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# Reduction and removal of Cr(VI) from aqueous solutions using modified byproducts of beer production

### Haojie Cui<sup>a,\*</sup>, Minglai Fu<sup>a</sup>, Shen Yu<sup>a</sup>, Ming Kuang Wang<sup>b</sup>

<sup>a</sup> Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, 1799 Jimei Road, Xiamen 361021, China <sup>b</sup> Department of Agricultural Chemistry, National Taiwan University, No. 1, Sec.4, Roosevelt Road, Taipei 106, Taiwan

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#### 1. Introduction

Pollution by hexavalent chromium (Cr(VI)) has received widespread attention, due to its acute toxicity and the wide use in various industries, including metallurgy, leather tanning, electroplating, and wood preservation. Several treatment methods for Cr(VI) removal from industry wastewater have been established, i.e., electrochemical precipitation, ion exchange, membrane ultrafiltration, reverse osmosis, reduction, and adsorption [1–5]. However, most of these methods are costly due to operational, treatment and sludge disposal costs. In recent years, biosorption has been developed, employing agricultural and fermentation wastes and various kinds of microorganisms as biomass. This can remove Cr(VI) from dilute aqueous solutions and offers low-cost, abundant raw materials, and an environmentally friendly process [6–12].

Numerous reports have been made on the removal of Cr(VI) from aqueous solutions using different organisms as adsorbents, including walnut hulls, bacteria, algae, fungi, seaweed, industrial byproducts and agricultural biowastes [13]. Various reports have explored how each material's capacity depends on reaction time, solution pH, temperature, material dosage, and type of biomaterials [8,12–14]. The mechanism for Cr(VI) biosorption is usually based on adsorption-coupled reduction, and electron transfer in the process of reduction and adsorption as well as the sorption

#### ABSTRACT

Biosorption, as an effective and low-cost technology treating industrial wastewaters containing Cr(VI), has become a significant concern worldwide. In this work, acid-modified byproducts of beer production (BBP) were used to remove Cr(VI) from aqueous solutions. Removal of Cr(VI) increases as the pH is decreased from 4.0 to 1.5, but the maximum of total Cr removal is obtained in a pH range from 2.0 to 2.5. Nearly 60% of the initial Cr(VI) ( $100 \text{ mg L}^{-1}$ ) was adsorbed or reduced to Cr(III) within the first 10 min at pH 2.0. The Cr(VI) removal capability of acid-modified BBP materials was almost completely retained after regenerating with acid. FT-IR and XPS spectra revealed that carboxylate and carboxyl groups on the surface of modified BBP materials play a major role in Cr(VI) binding and reduction, whereas amide and other groups play a minor role in the Cr(VI) removal process.

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sites involved in the redox reaction between Cr(VI) and biomass have been investigated [7,15,16]. Various reports have showed that the functional groups involved in the adsorption-coupled reduction reaction depend on the type of biomass; and amino, carboxyl, sulfonate, thiol, phenolic, and lignin, tannin groups of biomaterials have been reported as Cr(VI) sorption sites or electron-donor groups [6,17–23].

Although many types of biomass have been selected for removing Cr(VI) from aqueous solution, but there is little information on byproducts of beer production (BBP), which is most abundant residue from beer production. Moreover, the BBP materials contain many protons (solution pH approximately 3.7 with 1:10 of the relation m/v), which participate in the adsorption and reduction reactions between Cr(VI) and biomass materials [6–9]. In this study, our main objectives were to investigate the possible use of inorganic acid modified BBP as an alternative biosorbent material for removal of Cr(VI) ions from aqueous solutions. In batch studies, the effect of initial pH, isotherms, kinetics, and recovered BBP materials for the removal of Cr(VI) have been investigated. Finally, mechanism of Cr(VI) biosorption by BBP materials was characterized by Fourier Transform Infrared (FT-IR) and X-ray photoelectron spectroscopies (XPS).

#### 2. Materials and methods

#### 2.1. Materials and adsorbents

A byproduct of beer production (BBP) was kindly supplied by a beer producer from Xiamen, China. The raw BBP was washed with

<sup>\*</sup> Corresponding author. Tel.: +86 592 6190559; fax: +86 592 6190514. *E-mail address*: hjcui@iue.ac.cn (H. Cui).

