grafting of polyethylenimine (PEI) on the biomass surface. Due to the protonation of amine groups, the PEI-modified biomass was found to possess the zero point of ζ potential at pH 10.2, higher than the pristine biomass at pH 3.8. The aminated biosorbent was effective in removing anionic pentachlorophenol (PCP) and 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution. The sorption was pH-dependent and the sorption kinetic data were well described by the pseudo-second-order model. The sorption isotherms on the aminated biosorbent conformed to the Langmuir equation, with the maximum sorption capacity of 1.23 mmol/g for PCP and 1.22 mmol/g for 2,4-D. In the presence of Cu^{2+} or Pb^{2+}, the sorption capacities for both PCP and 2,4-D were further enhanced, attributed to the formation of surface complex. FTIR and ζ potential analysis before and after the sorption revealed that the amine groups on the biomass surface played an important role in the sorption of PCP and 2,4-D, due to the electrostatic interaction between the positive protonated amine groups and the negative PCP/2,4-D.

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1. Introduction

The removal of endocrine disrupting compounds (EDCs) from water has caused the attention of many researchers in recent years. Some strong polar EDCs, such as penta-cholorophenol (PCP) and 2,4-dicholorophenoxyacetic acid (2,4-D) are of great environmental concern because of their high solubility in water and toxicity to humans, animals and aquatic life [1,2]. PCP has been widely used as pesticide and wood preservative [1], and the US Environmental Protection Agency (EPA) has listed PCP as a priority pollutant because of its proven carcinogenicity and a large number of PCP-contaminated sites in the world [2]. 2,4-D is one of the most commonly used herbicides. Due to its wide application in agriculture, it was often detected in water environment [3]. Therefore, the development of an effective process for the pollutant removal from water or wastewater has been the concern of many researchers [3,4].

Biosorption has been regarded as a promising technology for the removal of pollutants from industrial wastewater. Since fungal biomass is produced as the byproduct or waste from food, beverage and pharmaceutical production, it may serve as a viable source for the development of inexpensive biosorbents. It was reported that the biosorbents such as algae, bacteria, fungi, and yeasts had been used to adsorb various pollutants, especially heavy metals [4–6]. Normally, the pristine mycelia were directly used as adsorbents to remove target compounds, but the sorption performance was not satisfactory due to the low sorption capacity [4,5].

In recent years, research interest has been focused on increasing the sorption capacity of the biomass through physical and chemical modification [7,8]. All these modifications were aimed at increasing the density of effective functional groups such as carboxylate, hydroxyl, sulfate, phosphate, amide, and amine groups on the biomass surface [9,10]. Among them, amine group is very effective in removing pollutants. It not only can chelate with cationic metal ions, but also adsorb anionic pollutants through the electrostatic interaction. Since the biomass is nonporous material and the adsorption of pollutants mainly occurs on the fungal biomass surface, increasing the sorption active sites on the surface is an effective approach to enhance the sorption capacity.

There are two methods to achieve high density of the functional groups on fungal biomass. One technique is the polymerization of monomer on the biomass, and our previous study showed that acrylic acid could be successfully polymerized on the biomass surface [11]. Alternatively, some polymers containing a lot of functional groups in one molecule can be adsorbed or grafted directly on biomass surface. For example, polyethylenimine (PEI) which contains a large number of primary, secondary and tertiary amine

groups in a molecule, exhibited good sorption ability for heavy metals when they were adsorbed or crosslinked on the adsorbent surface [12,13]. The long PEI chains can stretch in solution and provide more active sites for the sorption of adsorbates.

Most of the researchers generally used fungal biomass for the removal of heavy metals, while few researchers reported the removal of organic pollutants [4,5]. Biosorption may be an effective method to remove high concentration of PCP or 2,4-D from wastewater. In the present paper, the PEI-modified fungal biomass of *Penicillium chrysogenum* was prepared and used to remove the anionic PCP and 2,4-D from synthetic wastewater. The sorption behaviors including sorption kinetics, sorption isotherms, effect of pH and heavy metals on the sorption characteristics were investigated in detail. Finally, the sorption mechanism was studied through surface charge and FTIR analysis.

2. Materials and methods

2.1. Materials

The strain *P. chrysogenum* (No. 3.3890) was purchased from China General Microbiological Culture Center, Beijing, China, and the details of the mycelium preparation were described in our previous study [11]. Polyethylenimine (molecular weight 25,000, branched polymer $(-NHCH_2CH_2-)_x(-N(CH_2CH_2NH_2)CH_2CH_2-)_y)$, chloroacetyl chloride, pentachlorophenol (sodium salt, PCP) and 2,4-D were purchased from Sigma–Aldrich Company. Other chemicals were of analytical grade.

