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Surface-modified *Phanerochaete chrysosporium* as a biosorbent for Cr(VI)-contaminated wastewater

Gui-Qiu Chen[a,b,*], Wen-Juan Zhang[a,b], Guang-Ming Zeng[a,b], Jin-Hui Huang[a,b], Liang Wang[a,b], Guo-Li Shen[c]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, China
[c] State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China

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ABSTRACT

To improve the removal efficiency of heavy metals from wastewater, the surface of a fungal biomass was modified to obtain a high-capacity biosorbent for Cr(VI) in wastewater. The effects of pH, initial concentration, and sorption time on Cr(VI) removal by polyethylenimine (PEI)-modified *Phanerochaete chrysosporium* were investigated. The biomass adsorption capacity was significantly dependent on the pH of the solution, and the optimum pH was approximately 3.0. The maximum removal for Cr(VI) was 344.8 mg/g as determined with the Langmuir adsorption isotherm. Pseudo-first-order Lagergren model is better than pseudo-second-order Lagergren model when simulating the kinetic experiment results. Furthermore, an amount of Cr(VI) was reduced to Cr(III), indicating that some reactions occurred on the surface of the biomass leading to the reduction of Cr(VI). The point of zero potential for the modified biomass increased from an initial pH of 3.0 to a much higher value of 10.8, indicating that the PEI-modified biomass is better than the pristine biomass for adsorption of anionic adsorbates. Results showed that the PEI-modified biosorbent presented high efficiency in treating Cr(VI)-contaminated wastewater.

1. Introduction

Heavy metals can accumulate in vegetables, hydrophytes, and aquatic inhabitants, which are ultimately consumed by human beings as food. Chromium compounds are widely used in the manufacture of metal alloys and in other industries, such as leather tanning, electroplating, wood preservation, and electronics, leading to large amounts of Cr(VI)-contaminated wastewater being dumped into the bodies of water. Most chromium exists in the environment as Cr(VI) and Cr(III). Given that Cr(VI) has high mobility and a strong oxidation potential, it also has carcinogenic and mutagenic effects, posing a serious threat to human health. Moreover, it is also 500 times more toxic than Cr(III). According to the U.S. Environmental Protection Agency, the total chromium concentration in drinking water should be less than 0.1 mg/L. The World Health Organization has also established 0.005 mg/L as the maximum allowable emission standard of Cr(VI). Therefore, it is extremely important to control the levels of chromium in wastewater [1–3].

Various treatment technologies are available for the removal of Cr(VI) from wastewater, such as chemical reduction, electrochemical treatment, and ion exchange [4–6]. These techniques are expensive and have many disadvantages such as incomplete metal removal and high reagent and energy requirements; in addition, the toxic sludge or waste products must be disposed safely so that they do not harm the environment. Biosorption is an attractive treatment method for the removal of Cr(VI) from wastewater. There are many sources of inexpensive biosorbents that have strong adsorption capacity, enable easy separation, and promote the practical recovery of heavy metals.

Mycelial pellets of fungi have been reported to remediate heavy metal-polluted media in Finland [7] and China [8,9]. *Phanerochaete chrysosporium*, the model white-rot fungi, is known for its unique ability to degrade xenobiotics [10–12]. It can also be used to remove heavy metals from wastewater by adsorbing metals on its mycelium. The biosorption of heavy metals [Cd(II), Pb(II), and Cu(II)] from artificial wastewater by the dry fungal biomass of *P. chryosporium* was studied at concentrations ranging from 5 to 500 mg/L [13]. *P. chrysosporium* can also degrade the chlorinated organics in bleaching effluents from pulp and paper mills. Therefore, it can act as a biosorbent for waste sludge obtained from pulp and paper waste treatment facilities. Live, resting, and dead cells of *P. chrysosporium* show different biosorption capacities for Pb(II)

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* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Lushan South Road, Changsha, China. Tel.: +86 731 88822829; fax: +86 731 88823701.
E-mail addresses: gqchen@hnu.cn, guiqiuchen@gmail.com (G.-Q. Chen).

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[14]. Ülkü et al. found that it has a high capacity for the adsorption of a variety of heavy metals [10].