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deionized distilled water (DDW) several times, and then dried in an oven at 75 °C for 24 h. 100 g of the washed and dried raw BBP was treated with 1 L of 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 2 mol L<sup>-1</sup> HNO<sub>3</sub>, and 2 mol L<sup>-1</sup> HCl for 24 h, respectively, then washed with DDW several times and dried at 75 °C for 24 h to yield the acid-modified BBP materials. The mass loss is about 15% after treating with the three different acids. The modified BBP materials were labeled as BBP-S, BBP-N, and BBP-Cl. Hexavalent chromium solutions were prepared by dissolving appropriate amounts of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in DDW. A 0.1 mol L<sup>-1</sup> HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> solutions were used for initial pH adjustment, respectively. All reagents were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification.

#### 2.2. Batch experiments for Cr(VI) reduction and removal

Cr(VI)-reduction and Cr-removal capacities of raw and modified BBP materials were evaluated by measuring the time-dependent concentrations of Cr(VI) and total Cr in a batch system. In experiment to examine the pH effect,  $6.67 \text{ gL}^{-1}$  of dried BBP material was mixed with  $100 \text{ mg L}^{-1}$  of Cr(VI) solution at pHs of 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0, monitoring with pH-stat (TIM865, Titration Manager, Radiometer Analyzer). To screen efficient BBP materials for Cr(VI) reduction and Cr removal,  $6.67 \text{ g L}^{-1}$  of dried BBP materials was mixed with  $100 \text{ mg L}^{-1}$  of Cr(VI) solution at pH 2. To examine the effect of initial Cr(VI) concentration on the Cr(VI) reduction and Cr removal by the BBP materials,  $6.67 \text{ g L}^{-1}$ of dried BBP materials were contacted with 0, 5, 10, 20, 50, 100, 200, 300 and 400 mg L<sup>-1</sup> of Cr(VI) at pH 2. Regeneration and reuse of BBP-Cl studies were carried out using 2 mol L<sup>-1</sup> HCl. For this, exhausted adsorbent in a 250 mL conical flask was mixed with 100 mL of 2 mol L<sup>-1</sup> HCl solution and agitated in a shaker at 150 rpm for 4 h, after which, the adsorbent was washed five times with DDW in order to remove excess acid. It was again used as an adsorbent in more cycles to evaluate the reuse potential of the BBP-Cl. The flasks were agitated on a shaker at 250 rpm and 25 °C. The solution was intermittently sampled and centrifuged at 4000 rpm for 10 min, after which the Cr(VI) and total Cr concentrations of the supernatant were analyzed immediately. Batch experiments were conducted in duplicate, and average values are presented.

#### 2.3. Analysis of chromium

A standard colorimetric method was used to measure the concentrations of Cr(VI) in a visible spectrophotometer at 540 nm (vis-7220 model) [24]. The total concentration of chromium, i.e., Cr(VI)+Cr(III), in the remaining solution after sorption was determined by atomic absorption spectroscopy (AAS) (Thermo Element).

#### 2.4. FT-IR and XPS analyses

For a qualitative and preliminary analysis of the main functional groups that can be involved in Cr(VI) reduction and Cr uptake, FT-IR analysis of the solid phase was performed using a Fourier Transform Infrared spectrometer (FT-IR, Thermo Scientific Nicolet iS10). FT-IR spectra of the BBP materials before and after Cr(VI) contact were recorded. For the FT-IR study, approximately 2 mg of finely ground BBP materials was encapsulated in 200 mg of KBr to make translucent sample disks. Samples were scanned 15 times between 4000 and 400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

To investigate the oxidation state of chromium sorbed on the BBP materials surface, X-ray photoelectron spectroscopy (XPS) spectra of BBP loaded with Cr(VI) were recorded on a PHI Quantum 2000 Scanning ESCA Microprobe spectrometer with a Al K $\alpha$  incident X-ray beam. The X-ray source was operated at 35 W, and

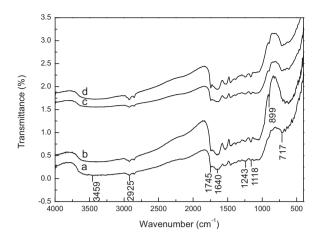


Fig. 1. FT-IR spectra of (a) raw BBP and acid treated BBP materials (b) BBP-N; (c) BBP-S; (d) BBP-CI.

the spectra were recorded at 15 kV. The analysis chamber pressure was  $5\times 10^{-8}$  Pa.