2.2. Preparation of aminated biomass

An amount of 0.5 g dried biomass was placed in 0.5 mL of pyridine in 30 mL of chloroform, followed by dropwise addition of 0.8 mL of chloroacetyl chloride. The reaction mixture was sealed and gently stirred at 25 °C for 8 h. The acylated biomass was rinsed with chloroform to remove any unreacted chloroacetyl chloride before being immersed in a mixture containing 10 g of PEI in 100 mL of N,N-dimethylformamide (DMF). After the reaction at 100 °C for 24 h, the modified biomass was rinsed with copious quantities of DMF, methanol, and deionized water. Finally, the biomass was freeze-dried to constant weight.

2.3. Adsorption experiments

Batch adsorption experiments were carried out in 250 mL flasks, each of which contained 100 mL of PCP or 2,4-D solution at pH 6. 0.02 g of biosorbent was added into a flask and the flask was shaken at 120 rpm in a thermostatic shaker at 25 °C for 24 h. During the studies of adsorption kinetics, the initial concentrations of PCP and 2,4-D were 0.174 and 0.226 mmol/L, respectively. The concentrations of residual adsorbate in solution were determined at the predetermined time. In the sorption isotherm experiments, the initial concentrations of PCP and 2,4-D were in the range of 0–1.04 and 0–1.31 mmol/L, respectively. The investigation on the effect of solution pH was conducted at an initial concentration of 0.347 mmol/L for both PCP and 2,4-D, with the solution pH varying from 5 to 10.8. In the sorption experiments of the effects of Cu^{2+} and Pb^{2+}, the biomass was first added in 0.2 mmol/L Cu^{2+} or Pb^{2+} solution, followed by the addition of PCP or 2,4-D solution at different concentrations at pH 6 after 10 min. After the sorption experiments, the biomass was filtered with a 0.45 μm membrane, and then the filtrate was adjusted to pH 7. The concentrations of PCP and 2,4-D in solution were determined using an UV–vis spectrometer (Agilent 8453, Germany) at 320 and 283 nm, respectively. The detention

limits for PCP and 2,4-D were 0.5 and 0.8 mg/L, respectively. Additionally, the control experiments (no PCP or 2,4-D) showed that there were no peaks at 320 and 283 nm in the spectra after 24 h sorption, verifying the determination reliable.

2.4. ζ potential measurement

0.05 g of the aminated biomass was added into a conical flask containing 100 mL of 1 mmol/L PCP/2,4-D, or 0.2 mmol/L Cu^{2+}/Pb^{2+}. The flask was shaken at 120 rpm in a thermostatic shaker at 25 °C for 24 h, and then the biomass was filtrated and rinsed with deionized water, and finally dried at 60 °C for 12 h. During the ζ potential measurement, 0.1 g of dried biomass was put into 100 mL of deionized water and the mixture was stirred for 2 h. The solution pH was adjusted with 0.1 M NaOH or 0.1 M HCl. After 1 h, the equilibrium solution pH was recorded, and the mixture was used to conduct ζ potential measurement with a Zeta-Plus4 instrument (Brookhaven Corp., USA). All the ζ potential measurements were conducted five times, and their average values were adopted.

2.5. FTIR spectroscopy

The samples of the aminated biomass before and after PCP and 2,4-D sorption were analyzed with a Magna-560 ATR-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}.

3. Results and discussion

3.1. Surface modification

Our previous study found that some hydroxyl and amine groups were present on the surface of fungal biomass [14]. During the surface modification in this study, the acylchlorine groups in chloroacetyl chloride molecules first reacted with the hydroxyl and amine groups on the biomass surface. The acylated biomass then reacted with the amine groups in PEI molecules through the nucleophilic substitution, which was verified by FTIR analysis [15]. Although the PEI molecules were successfully grafted on the fungal biomass using 4-bromobutyryl chloride in our previous papers [13,14], the use of chloroacetyl chloride in place of 4-bromobutyryl chloride in this preparation can decrease the preparation cost since chloroacetyl chloride is much cheaper. The proposed schematic diagram for the chemical reactions in this preparation is shown in Fig. 1. It can be seen that the PEI molecules were grafted on the biomass surface after the modification. As there are many amine groups in one branched PEI molecule, the grafted PEI on the modified biomass surface can provide many active sorption sites for the specific pollutants, resulting in the enhanced sorption capacity. When the amine groups are protonated in solution, the anionic pollutants such as PCP and 2,4-D can be adsorbed on the PEI-modified biomass through the electrostatic interaction, shown in Fig. 1.