To obtain a biosorbent with a high capacity for Cr(VI) absorption, we cultured *P. chrysosporium* in a potato medium to produce mycelial pellets. Polyethylenimine (PEI) was used to modify the mycelial pellets to increase the amounts of functional groups on the biomass surface, which will adsorb Cr(VI) from the wastewater. The adsorption capacity of the biosorbent was evaluated by studying the equilibrium adsorption isotherms and kinetic models of Cr(VI) in batch experiments. To determine the best biosorption conditions, factors, such as pH, adsorption time, and initial concentration, were examined. The zeta potential was used to understand the characteristic changes of the biomass surface after modification.

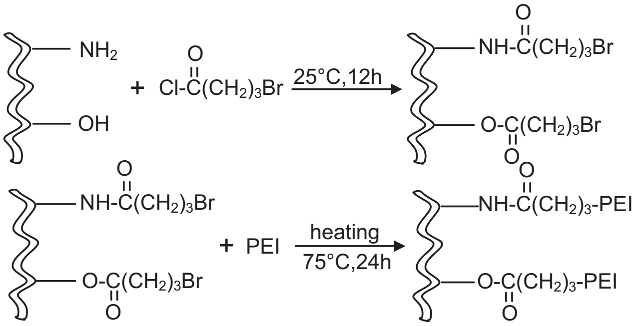

Fig. 1. Process of branched PEI on the biomass surface.

2. Materials and methods

2.1. Micro-organism source

P. chrysosporium (BKMF-1767) was purchased from the China Center for Type Culture Collection (Wuhan, China).

2.2. Preparation of mycelial pellets

P. chrysosporium was cultured at 30 °C for 7 days in a solid culture medium. *P. chrysosporium* spores on an agar plate were scraped into sterile water to form a spore suspension. The turbidity of the suspension was adjusted to 60% (MODEL-21907, USA). Then, 1 mL of the spore suspension was added per 100 mL culture medium. Quantitative suspensions were added to the liquid medium, then the mixtures were cultured for 37–42 h at 30 °C and 120 rpm. Potato-dextrose agar (PDA) was used as both solid and liquid media. Mycelia balls were collected, and parts were placed in an oven (40 °C, 4 h). These mycelia balls were modified by a series of processes as described below. The modified mycelia balls were freeze-dried for 24 h until they reached a constant weight. The modified biosorbent was used to adsorb simulated Cr(VI)-contaminated wastewater.

2.3. Surface modification of *P. chrysosporium*

Ten grams of dried biomass was added to a mixture of 2.5 mL pyridine and 95 mL chloroform. Then, 5 mL of 4-bromobutyryl chloride was added dropwise. The reaction mixture was sealed, and gently stirred at 25 °C for 12 h. The acylated biomass was rinsed with chloroform to remove any unreacted 4-bromobutyryl chloride before immersing it in a mixture of 10 g PEI (molecular weight, 10,000 Da) and 0.1 g KOH in 90 mL tert-amyl alcohol. After the mixture was stirred at 75 °C for 24 h, the modified biomass was rinsed with copious quantities of methanol and deionized water. Finally, the biomass was freeze-dried to a constant weight. The modification process is shown in Fig. 1.

2.4. Zeta potential measurement

About 0.1 g freeze-dried biomass was placed in 100 mL deionized water. The mixture was stirred for 2 h. A pH series from 1.0 to 11.0 was prepared by adjusting with 0.1 mol/L NaOH or 0.1 mol/L HCl. After 1 h of stabilization, the supernatant was decanted, and used for potential measurements with a Zeta-Plus4 instrument (Brookhaven Corp., USA).

2.5. Effect of pH

A 200 mg/L chromium solution and 0.5 g/L biomass were used in the experiments. Different volumes of acid (0.1 mol/L HCl) or alkali (0.1 mol/L NaOH) were added to adjust the pH of the mixture. The pH of the solution was varied from 2.0 to 11.0. The flask was shaken in a thermostatic shaker at 25 °C for 6 h. The total chromium concentrations in the samples were analyzed using an inductively coupled plasma emission spectrometer (ICP-ES, Perkin–Elmer Optima 3000, USA). The colorimetric method was used to determine the Cr(VI) concentration. The pink complex formed by 1,5-diphenylcarbazide and hexavalent chromium was measured at 540 nm, using a spectrophotometer (720-Spectrophotometer, 7230G, Shanghai, China).