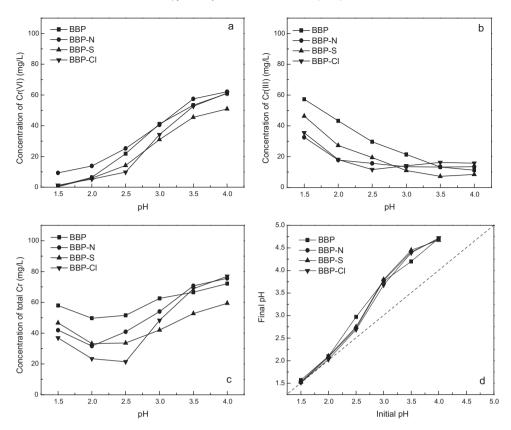
#### 3. Results and discussion

# 3.1. Characterization of surface functional groups on BBP materials

FT-IR spectroscopy was used to investigate the major functional groups involved in the Cr(VI) reduction and adsorption processes. The infrared spectra of the raw BBP and the three acid-modified BBP materials are shown in Fig. 1. The broad absorption band around 3459 cm<sup>-1</sup> indicates the existence of –OH stretching, thus showing the presence of hydroxyl groups on the four BBP materials surface [25]. FT-IR spectra of absorption vibration observed at 2925 cm<sup>-1</sup> are associated with the special vibration of C-H stretching of -CH<sub>2</sub> groups [11]. The FT-IR absorption vibration at 1745 cm<sup>-1</sup> was attributed to the stretching vibration of free carbonyl from carboxylic groups [16]. The relatively broad vibration mode at 1640 cm<sup>-1</sup> can be attributed to the stretching vibration of carboxylate anion [6]. The FT-IR bending modes at about 1243 and  $1118 \text{ cm}^{-1}$  represent  $-SO_3$  stretching [25,26], which was also observed in the FT-IR spectra of the four BBP materials. The intense FT-IR bending mode at 717 cm<sup>-1</sup> was caused by the special vibration of -CN stretching [21]. Almost no significant changes of the functional group were visible after acid modification, but the intensity of bending mode at 899 cm<sup>-1</sup> became strong, indicating that the acid modification promote the formation of carbohydrate units [6].

#### 3.2. Effect of pH on Cr(VI) adsorption and reduction

Earlier studies have indicated that solution pH is an important parameter affecting sorption and reduction of Cr(VI) [6,8,21,27]. Fig. 2 demonstrates that the conversion of Cr(VI) depends mainly on the pH of the aqueous solutions with the raw and three acid modified BBP materials, and the remaining concentrations of Cr(VI) in aqueous solutions increase with increasing pH (Fig. 2a), indicating that it is suitable for reduction of Cr(VI) by controlling the solution pH  $\leq$  2. In addition, the Cr(III) concentrations in solutions decrease with increasing pH, and the Cr(III) concentration for the raw BBP treatment is higher than that of BBP-N, BBP-S and BBP-Cl treatments (Fig. 2b). As shown in Fig. 2c, the concentrations of total Cr first decrease with increasing pH from 1.5 to 2.5, and then begin to increase with further increase of pH in aqueous solutions. The initial and final pH values of Cr(VI) solutions after 24 h con-



**Fig. 2.** Effect of initial pH on reduction of Cr(VI) (a) soluble Cr(VI); (b) soluble Cr(III); (c) soluble total Cr; (d) pH variation after contacting the four BBP materials with Cr(VI) solutions (100 mg L<sup>-1</sup> of initial Cr(VI) concentration, 6.67 g L<sup>-1</sup> of BBP materials, contact for 24 h).

tact with the four BBP materials are shown in Fig. 2d. The solution pH increases very slightly after coming into contact with four BBP materials with Cr(VI) at solution pH 1.5 and 2.0, and the solution pH increases markedly in all the cases as a result of 24 h contact with the four BBP materials at initial solution pH above 2.5 (Fig. 2d). Moreover, the mass loss is about 10–15% for the raw BBP materials at initial pH from 3.0 to 1.0, and there is no significant weight loss for the other three acid modified BBP materials. As can be seen in Fig. 2, it is suitable to reduce Cr(VI) and remove total Cr in aqueous solutions in a pH range of 2.0–2.5. Therefore, the solution pH of 2.0 was fixed for adsorption and reduction of Cr(VI) for further studies.