3.2. ζ potential analysis

To investigate the change of biomass surface charge before and after the surface modification, the ζ potentials as a function of solution pH were measured. As shown in Fig. 2, the ζ potentials decrease with increasing solution pH. The zero point of ζ potential of the pristine biomass is at pH 3.8, while that of the aminated biomass is achieved at pH 10.2, which is due to the protonation of amine groups in PEI molecules on the biomass surface. Thus, the ζ potential of the aminated biomass is positive at pH < 10.2. From the
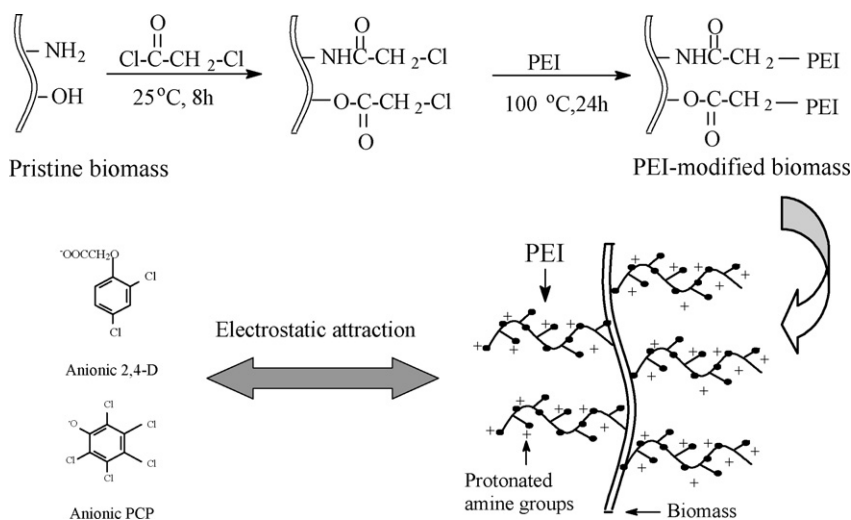
Fig. 1. Schematic diagram illustrating the graft of branched PEI on the biomass and sorption of anionic pollutants.

electrostatic interaction point of view, the aminated biomass can be expected to provide good adsorption performance for anionic adsorbates.

Other researchers also reported that the zero point of ζ potential was increased significantly after the addition of PEI on the solid surface. When the silicon carbide powder was covered with PEI, its isoelectric point changed from pH 2 to 10.5 [16]. Tang et al. reported that the zero charge point of nano-zirconia powder shifted from pH 6 to pH 10.5 when PEI was used as a dispersant to stabilize the powder suspension [17]. The zero point of ζ potential of the PEI-modified fungal biomass in our study is in accordance with the one reported in other studies. The commercial branched PEI employed in this study contains the primary, secondary and tertiary amine groups in the ratio of about 1:2:1, which has great proton sponge effect [18]. It was reported that the zero charge point of the PEI molecule was approximately at pH 10.8 [19].

3.3. Sorption kinetics

Predicting the sorption rate for a given system is one of the important factors in the adsorption system design as the sorption kinetics controls the retention time and the reactor dimensions. The sorption rate constants are important physicochemical parameters to evaluate the quality of adsorbents. Fig. 3 shows the sorption
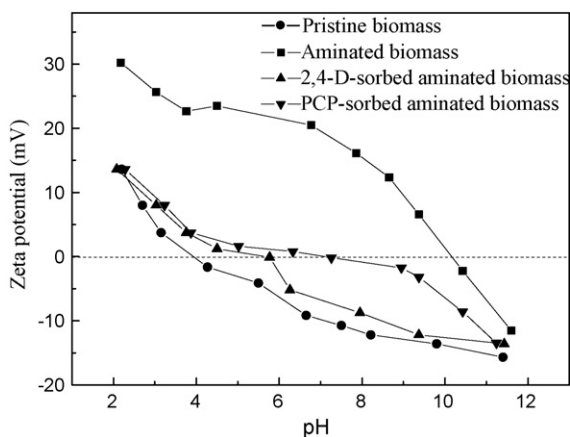
kinetics of PCP and 2,4-D on the aminated biomass at different solution pH. The sorption profile is smooth and continuous, leading to the equilibrium. For both PCP and 2,4-D, the sorption capacity was enhanced at lower solution pH. As the aminated biosorbents could be protonated at pH 4, the anionic adsorbates should be adsorbed via the electrostatic interaction. It is noticeable that the adsorbents still had higher sorption capacity for PCP at pH 4 although only about 15% PCP could be in anionic form at pH 4. The reasonable interpretation is that the neutral PCP molecules could be dissociated to maintain the equilibrium after the anionic species had been adsorbed on the adsorbents.