2.6. Effect of adsorption time

Batch adsorption experiments were performed in 250 mL flasks, each containing 100 mL chromium solution prepared with potassium dichromate ($K_2Cr_2O_7$). Next, 0.05 g biosorbent was added to the flask, and shaken at 120 rpm in a thermostatic shaker at 25 °C. The initial chromium concentration was 200 mg/L. Samples were intermittently removed from the flask to determine the chromium remaining in the solution at 15 and 30 min, and 1, 2, 3, 6, and 9 h. The total volume of samples withdrawn did not exceed 1.5% of the initial volume (100 mL) for each sampling. The change in volume was not considered during calculation.

2.7. Effect of initial concentration

A series of Cr(VI) solutions with concentrations of 100, 150, 200, 250, and 300 mg/L was prepared to determine the equilibrium isotherms. Next, 0.05 g biosorbent was added to the solutions. An acid or alkali was added to maintain the optimum adsorption pH as determined above. The mixtures were shaken in a thermostatic shaker at 25 °C for 6 h. The final concentration of Cr(VI) and total chromium were analyzed using the same method as described above.

The metal uptake q (mg Cr/g biosorbent) was calculated from the mass balance using the following equation:

$$q = \frac{(C_0 - C_t)V}{W} \times 1000 \quad (1)$$

$$\text{Removal efficiency}\,(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where C_0 and C_t are the initial and final metal concentrations (mg/L), and W and V are the biomass weight (g) and solution volume (mL), respectively. The change in the working volume due to the addition of NaOH or HCl was negligible in these experiments.

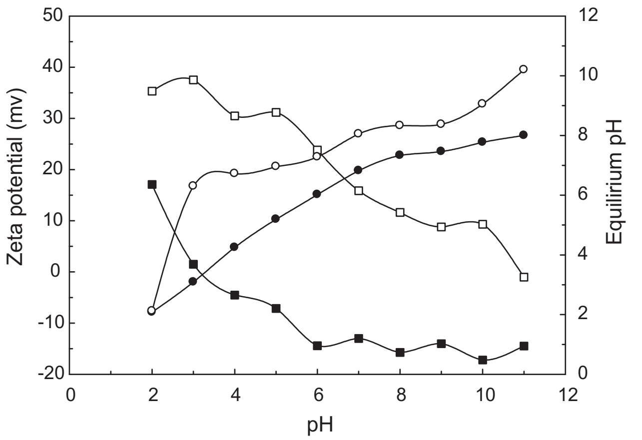

Fig. 2. Change of zeta potential and pH of the pristine and modified biomass (under the conditions of: biosorbent dosage = 0.1 g, rotate speed = 120 rpm, temperature = 25 °C, adsorption time = 2 h; (■) zeta potential of Pristine biomass; (□) zeta potential of modified biomass; (●) equilibrium pH of pristine biomass; (○) equilibrium pH of modified biomass).

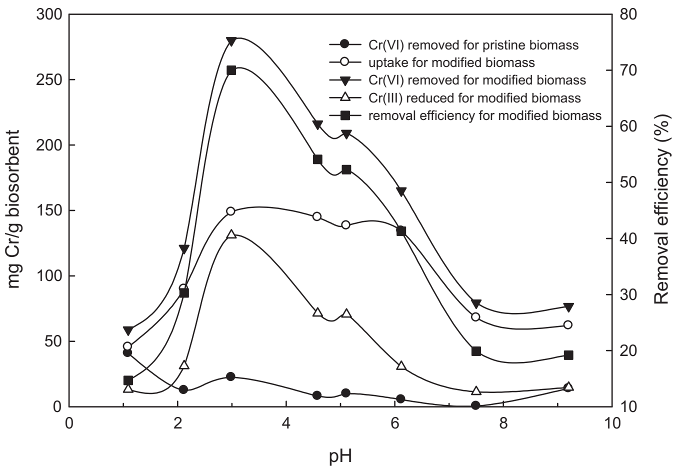

Fig. 3. Effect of initial pH on biosorption (under the conditions of: biosorbent dosage = 0.05 g, rotate speed = 120 rpm, temperature = 25 °C, adsorption time = 6 h and C_0 (Cr(VI)) = 200 mg/L).