#### 3.3. Kinetic studies

The effects of time on adsorption and reduction of Cr(VI) for the four BBP materials were investigated and are shown in Fig. 3a, which indicates that nearly 60% of the initial Cr(VI) was adsorbed or reduced to Cr(III) for the four BBP materials within the first 10 min, and Cr(VI) disappeared in aqueous phase for the raw BBP, BBP-S, and BBP-Cl within 96 h, but the Cr(VI) removal rate for BBP-N is slower than other three BBP materials. In order to investigate the mechanism of sorption and reduction of Cr(VI), the pseudo-firstorder and pseudo-second-order kinetic models have been used to fit the experimental data, and the adsorption and reduction rate constants  $k_1$  and  $k_2$ , along with correlation coefficients  $R^2$ , are listed in Table 1. Comparing with linear correlation coefficient  $R^2$ , kinetics data for the adsorption and reduction of Cr(VI) from aqueous solution were in good agreement with pseudo-second-order rate equation, which considers the rate-limiting step as chemisorption through sharing or exchange of electrons between adsorbate and adsorbent [11].

Furthermore, Cr(III) appears in the supernatant liquid after the four BBP materials were immersed in Cr(VI) solutions, and the con-

 Table 1

 Kinetic parameters for Cr(VI) ion adsorption and reduction on BBP materials.

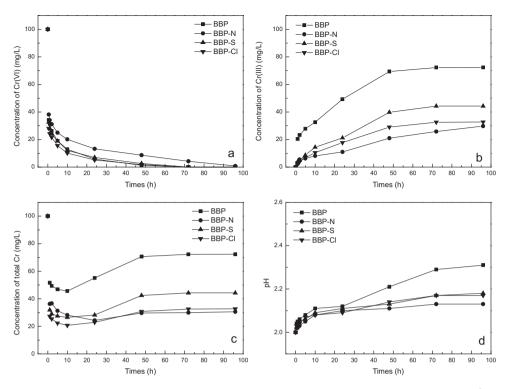
Adsorbent	Pseudo-first-order <sup>a</sup>		Pseudo-second-order <sup>b</sup>	
	$k_1 (\min^{-1})$	$R^2$	$k_2$ (g/(mg min))	<i>R</i> <sup>2</sup>
BBP	2.273	0.9095	0.2716	0.9621
BBP-N	2.427	0.9265	0.3297	0.9685
BBP-S	2.509	0.9341	0.3218	0.9738
BBP-Cl	2.883	0.9439	0.3860	0.9775

<sup>a</sup> The kinetic model as proposed  $\log(q_e - q_t) = \log q_e - k_1^* t/2.303$ ,  $q_e$  and  $q_t$  are the amounts of Cr(VI) adsorption and reduction (mg/g) at equilibrium and at any instant of time t (min), respectively, and  $k_1$  is the rate constant of pseudo-first-order adsorption (min<sup>-1</sup>).

<sup>b</sup> The kinetic model as proposed  $t/q_t = 1/(k_2^*q_e^2) + t/q_e$ ,  $q_e$  and  $q_t$  are the amounts of Cr(VI) adsorption and reduction (mg/g) at equilibrium and at any instant of time t (min), respectively, and  $k_2$  is the equilibrium rate constant of pseudo-second-order adsorption (g/(mg min)).

centrations of Cr(III) all increase with increasing contact time, and attain equilibrium within 96 h (Fig. 3b). The presence of Cr(III) in the solutions indicates that BBP materials can reduce Cr(VI) to Cr(III) under the present experimental conditions. However, the Cr(III) concentration in solution with raw BBP treatment was higher than that of BBP-N, BBP-S and BBP-Cl treatments, which indicates that the acid-modified BBP materials is higher adsorption capacity for Cr(III) than that of raw BBP material.

On the other hand, the concentrations of total Cr firstly decrease with longer contact time within 10 h, and then begin to increase slightly with further increasing of contact time until attaining equilibrium within 96 h (Fig. 3c). It has been proposed that Cr(VI) was abiotically removed from an aqueous system by biomass through a adsorption-coupled reduction mechanism [17]. The reduction of Cr(VI) would lead to protons consumed and solution pH increase, resulting in an decrease of binding of anionic Cr(VI) ion species with the positively charged groups on the surface of BBP [11]. Similar



**Fig. 3.** Effect of time on the adsorption and reduction of Cr(VI)(a) soluble Cr(VI); (b) soluble Cr(III); (c) soluble total Cr; (d) solution pH (100 mg L<sup>-1</sup> of initial Cr(VI) concentration, 6.67 g L<sup>-1</sup> of BBP materials, initial pH 2).