To investigate the adsorption mechanism and rate-controlling steps, the kinetic data were described by the pseudo-first-order and pseudo-second-order models, respectively (see Fig. 3 and Table 1). For the first-order plot, the correlation coefficients were in the range of 0.844–0.902, and especially the calculated q_e values were not consistent with the experimental ones, suggesting that the sorption of PCP and 2,4-D was not the first-order reaction. It was reported that the first-order model did not fit the kinetic data well over the entire range of contact time in many cases [20].

The second-order model, put forward by Ho and McKay [21], was used to describe chemisorption involving valency forces through sharing or exchange of electrons between adsorbents and adsorbates [22]. As shown in Fig. 3a and b, the pseudo-second-order model described the experimental data well with the high correlation coefficients (see Table 1), indicating the possible chemisorption occurred between the modified biomass and PCP/2,4-D. Since the amine groups were protonated, the

Fig. 2. ζ potentials of the pristine biomass, aminated biomass before and after the sorption of PCP and 2,4-D as a function of solution pH.

Table 1
Kinetic parameters of the pseudo-first-order and pseudo-second-order equations for PCP and 2,4-D sorption on the aminated adsorbent.

Adsorbates	Pseudo-first-order[a]			Pseudo-second-order[b]		
	k_1	q_e	R^2	k_2	υ_0	R^2
PCP (pH 4)	1.04	0.60	0.902	2.10	0.92	0.978
PCP (pH 6)	1.00	0.49	0.844	2.42	0.71	0.945
2,4-D (pH 4)	0.92	0.69	0.847	1.54	0.90	0.956
2,4-D (pH 6)	0.98	0.53	0.880	2.18	0.74	0.974

q_e: sorption amount at equilibrium, mmol/g; k_1: rate constant of pseudo-first-order adsorption, 1/h; k_2: rate constant of pseudo-second-order adsorption, g/(mmol h); υ_0: initial sorption rate, mmol/(g h).

[a] $q_t = q_e(1 - e^{-k_1 t})$.

[b] $t/q_t = (1/k_2 q_e^2) + (t/q_e) = (1/\upsilon_0) + (t/q_e)$.
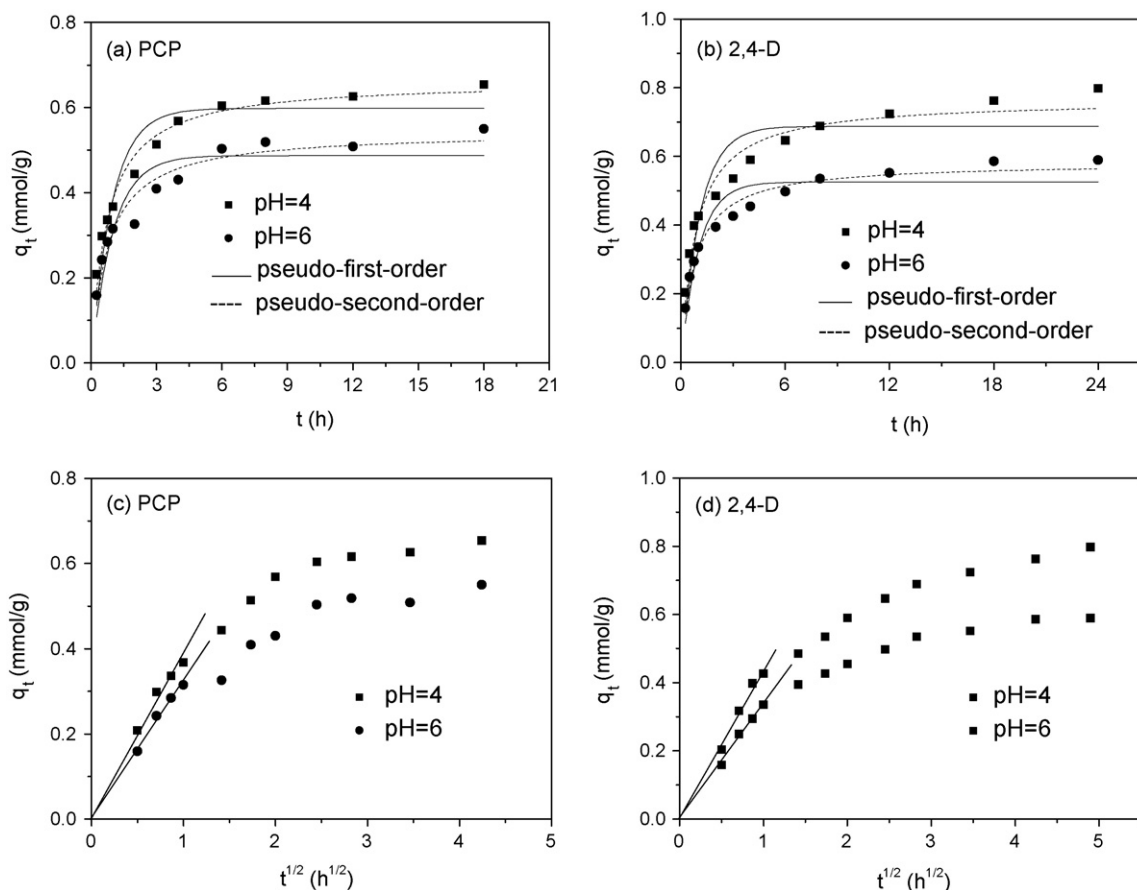
Fig. 3. Sorption kinetics of PCP and 2,4-D on the aminated biomass at pH 4 and pH 6. (a) Modeling result for PCP using the pseudo-first-order and pseudo-second-order equations; (b) modeling result for 2,4-D using the pseudo-first-order and pseudo-second-order equations; (c) modeling result for PCP using the intraparticle diffusion model; (d) modeling result for 2,4-D using the intraparticle diffusion model.