3. Results and discussion

3.1. Zeta potential measurement

The potential and equilibrium pH of the pristine and modified biomass in solutions at different pH values are shown in Fig. 2. All experiments were performed in triplicate, and the average value was used. Compared to the initial pH, the pH values in the solution of the pristine and modified biomasses increased as the reaction progressed, which may be due to the consumption of H^+ during chromium removal. Furthermore, H^+ may have participated in the protonation of the amine groups in the biomass surface and reduction of Cr(VI).

Fig. 2 shows that the point of zero potential for the pristine biomass was pH 3.0. In contrast, the point of zero potential for the modified biomass was much higher, i.e., 10.8, which could be attributed to the protonation of amine groups of the PEI molecules on the biomass surface. The potential of the modified biomass was positive at pH < 10.8, whereas the potential of the pristine biomass was positive at pH < 3.0. Other researchers have also reported that the point of zero potential increases significantly after PEI is added to a solid surface. When the PEI is covered with silicon carbide powder, its isoelectric point changes from pH 2.0 to 10.5 [15]. Tang et al. reported that the point of zero charge of nano-zirconia powder shifts from pH 6.0 to 10.5 when PEI is used as a dispersant to stabilize the powder suspension [16]. Considering the electrostatic interactions, the PEI-modified biomass could be expected to adsorb anionic adsorbates better than the pristine biomass since the surface interactions between the adsorbent and adsorbate in the solutions were enhanced.

3.2. Effect of pH on biosorption

The pH is one of the most important parameters that determines the biosorption of metal ions from aqueous solutions [17]. The removal of Cr(VI) from the solution depends greatly on the pH of the solution, which also affects the uptake ability [6]. The pH not only influences the properties of a sorbent surface, but also affects metal speciation in the solution. Some researchers report an optimum pH ranging from 2.0 to 3.0 for the maximum sorption of Cr(VI) using the seaweed biomasses of *Sargassum* and *Ecklonia* spp. [18,19]. However, the optimum pH increases with contact time [20]. The Cr (VI) sorption capacities were higher than 50 mg/g when pH values were above 7.0, indicating that the PEI-modified biomass is capable of adsorbing anionic chromium in a neutral pH solution. In contrast, most sorbents show low sorption capacity for anionic Cr(VI) ions at pH values above 5.0 [18,21]. The difference in performance is closely associated with the functional groups on the sorbent surface. Given that negatively charged groups, such as carboxyls, are the most abundant functional groups on the sorbent surface at pH values above 5.0, and electrostatic repulsion prevents Cr(VI) from approaching these groups. In contrast, amine groups can be protonated even at pH values above 10.0, allowing sorption to occur through electrostatic attraction in solutions at a higher pH.

In this study, experiments were performed to examine the uptake, reduction, and removal efficiency of chromium from chromium-containing solutions (200.00 mg/L) of various pH values. The sorption phenomena varied at different pH values (pH range, 1.0–10.0, Fig. 3). Chromium uptake increased from 45.6 mg/g at pH 1.09 to 148.8 mg/g at pH 2.99. Maximum chromium uptake occurred at a pH of approximately 3.0. Optimum Cr(VI) sorption occurred at pH 3.0. At this pH, Cr(VI) removal, the sum of Cr uptake and Cr(III), reached a maximum value of 279.9 mg/g. Chromium uptake by the pristine biomass was only 22.5 mg/g under optimal conditions, which was much lower than the adsorption capacity of the modified biomass. When the pH is very low, *P. chrysosporium* is protonated as a result of the large number of H^+ ions. The higher the degree of protonation, the greater the degree of repulsion of *P. chrysosporium* by heavy metal ions. This may be due to the competition of H^+ and heavy metal ions for the adsorption sites, impeding the dissociation of active groups and resulting in low adsorption capacity. When the pH is very high, the OH^- and functional groups on the surface of the cell wall of *P. chrysosporium* compete for the heavy metal ions, decreasing the adsorption capacity. The adsorption sites of the biomass increased significantly after it was modified with PEI, considerably increasing the adsorption capacity of the original biomass when the pH was approximately 3.0. During adsorption, redox reactions and the chelation of amine groups on the surface lead to the consumption of H^+ in solution, and as a result, the pH of the solution rises as adsorption occurs.

