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*Journal of* Hazardous Materials

Journal of Hazardous Materials 150 (2008) 446-452

www.elsevier.com/locate/jhazmat

# Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste—Rice straw

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#### Abstract

The removal of Cr(VI) from aqueous solution by rice straw, a surplus agricultural byproduct was investigated. The optimal pH was 2.0 and Cr(VI) removal rate increased with decreased Cr(VI) concentration and with increased temperature. Decrease in straw particle size led to an increase in Cr(VI) removal. Equilibrium was achieved in about 48 h under standard conditions, and Cr(III), which appeared in the solution and remained stable thereafter, indicating that both reduction and adsorption played a part in the Cr(VI) removal. The increase of the solution pH suggested that protons were needed for the Cr(VI) removal. A relatively high level of  $NO_3^-$  notably restrained the reduction of Cr(VI) to Cr(III), while high level of  $SO_4^{2-}$  supported it. The promotion of the tartaric acid modified rice straw (TARS) and the slight inhibition of the esterified rice straw (ERS) on Cr(VI) removal indicated that carboxyl groups present on the biomass played an important role in chromium remediation even though were not fully responsible for it. Isotherm tests showed that equilibrium sorption data were better represented by Langmuir model and the sorption capacity of rice straw was found to be 3.15 mg/g.

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Keywords: Rice straw; Cr(VI) removal; Reduction; Adsorption; Isotherm

# 1. Introduction

Growing attention is being given to health hazards caused by the existence of heavy metals in the aqueous environment and their accumulation in living tissues poses a serious health problem. Chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern [1]. Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production [2]. Extensive use of chromium results in large quantities of chromium-containing effluents which need an exigent treatment.

In general, the physico-chemical treatment technologies for removing chromium from industrial waste include ion-exchange, electrodepositing, chemical precipitation and

0304-3894/\$ – see front matter © 2007 Published by Elsevier B.V. doi:10.1016/j.jhazmat.2007.04.126

adsorption [3]. Since these methods are often very costly, requiring high energy input or large quantities of chemical reagents, using biologic methods for removal of chromium offers a potential alternative [4]. New approaches for removing chromium from wastewaters using bacteria [5-7], fungi [3,8], algae [9] and various kinds of plants [10,11] have been reported. Although these materials presented good performance under laboratory conditions, their use for large-scale effluent treatment may not be suitable due to their relatively poor nature abundance, continuous nutrient requirement and constraints of various physiological factors such as Cr(VI) toxicity for living of cells. On the other hand, the successful use of many other low-cost natural materials, such as sawdust [12], rice husk [13], peanut shells [14,15], which could conquer the disadvantages mentionedabove, may show higher potential for the removal of Cr(VI) from aqueous environment and thus gain important reliability and more attention during recent years.

In this sense, many byproducts of agriculture may be good candidates in the detoxification of Cr(VI). In South China, rice is a very common and abundant crop and its byproduct-rice straw, which is 1.35 times more than the grain harvested in the field, is being considered as a significant waste disposal problem nowa-

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days [16]. In addition, rice straw is a fibrous material typical of most agricultural residues and the presence of compounds such as cellulose, hemi-cellulose, lignin and silica in this material, with binding sites capable to tack up metals also suggests the use of rice straw may hold the potential in the detoxification of chromium in a more environmental-friendly and cost-effective manner.

However, the use of rice straw for removal of Cr(VI) from aqueous solution has not been described. Thus providing useful information about the removal characteristics of rice straw may be essential for understanding its Cr(VI) removal capacity and give us a new direction to select biologic materials which are competent for the remediation of chromate pollution.

The aims of the present investigation are to detect the performance of rice straw on Cr(VI) removal from aqueous solution and to evaluate the effect of various parameters including pH, initial Cr(VI) concentration, temperature, straw particle size, different concentrations of  $NO_3^-$  and  $SO_4^{2-}$  and specific modifications. Furthermore, sorption isotherms are conducted and the potential application of rice straw for the detoxification of Cr(VI) is discussed.

# 2. Materials and methods

#### 2.1. Samples and reagents

The air-dried rice straw was obtained from a local rice mill in Changsha, China and was passed through different sieve size. The fraction of particle between 150 and 380  $\mu$ m was selected. Rice straw was washed several times with distilled water and was dried at 50 °C. The dried rice straw was stored in a desiccator, until used for the following batch experiments.