corresponding anions around the protonated amine groups could be exchanged by the anionic PCP or 2,4-D in the sorption process. For both PCP and 2,4-D, the initial sorption rate (v_0) at pH 4 (0.85 mmol g^{-1} h^{-1} for PCP, 0.65 mmol g^{-1} h^{-1} for 2,4-D) is higher than that at pH 6 (0.6 mmol g^{-1} h^{-1} for both PCP and 2,4-D), suggesting the fast adsorption at low solution pH during the initial stage for both PCP and 2,4-D.

The intraparticle diffusion model ($q_t = k \cdot t^{1/2}$) was also used to model the sorption kinetic data in this study, which was often used to describe the sorption kinetics of porous adsorbents [23]. During the initial 1 h, the plot of q_t versus $t^{1/2}$ for the experimental data obtained at each solution pH indeed gives a linear relationship. The results confirm that PCP and 2,4-D adsorption on the sorbent during the initial stage followed the diffusion-controlled adsorption kinetics. Although the mycelia were almost nonporous, the biomass pellets used were composed of many mycelia and the pellets were porous. Especially, after the long molecules of PEI were grafted on the biomass surface, the adsobates had to overcome the resistance to diffuse and adsorb on the active sites. During the later stage, the adsorption process was the most likely attachment-controlled process after some adsorbates had been adsorbed on the biomass surface.

3.4. Sorption isotherms

Langmuir equation assumes monolayer coverage of adsorbate over a homogenous adsorbent surface and it has been successfully applied to many sorption processes [11]. The Langmuir equation is expressed as follows:

$$q_e = \frac{q_m C_e}{(1/b) + C_e} \tag{1}$$

where q_m is the maximum adsorption capacity (mmol/g); b is the sorption equilibrium constant (L/mmol), indicating the sorbent affinity; C_e is the equilibrium concentration of adsorbate in solution (mmol/L).

The sorption isotherms of PCP and 2,4-D on the pristine and PEI-modified biomass are shown in Fig. 4. It can be found that the sorption capacity for both PCP and 2,4-D increased significantly after the modification. The Langmuir equation was used to fit the experimental data (see Fig. 4), and the corresponding parameters are given in Table 2. The Langmuir model described the experimental data well according to their correlation coefficients (R^2),

Table 2
Calculated equilibrium parameters using the Langmuir equation.