3.3. Effect of adsorption time on biosorption

The removal of Cr(VI) and Cr(III) in the experiment is shown in Fig. 4. Chromium uptake increased from 42.4 mg/g at 15 min to 149.6 mg/g at 180 min. When the adsorption time was up to 180 min, the adsorption reached equilibrium. At this point, Cr(VI) removal reached the maximum value of 270.0 mg/g, while the

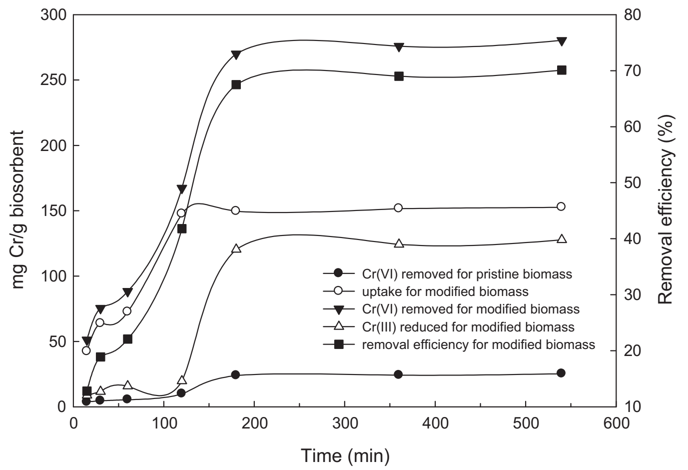

Fig. 4. Effect of contact time on biosorption (under the conditions of: pH = 3.0, biosorbent dosage = 0.05 g, rotate speed = 120 rpm, temperature = 25 °C and C_0 (Cr(VI)) = 200 mg/L).

removal efficiency was 67.5%. After the first 3 h, the unit adsorption capacity of Cr(VI) increased rapidly. However, the adsorption capacity of the pristine biomass was only 23.9 mg/g after 180 min. When *P. chrysosporium* is exposed to wastewater that contains heavy metals, its cell wall first makes contact with the heavy metal in the wastewater. In addition, a large number of active groups aggregate on the surface of the modified biomass, increasing the number of adsorption sites on the surface. These active groups coordinate with the heavy metal ions during adsorption. As the adsorption capacity increases, the adsorption of metal ions on the surface of the cell wall gradually reaches saturation. The repulsion produced by the heavy metal ions on the cell wall is enhanced, resulting in an increase in the resistance of free heavy metal ions to the cell surface. Consequently, the time taken to reach adsorption saturation increases.

3.4. Effect of the initial concentration of chromium on biosorption

As shown in Fig. 5, the adsorption capacity increased as the concentration of heavy metals increased, until the concentration reached 250 mg/L. Subsequently, the unit adsorption capacity began to decline, indicating that the optimum experimental heavy metal concentration was approximately 250 mg/L. At this point, maximum removal of Cr(VI) was 283.05 mg/g, whereas the maximum uptake of Cr(VI) was 155.20 mg/g. A considerable quantity of Cr(III) (127.8 mg/g) was produced in this condition. At a pH of approximately 3.0, chromium was removed with an efficiency of 46.4–68.9%. The results showed that Cr(VI) was reduced in the wastewater, thus the toxicity of Cr(VI)-contaminated wastewater was greatly reduced. Therefore, this modified absorbent can be considered a prospective treatment material for Cr(VI)-contaminated wastewater. Because the pristine biomass had low adsorption capacity, it was not used for follow-up experiments.