All reagents were of analytical grade and the stock solution (1 mg/ml) was prepared by dissolving the exact quantities of  $K_2Cr_2O_7$  in deionized water. Before mixing all chemical solutions, each chemical was separately dissolved in deionized water and autoclaved  $(121 \,^{\circ}C)$  for 20 min.

#### 2.2. Batch experiments and isotherm studies

Batch experiments were conducted in 250 ml flasks with a working volume of 100 ml agitated on a shaker at 150 rpm under anaerobic conditions. The solution pH was adjusted to the desired value using 10% (w/v) NaOH and 10% (w/v) HCl. Each experiment was performed in replicate and the mean values were taken into account. The following set of factors was chosen as the standard conditions: 10 g/l of rice straw ( $\leq 150 \text{ }\mu\text{m}$ ), 100 mg/l of initial Cr(VI) concentrations at pH 2.0, 47 °C. To determine the effects of pH variation on Cr(VI) removal, pH of 2–6 were used at room temperature  $(27 \,^{\circ}\text{C})$ ,  $40 \,\text{mg/l}$  of initial Cr(VI) concentration; and of initial Cr(VI) concentration variation, concentrations of 40, 60, 100, 150 and 200 mg/l were used at pH 2.0, 27 °C. The effect of temperature was studied in the range 27-47 °C, which was controlled using a water bath at pH 2.0, 100 mg/l of initial Cr(VI) concentration. In the experiments with different straw particle size, sizes between 150 and 380 µm were used at pH 2.0, 100 mg/l of initial Cr(VI) concentration and

47 °C. The solution pH variation was determined to discuss the action of protons in Cr(VI) removal by rice straw. In order to research the effect of  $NO_3^-$  and  $SO_4^{2-}$  on reduction of Cr(VI) to Cr(III), experiments with different amounts of  $NO_3^{-1}$  and  $SO_4^{2-1}$ were conducted under standard conditions, in which NO3<sup>-</sup> concentrations varied from 100 to 500 mg/l; SO<sub>4</sub><sup>2-</sup> concentrations varied from 100 to 800 mg/l. Treatment reagents which contain or could breach the carboxyl groups were chosen according to the reported significant influence of this functional group in the adsorption of various kinds of metals [1,9,17,18]. Modification of rice straw with tartaric acid (TARS) was carried out using the method reported by Marshall et al. [14]. Rice straw was mixed in a ratio of 1 g straw to 7 ml of 1.2 M tartaric acid and the acid/straw slurry was dried overnight at 50 °C. The material was subsequently heated at 90 °C for 90 min, then washed with 200 ml distilled water per each gram to remove excess tartaric acid and was dried at 50 °C overnight. Treatment causes esterification of carboxyl groups present on the biomass was performed using the method reported by Kapoor and Viraraghavan [19]. The rice straw was mixed in a ratio of 1 g straw to 100 ml of anhydrous methanol and 1 ml of concentrated hydrochloric acid with continuous agitation on a rotary shaker for 6 h at 200 rpm. Then the esterified rice straw (ERS) was washed and dried as described above. Cr(VI) removal experiments using these modified rice straw were conducted to determine the role of carboxyl groups present on the biomass under standard conditions. Cr sorption isotherms were conducted at straw dose 5-25 g/l and keeping the Cr(VI) concentration constant at 40 mg/l.

# 2.3. Analysis

Samples were drawn at proper time intervals and centrifuged at 5000 rpm for 10 min, then filtrated. Cr(VI) concentration in the supernatant was determined using a colorimetric method [20]. The absorbance of Cr(VI) in acidic solution was measured at 540 nm by UV754N spectrophotometer. To estimate total Cr, Cr(III) was first converted to Cr(VI) by oxidizing with excess potassium permanganate before the 1,5-diphenycarbazide reaction. The Cr(III) concentration was calculated from the difference between total Cr and Cr(VI). The solution pH variation was determined using a pH-meter (pHS-25). Cr(VI) removal efficiency was calculated according to the following equation:

$$Cr(VI) \text{ removal efficiency } (\%) = \frac{(C_i - C_f) \times 100}{C_i}$$
(1)

where  $C_i$  is the initial Cr(VI) concentration (mg/l);  $C_f$  is the final Cr(VI) concentration (mg/l).