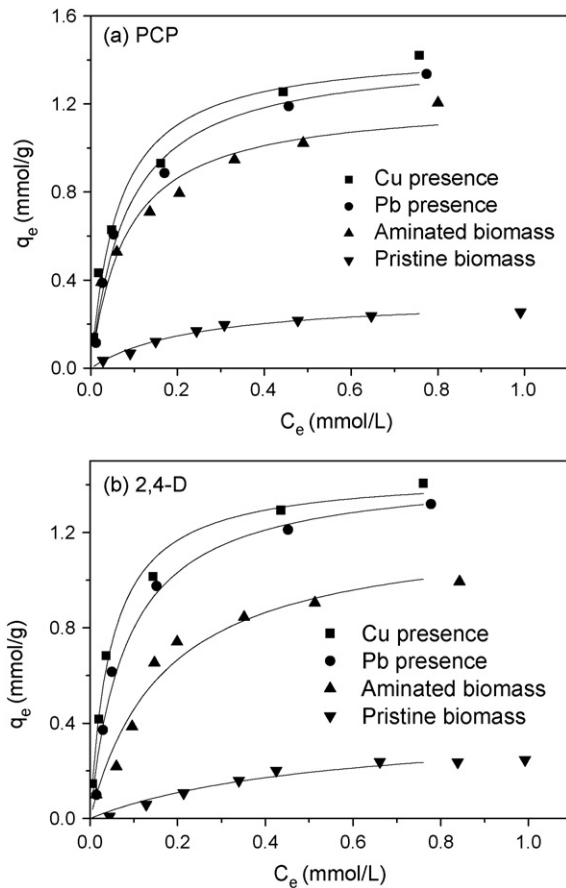| Adsorbates	Adsorbents	Langmuir equation		
		q_m (mmol/g)	b (L/mmol)	R^2
PCP	Pristine biomass	0.33	4.06	0.983
	Aminated biomass	1.23	12.16	0.963
	Pb effect	1.43	11.95	0.985
	Cu effect	1.45	15.94	0.973
2,4-D	Pristine biomass	0.40	1.85	0.964
	Aminated biomass	1.22	5.96	0.963
	Pb effect	1.46	12.09	0.982
	Cu effect	1.45	20.67	0.992

Fig. 4. Effect of Cu^{2+} and Pb^{2+} on the sorption of (a) PCP and (b) 2,4-D on the aminated biomass at 25 °C.

indicating the possible monolayer sorption of PCP and 2,4-D on the biomass surface. The maximum sorption capacities (q_m) of the pristine and aminated biomass are 0.33 and 1.23 mmol/g for PCP, 0.40 and 1.22 mmol/g for 2,4-D, respectively. The sorption capacity increased by 2.7 times for PCP and 2.1 times for 2,4-D after the PEI-modification. Some studies were conducted to remove PCP and 2,4-D using the various adsorbents such as activated carbon, activated sludge, fly ash, blast furnace slag, almond shell, fungal mycelia, pine bark, and chitosan [1,20,24–31]. Normally, their sorption capacities for the two adsorbates were less than 1 mmol/g, but Wu et al. reported that the sorption capacity reached 728.3 mg/g (3.3 mmol/g) for 2,4-D using the KOH-activated carbon [32].

Heavy metals are commonly present in wastewater with organic pollutants, which may directly affect the sorption behavior of adsorbents for the target compounds. The effects of Cu^{2+} and Pb^{2+} on the sorption of PCP and 2,4-D on the aminated biomass were investigated in this study. As shown in Fig. 4, the sorption capacity for both PCP and 2,4-D increased significantly in the presence of Cu^{2+} and Pb^{2+}, and Cu^{2+} had greater effect than Pb^{2+}. The Langmuir equation can also fit the experimental data well. In the presence of Cu^{2+}, the maximum sorption capacity increased by 18% for PCP and by 19% for 2,4-D. Similarly, the maximum sorption capacity increased by 16% for PCP and by 20% for 2,4-D in the presence of Pb^{2+}.

Many researchers reported that heavy metals could enhance the sorption capacity of the adsorbents for organic pollutants [33,34]. Zhu et al. proposed two specific sorption mechanisms including cation–π interaction and π H-bonding for π-donor compounds to explain the enhanced sorption for phenanthrene [33], but PCP and 2,4-D are non-π-donor due to the chlorine substitution, and