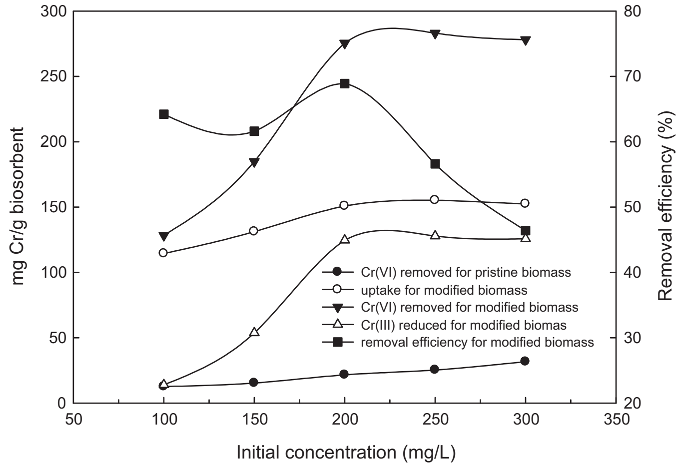

Fig. 5. Effect of different initial concentration on biosorption (under the conditions of: pH = 3.0, biosorbent dosage = 0.05 g, rotate speed = 120 rpm and temperature = 25 °C).

The Langmuir (3) and linearized Freundlich (4) isotherm models are often used to simulate sorption behavior to determine maximum sorption capacity. The following models are usually used.

$$\frac{C_e}{Q} = \frac{1}{Q_m \cdot k} + \frac{C_e}{Q_m} \tag{3}$$

$$\lg Q = \lg K_F + \frac{1}{n} \lg C_e \tag{4}$$

where Q_m is the maximum adsorption capacity of the sorbent (mg/g), Q is the equilibrium adsorption capacity (mg/g), and C_e is the equilibrium concentration in solution (mg/L).

The data shown in Fig. 4 were used to simulate the adsorption performance with the Langmuir and linearized Freundlich isotherm models. The maximum adsorption capacity of this biomass was determined by the Langmuir isotherm model, and found to be 344.8 mg/g at a pH of approximately 3.0, where k was 0.03. The values of K_F and $1/n$, which are the Freundlich constants representing the adsorption capacity and intensity of adsorption, respectively, were 19.6 L/g and 0.54 respectively.

A previous study reported the capacity of low-cost biodegradable adsorbents developed from naturally and abundantly available sawdust to remove Cr(VI) from aqueous solutions and synthetically prepared industrial effluents used in electroplating and tannery industries [22]. The maximum uptake of chromium from chromate-contaminated water by a by-product of *Lentinus edodes* was 21.5 mg/g [23]. Adsorption with a silica-based adsorbent prepared by radiation-induced grafting was an effective and versatile method for removing Cr(VI) [24]. The sorption capacity of the PEI-modified biomass for Cr(VI) was compared to that of several adsorbents as reported in the literature (Table 1). In this study, the sorption capacity of the PEI-modified biomass for Cr(VI) was the highest among all the sorbents examined.

3.5. Kinetic modeling

Kinetic models were established to find the potential rate-controlling steps involved in biosorption. The adsorption rate was normally high at first, but decreased after equilibrium was reached [28]. Two kinetic models, pseudo-first-order Lagergren (5) and pseudo-second-order kinetic (6) models, were used to evaluate the biosorption kinetics of modified *P. chrysosporium*. The following models are usually used.

$$\log(q_e - q) = \log q_e - \frac{k_a}{2.303} t \tag{5}$$

$$\frac{t}{q} = \frac{1}{k_b q_e^2} + \frac{t}{q_e} \tag{6}$$

where q and q_e are the adsorbed amounts (mg/g) at time (t) (min) and at equilibrium time, respectively, k_a (min^{-1}) is the rate constant of the first-order biosorption, and k_b is the rate constant of the second-order biosorption [g/(mg min)].

The value of q_e was 276.5 mg/g according to the pseudo-first-order Lagergren model at a pH of approximately 3.0, whereas k_a was 0.003 min^{-1}. The values of q_e and K_b were 333.33 mg/g and 0.00003 g/(mg min), respectively. The results showed that the q_e

Table 1
Comparison of maximum sorption capacities of various sorbents for Cr(VI).