results were also obtained in the other study [28]. Moreover, the total Cr concentration in solution for raw BBP treatment is higher than that of BBP-N, BBP-S and BBP-Cl treatments, and the Cr(VI) removal rate order was BBP-Cl>BBP-S>BBP-N>raw BBP (Fig. 3c). This result indicates that the inorganic acid modified BBP materials can improve the removal of total Cr from aqueous solutions. The solution pHs increase very slightly after coming into contact with the three acid modified BBP materials with Cr(VI), and the solution pH increases markedly in the case as a result of 96 h contact with the raw BBP material (Fig. 3d).

#### 3.4. Reduction of Cr(VI) into Cr(III) affected by Cr concentrations

Fig. 4 shows the effect of initial Cr(VI) concentration on Cr(VI) adsorption and reduction by the raw and three acid-modified BBP materials. It is generally observed that the adsorption and reduction of Cr(VI) increase with higher initial Cr(VI) concentrations, and almost all of the Cr(VI) was adsorbed and converted into Cr(III) when the initial Cr(VI) concentrations were lower than  $100 \text{ mg L}^{-1}$ (Fig. 4a). Moreover, reductions of Cr(VI) by the four BBP materials are very similar under different Cr(VI) concentrations (Fig. 4a), indicating that the pretreatment of raw BBP with inorganic acids has few effect on Cr(VI) reduction. Furthermore, almost no Cr(III) could be detected in the supernatants of the contacted solutions with initial Cr(VI) concentration lower than 50 mg L<sup>-1</sup>, and the concentration of Cr(III) in solution increase with higher initial Cr(VI) concentration (Fig. 4b), indicating that Cr(III) in solution as a product of Cr(VI) reduction is related to the initial Cr(VI) concentration. However, there were different concentrations of Cr(III) in the solutions after contacting the four BBP materials with above  $50 \text{ mg L}^{-1}$ of initial Cr(VI) solutions and the Cr(III) concentrations of the solutions for the BBP-N, BBP-S and BBP-Cl treatment were obviously lower than that of the raw BBP treatment (Fig. 4b). To optimize the design of an adsorption system for removing Cr from solutions, the Langmuir and Freundlich isotherms were applied to fit the equilibrium data in this study. The correlation coefficients for the four BBP materials from the Langmuir model and Freundlich equation showed that the Freundlich equation was more in correlation with the experimental data (Fig. 4c), and the correlation coefficients ( $R^2$ ) were 0.941, 0.926, 0.931, and 0.938 for BBP, BBP-N, BBP-S, and BBP-Cl samples, respectively. The results indicate that the inorganic acid modified BBP materials are more suitable for reduction and removal of Cr(VI) solutions with high concentration than that of raw BBP materials.

#### 3.5. Regeneration and reuse studies of BBP

For the sustainability of an adsorption process, the adsorbents should have good desorption and reuse potential. The acid-modified BBP materials could be regenerated by treating with a corresponding inorganic acid. As shown in Fig. 5a, the concentrations of Cr(VI) in the solution after contact with regenerated BBP-Cl materials in second and third regenerations with Cr(VI) solutions increase slightly compared to that of first treatment. But the Cr(VI) concentration still could be found to sharply decreased and was finally below the lower limit of detection for analytical method employed. In addition, the concentration of Cr(III) and total Cr in the contacted solutions are similar between fresh BBP-Cl and the two regenerated BBP-Cl materials treatment (Fig. 5b and c). Therefore, the reduction and removal rate for Cr(VI) was almost completely retained after regenerating with acid. The solution pHs increase very slightly after coming into contact with the recovered BBP materials with Cr(VI) (Fig. 5d). There was approximately 10% weight loss in the first recovery and a total of 18% of the weight was lost in the second recovery with 2 mol L<sup>-1</sup> HCl. However, there was no significant weight loss for the third recovery.