thus these interactions cannot occur. In our study, we first put the biosorbents in the heavy metal solution, and then the organic pollutants were added. The metal ions were first adsorbed on the amine groups on the biomass surface via the chelation interaction, and the adsorbed metal ions then adsorbed PCP or 2,4-D through the electrostatic interaction. Our preliminary experiments showed that the sorption amount of organic pollutants also increased when the biosorbents were put into the mixture solution of heavy metal and organic pollutant simultaneously, but it was lower than that obtained when metal ions were first added. In fact, not all the active sites were occupied by the heavy metals after 10 min sorption, and the metal ions and organic pollutants also competed with each other in the following sorption process. Due to the higher valency charge of Cu^{2+} or Pb^{2+} than the protonated amine group, more PCP or 2,4-D molecules were adsorbed on the adsorbent surface. In addition, Cu^{2+} showed the greater effect on the sorption of PCP and 2,4-D on the biomass than Pb^{2+}, which was related to the higher sorption amount of Cu^{2+} on the biosorbent than that of Pb^{2+} according to our previous study [14]. It is known that Pb^{2+} has a coordination number of 6, while Cu^{2+} has a coordination number of 4. Therefore, more amine groups on the biomass surface may chelate with Pb^{2+}, resulting in the lower sorption capacity.

3.5. Effect of pH

The effect of solution pH on the sorption of PCP and 2,4-D onto the aminated biomass is shown in Fig. 5. It can be seen that the sorption amount for both PCP and 2,4-D decreases with increasing solution pH. Solution pH not only influences the surface property of the biomass, but also affects the adsorbate speciation in solution. As the pK_a values of PCP and 2,4-D are 4.75 and 2.64, respectively, all 2,4-D and most PCP molecules exist as anions in solution at pH above 5. After the anionic PCP species were adsorbed on the biomass, the neutral PCP molecules were dissociated to maintain the equilibrium defined by the pH–pKa relationship [35]. Obviously, the anionic PCP and 2,4-D were adsorbed on the adsorbents. It is interesting to find that the solution equilibrium pH increased after the sorption of PCP and 2,4-D when the initial pH was below 10 (see Fig. 5), which was attributed to the protonation of amine groups on the aminated biomass. Some amine groups grafted on the biomass surface were protonated at low solution pH and the biomass surface was positive. Therefore, the electrostatic interaction played an important role in the sorption of PCP and 2,4-D on the aminated biomass. With the increase of solution pH, the number of the protonated amine groups decreased, resulting in the decrease of sorption amount.
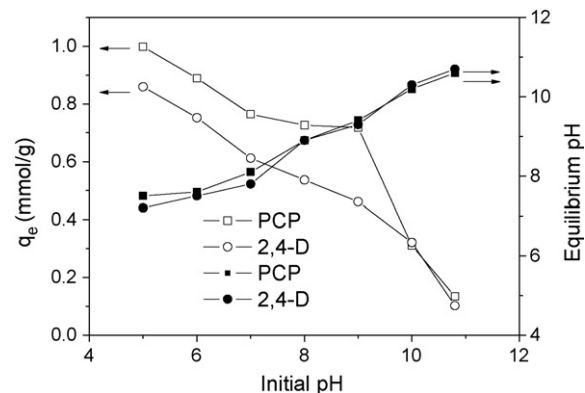

Fig. 5. Effect of solution pH on the sorption of PCP and 2,4-D on the aminated biomass.

3.6. Sorption mechanism

Fig. 6 shows the FTIR spectra of the aminated biomass before and after the sorption of PCP and 2,4-D, respectively. The peaks at 3338, 1655, 1551, 1080, and 1039 cm^{-1} are observed in the spectrum of the aminated biomass (Fig. 6a). 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 peaks at 1080 and 1039 cm^{-1} assigned to the alcoholic C–O and C–N stretching vibration [17], thus showing the presence of hydroxyl and amine groups on the biomass surface. The band at 1551 cm^{-1} is attributed to the N–H bending [17], and the strong peak at 1655 cm^{-1} can be assigned to the C=O stretching in carboxyl or amide groups, verifying that the PEI molecules were chemically grafted on the biomass surface.

As shown in Fig. 6b and c, the broad overlapping peak shifted to 3280 cm^{-1} after the sorption of PCP and 2,4-D, suggesting that hydroxyl or amine groups were involved in the adsorption. Additionally, the peak at 1655 cm^{-1} assigned to the C=O stretching did not shift after PCP adsorption, but shifted to 1664 cm^{-1} after 2,4-D adsorption, which may be due to the effect of carboxyl groups in 2,4-D molecules. The peak at 1551 cm^{-1} assigned to N-H bending shifted to 1529 and 1479 cm^{-1} after PCP and 2,4-D adsorption, respectively, indicating that the amine groups were involved in the sorption.