Sorbents	T (°C)	pH	Q_m (mg/g)	K_F (L/mg)	Ref.
PEI-modified biomass of *P. chrysosporium*	25	3.0	344.8	19.6	This study
By-product of *Lentinus edodes*	25	3.9–4.4	21.5	0.15	[23]
Sawdust	25	1.0	41.5	/	[22]
Brown seaweed *S. siliquosum*	30	3.6–4.2	15.9	0.02	[18]
Silica-based adsorbent	25	3.5	68	/	[24]
4-VP and HEMA mixture-modified (PET) fibers	25	3.0	4.93	6.84 (mg/g)	[25]
APTS-treated biomass of *Rhizopus nigricans*	30	2.0	200	74.19 (mg/g)	[26]
Leaf mould	25	2.0	43	3.8 (mg/g)	[27]

values fit the experimental data better by a pseudo-first-order kinetic model than by a pseudo-second-order kinetic model. Thus, the pseudo-first-order kinetic model was preferable for the adsorption of Cr(VI) by PEI-modified *P. chrysosporium*.

3.6. Sorption mechanisms

To understand the sorption mechanisms of Cr(VI) anions in a solution onto the modified biomass, it is necessary to consider Cr(VI) speciation and biomass surface properties in solutions with different pH values. The Cr(VI) speciation is determined by both pH and chromium concentration.

The Cr(VI) exists in the solution in different forms at different pH values [29]. For example, Cr(VI) mainly exists as $HCrO_4^-$ at pH 1, whereas it exists as $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$ at pH 2–6. As the pH value continues to rise, Cr(VI) changes from its existing form into CrO_4^{2-} and $Cr_2O_7^{2-}$.CrO_4^{2-} is the only form that exists at pH values greater than 7.5. Under acidic and alkaline conditions, the following reactions occur:

$$2OH^- + Cr_2O_7^{2-} \leftrightarrow 2Cr_2O_4^{2-} + H_2O \qquad (7)$$

$$Cr_2O_7^{2} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O \qquad (8)$$

The surface of the PEI-modified biomass exhibited a positive zeta potential at pH values below 10.8. The amine groups (–NH–, –N <, –NH_2) were protonated at pH values below 10.8 and adsorbed anionic hexavalent chromium (CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$) via electrostatic attraction (–NH_2 as the representative species):

$$-NH_3^+ + HCrO_4^- \rightarrow -NH_3^+{-}HCrO_4^- \qquad (9)$$

$$-NH_3^+ + CrO_4^{2-} \rightarrow -NH_3^+{-}CrO_4^{2-} \qquad (10)$$

$$-NH_3^+ + CrO_7^{2-} \rightarrow -NH_3^+{-}Cr_2O_7^{2-} \qquad (11)$$

The converted Cr(III) species may be chelated on the amine groups on the biomass surface. At different pH values, different Cr(III) species exist in solution [30]. Therefore, the possible sorption mechanisms may be as follows (–NH_2 as a representative):

$$-NH_2 + Cr^{3+} \rightarrow -NH_2Cr^{3+} \qquad (12)$$

$$-NH_2 + Cr(OH)^{2+} \rightarrow -NH_2Cr(OH)^{2+} \qquad (13)$$

$$-NH_2 + Cr(OH)_2^+ \rightarrow -NH_2Cr(OH)_2^+ \qquad (14)$$

From the above equation, Cr(III) and Cr(VI) exist in the solution, as well as on the surface of the biomass. Fig. 3 shows the distribution of Cr(III) and Cr(VI) species in the solution after sorption onto the PEI-modified biomass at different pH values. The residual Cr(VI) concentration in the solution was the lowest at pH 3.0, and it increased with increasing pH, whereas the Cr(III) concentration decreased with increasing pH over the same pH range.

4. Conclusions

PEI-modified *P. chrysosporium* is an effective biosorbent for Cr(VI), and has good potential for use in chromium removal in Cr(VI)-contaminated wastewater. The point of zero potential changed from pH 3.0 to 10.8 after the biomass was modified, which is attributed to the protonation of the amine groups in the PEI molecules on the biomass surface. An important parameter that affects the sorption of metal ions is pH. The optimal pH for adsorption is 3.0. A pH that is higher or lower than 3.0 would decrease the adsorption capacity of the modified biomass. According to the Langmuir adsorption isotherm, Cr(VI) removal reached a maximum of 344.8 mg/g. During adsorption, a large amount of the toxic Cr(VI) was reduced to the less toxic Cr(III), and about 32.5% of Cr(VI) was reduced to Cr(III) in the solution under optimal conditions. The process of adsorption of Cr(VI) ions by PEI-modified *P. chrysosporium* was successfully described by a pseudo-first-order model.

Acknowledgments

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