#### 3.6. Mechanisms of Cr(VI) adsorption and reduction

The aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent. In this study, the pH values of initial solutions were adjusted to below 4.0,

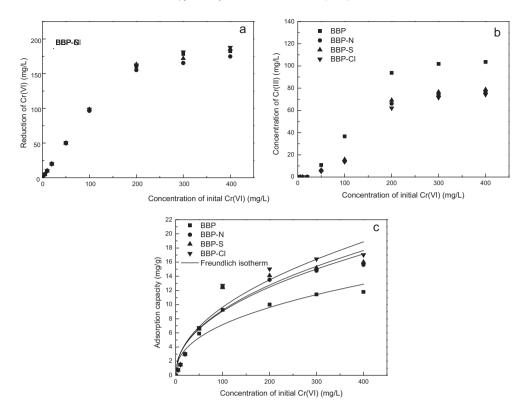
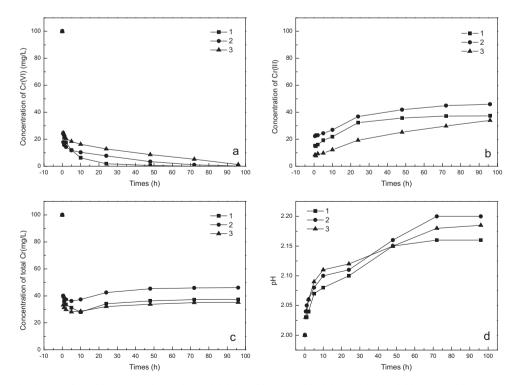


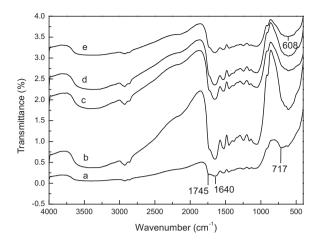
Fig. 4. Effect of initial Cr(VI) concentration on adsorption and reduction of Cr(VI) for BBP materials (a) reductions of Cr(VI); (b) soluble Cr(III); (c) adsorption of Cr (6.67 g L<sup>-1</sup> of BBP materials, pH 2, contact for 24 h).

and the acid chromate ion species ( $\text{HCrO}_4^-$ ) was the major form of Cr(VI) at this range of pH value [29]. With lower pH of the aqueous phase, there is easier protonation of functional groups such as amino, carboxyl and sulfonate groups of biomaterials [30,31]. Thus, low pH makes the BBP material surfaces more positive. When

the positive surface charge of the BBP materials is higher, the removal rate of Cr(VI) in the aqueous phase is faster, since the binding of anionic Cr(VI) species with the positively charged groups is enhanced as a result of electrostatic interaction. Low pH also accelerates the redox reactions in aqueous and solid phases, since the



**Fig. 5.** The adsorption and reduction of Cr(VI) by recovered BBP-CI materials (a) soluble Cr(VI); (b) soluble Cr(III); (c) soluble total Cr; (d) pH variation during contacting the recovered BBP materials with Cr(VI) solutions (100 mg L<sup>-1</sup> of initial Cr(VI) concentration, 6.67 g L<sup>-1</sup> of BBP materials, initial pH 2).



**Fig. 6.** FT-IR spectra of (a) untreated BBP-Cl and BBP-Cl contacted 24 h with different concentrations of Cr(VI) solution (b)  $10 \text{ mg L}^{-1}$ ; (c)  $50 \text{ mg L}^{-1}$ ; (d)  $100 \text{ mg L}^{-1}$ ; (e)  $200 \text{ mg L}^{-1}$  (6.67 g L<sup>-1</sup> of BBP-S materials, initial pH 2).

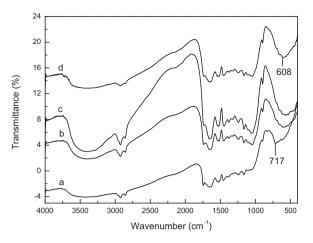
protons participate in these reactions as Eq. (1) [8].

$$HCrO_4^{-}+7H^{+}+3e \leftrightarrow Cr^{3+}+4H_2O$$
(1)

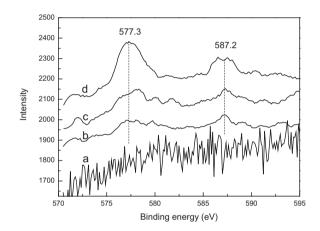
Therefore, the adsorption and reduction of higher amounts of  $HCrO_4^-$  ions would lead to a large number of hydroxide ions released and protons consumed, which results in higher pH (Fig. 2d). The CN-groups of biomaterials could serve as electrondonor groups in the process of reduction-sorption [16]. Meanwhile, cationic  $Cr^{3+}$  ions in aqueous phase can bind to negatively charged groups, such as carboxyl and sulfonate groups, and thus its removal efficiency decreases with lower pH (Fig. 2c) [6,17].