The surface charge on the aminated biomass played an important role in the sorption of anionic pollutants. To investigate the change of the biomass surface charge before and after the sorption of PCP and 2,4-D, the zeta potentials as a function of solution pH were measured. As shown in Fig. 2, the zero point of ζ potential of the aminated biomass was at pH 10.2, while that of the biomass after PCP and 2,4-D sorption decreased to 6.4 and 5.2, respectively. Once the anions were adsorbed on the aminated surface, the positive charge would be neutralized from the electrostatic interaction point of view, resulting in the decrease of zero point of ζ potential.

Fig. 7 shows the ζ potentials of the aminated biomass after Cu^{2+} and Pb^{2+} sorption. It is found that the zero points of ζ potential of the Cu-sorbed and Pb-sorbed biomass are at pH 10.8 and 10.4, respectively, a little higher than that of the aminated biomass. The metal ions may chelate with amine groups on the biomass surface and increase the positive charge on the surface, which is associated with the higher sorption capacity of the aminated biomass for PCP or 2,4-D in the presence of Cu^{2+} or Pb^{2+}, shown in Fig. 4.
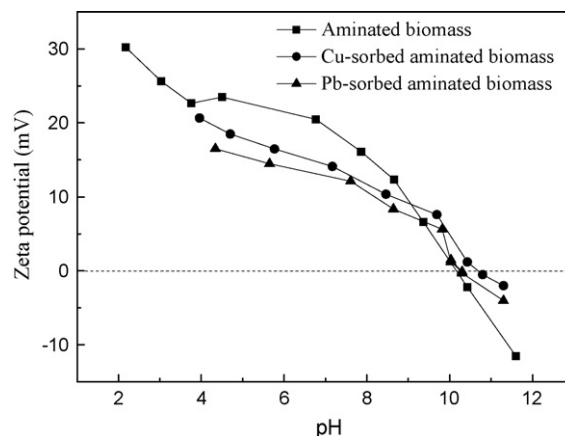
Fig. 7. Effect of the adsorbed Cu^{2+} and Pb^{2+} on the zeta potentials of the aminated biomass.

According to the above results, the amine groups (–NH–, –N<, –NH$_2$) on the biomass surface were protonated at pH below 10.2, and then adsorbed the anions in solution via the electrostatic interaction. As PCP and 2,4-D existed as anions in solution in the studied pH range of 5–10, the electrostatic attraction played an important role in the sorption process at pH below 10.2. With further increasing solution pH above 10.2, the electrostatic attraction disappeared, leading to the decrease of the adsorption amount.

4. Conclusions

The PEI macromolecules were successfully grafted on the fungal biomass surface through a two-step reaction. Since lots of amine groups are present in one PEI molecule, the grafted PEI molecules can stretch in solution and provide many active adsorption sites for PCP and 2,4-D, thus achieving high sorption capacities. Moreover, the PEI-modified biomass had a high zero point of ζ potential at pH 10.2 as the amine groups in PEI molecules were easily protonated in solution. Therefore, the electrostatic attraction between the positive protonated amine groups and the negative adsorbates played an important role in the sorption of PCP and 2,4-D, which was verified by FTIR analysis and ζ potential measurement. In addition, the sorption of heavy metal ions (Cu^{2+} or Pb^{2+}) on the biomass also increased the zero point of ζ potential of the aminated biomass. The sorption kinetics and isotherms were well described by the pseudo-second-order and Langmuir equations, respectively, indicating the possible chemisorption and monolayer sorption. This research revealed that the strong polar EDCs could be effectively removed from aqueous solution using the aminated adsorbent obtained by a simple surface modification.
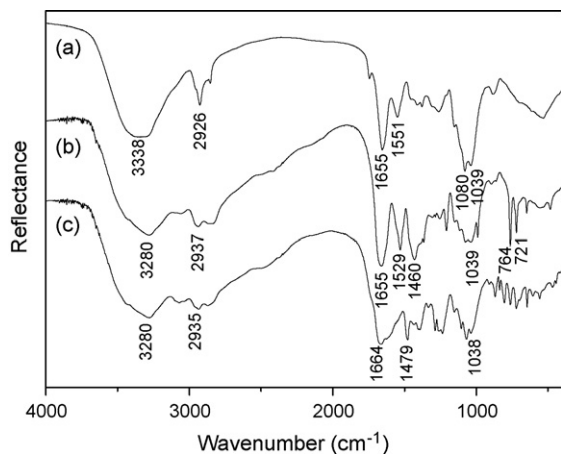
Fig. 6. FTIR spectra of the aminated biomass before and after the sorption of PCP and 2,4-D. (a) Aminated biomass; (b) PCP-sorbed aminated biomass; (c) 2,4-D sorbed aminated biomass.

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