The adsorption and reduction of Cr(VI) induces some substantial modification of the FT-IR spectra. The FT-IR spectra corresponding to the BBP-Cl loaded with Cr(VI) exhibit an apparent shift in the bending mode at 717 cm<sup>-1</sup> and a decrease in the ratios of the COOH  $(1745 \text{ cm}^{-1})$  and COO-  $(1640 \text{ cm}^{-1})$  groups intensities (Fig. 6), indicating that the amide, carboxylate, and carboxyl groups are involved in the chemical adsorption and reduction of Cr(VI). The decreased intensity of bending mode at 1745 cm<sup>-1</sup> indicates that more Cr ions bonded with carboxyl groups at higher Cr(VI) concentration. This result is in agreement with the AAS analysis, which showed that almost no Cr(III) can be detected in the supernatants of the contacted solutions with initial Cr(VI) concentration lower than 50 mg  $L^{-1}$  (Fig. 4b). Moreover, compared with the FT-IR spectra of the new BBP-Cl and the regenerated BBP-Cl materials, there was a clear bending mode shift at 717 cm<sup>-1</sup> (Fig. 7), similar to that of the Cr-load BBP-Cl (Fig. 6). This result suggests that the functional amide group cannot be recovered after regeneration with 2 mol L<sup>-1</sup> HCl. On the other hand, the adsorption and reduction rates of new BBP-Cl and regenerated BBP-Cl materials for Cr(VI) are similar between (Fig. 5). These results indicate that carboxylate and carboxyl groups specifically play a major role in Cr(VI) binding sites for BBP and reduction, whereas amide and other groups play a minor role in Cr(VI) chemical binding and reduction.

Many studies have shown that Cr(VI) is removed from the aqueous phase by nonliving biomass materials through an adsorption-coupled reduction mechanism [6–8,11,15], and Cr(VI)can be reduced from an aqueous system by biomaterials through both direct and indirect reduction mechanisms [7,15]. To characterize the main mechanism of Cr(VI) removal, it is very important to verify the oxidation state of the chromium bound to the biomaterial. As illustrated in Fig. 8, two main contributions of  $Cr_{2p}$ peaks of chromium sorbed in BBP-Cl appeared close to the binding energies of 577.3 and 587.2 eV, and the intensity of the two peaks increased with increasing immersion time because more chromium



**Fig. 7.** FT-IR spectra of (a) new BBP-Cl; (b) first regenerated BBP-Cl; (c) second regenerated BBP-Cl; (d) third regenerated BBP-Cl.



**Fig. 8.** XPS spectra of BBP-Cl loaded with  $100 \text{ mg L}^{-1}$  Cr(Vl) under an immersion time of (a) 0 min, (b) 10 min, (c) 2 h, and (d) 24 h at pH 2.0.

is bound to the BBP-CI. These values are similar to the binding energy of the references in Cr(III) but are different from the binding energy in Cr(VI) [6,7,15,16]. Therefore, Cr(III) is present on the surface of BBP-Cl biomass when it is immersed in Cr(VI). These results imply that the adsorption process involves the reduction of Cr(VI) into Cr(III) with its subsequent partial sorption. Moreover, batch removal experiments have shown the Cr(VI) concentration sharply decreases in the first 10 min (Fig. 3), but no significant bands of Cr(VI) appeared in the XPS spectrum corresponding to the BBP-Cl loaded with Cr(VI) for the same time (Fig. 8). These results imply that the redox reaction occurring on the BBP materials surface can be extremely fast, and more reduced Cr(VI) will be loaded on the surface of modified BBP materials with prolonged the reaction time.

#### 4. Conclusions

Raw BBP and three acid modified BBP biomaterials were used for reduction and removal of Cr(VI) from aqueous solutions. The amide, carboxylate, and carboxyl groups on the surface of modified BBP materials are involved in the biosorption and reduction of Cr(VI). The carboxylate and carboxyl groups play major roles in Cr(VI) binding and reduction, whereas the amide group plays a minor role in Cr(VI) chemical binding site on BBP and reduction. The biosorption and reduction process is fairly fast, and a pH range from 2.0 to 2.5 is suitable for the Cr(VI) reduction and removal. The adsorption and reduction capabilities of acid-modified BBP materials for Cr(VI) can be recovered by treating with corresponding acid treatment. Thus, the acid modified BBP materials can be used as a biomass for reduction and removal of Cr(VI) from aqueous solutions.

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