#### 3. Results and discussion

#### 3.1. Effect of pH

pH value is an important parameter affecting chemical and biological reactions in wastewaters [21]. Thus changes in pH could affect the removal of Cr(VI) in the rice straw solution. The results of Cr(VI) removal in the pH-effect experiment are



Fig. 1. Effect of pH on Cr(VI) removal by rice straw (40 mg/l of Cr(VI) concentration, 10 g/l of biomass concentration). Initial pH value of solution was adjusted to 2–6, respectively.

presented in Fig. 1. As seen in this figure, an optimal pH value for Cr(VI) removal by rice straw was 2.0. Many previous studies showed that the solution pH of wastewaters containing chromium was generally very acidic and the complete removal of Cr(VI) was observed only at highly acidic pH such as 2.0 [22–25]. Our study also finds the same results. Only 68.3%, 26.1%, 24.3% and 16.0% of Cr(VI) were removed from the solution in the pH variation of 3–6 at time of 132h, respectively (data not shown). These phenomena may be explained by that at low pH the surface of rice straw will be surrounded by a high quantities of hydronium ions (H<sup>+</sup>), which will promote the approach of negatively charged  $Cr_2O_7^{2-}$  [9]. The more positive the surface charge of the biomass, the faster the removal rate of Cr(VI) in the rice straw solution, since the binding of anionic Cr(VI) ion species is enhanced. Therefore, solution pH is of great importance for Cr(VI) removal by rice straw.

#### 3.2. Effect of initial Cr(VI) concentration

The effect of initial Cr(VI) concentration on Cr(VI) removal was investigated over a range of 40–200 mg/l. As shown in Fig. 2, the Cr(VI) removal rate increased as Cr(VI) concentration decreased. For an initial concentration of 40 mg/l, Cr(VI)



Fig. 2. Effect of initial Cr(VI) concentration on Cr(VI) removal by rice straw (pH 2.0, 10 g/l of biomass concentration). Initial Cr(VI) concentration in the solution was adjusted to 40, 60, 100, 150 and 200 mg/l, respectively.



Fig. 3. Effect of temperature on Cr(VI) removal by rice straw (pH 2.0, 100 mg/l of Cr(VI) concentration, 10 g/l of biomass concentration). Cr(VI) removal were performed at the temperature of 27, 37 and 47  $^{\circ}$ C, respectively.

was completely removed from the solution at 24 h, whereas the complete removal of 100 mg/l of Cr(VI) required about 108 h of contact time (data not shown). However, even at the highest concentration of 200 mg/l, Cr(VI) removal could be observed, although complete Cr(VI) removal was not found for this initial concentration over 9 days (data not shown). The drop in Cr(VI) removal rate with higher initial concentration may be due to the restriction of adsorption sites present on the surface of rice straw. At lower initial concentrations, sufficient adsorption sites are available for the sorption of Cr(VI). However, the numbers of Cr(VI) are relatively higher as compared to availability of adsorption sites at higher Cr(VI) concentrations.

#### 3.3. Effect of temperature

Temperature may play an important role in the process of Cr(VI) removal. So batch experiments were performed under three different temperatures: 27, 37 and 47 °C to examine the effect of temperature on Cr(VI) removal by rice straw. The results of the temperature dependency of Cr(VI) removal are presented in Fig. 3 which shows complete removal in the whole range of 27–47 °C. Increasing temperature greatly enhanced the Cr(VI) removal rate, and decreased the contact time required for complete Cr(VI) removal, which took 108, 84 and 48 h at 27, 37 and 47 °C experiments, respectively.

# 3.4. Effect of straw particle sizes

The rate of Cr(VI) removal by rice straw of different particle size, which were  $x \le 150 \,\mu\text{m}$ ,  $150 \,\mu\text{m} \le x \le 250 \,\mu\text{m}$ ,  $250 \,\mu\text{m} \le x \le 380 \,\mu\text{m}$  are shown in Fig. 4. It was observed that the decrease of straw particle size resulted in reducing the complete removing time from 60 h for  $150 \,\mu\text{m} \le x \le 250 \,\mu\text{m}$  to 48 h for  $x \le 150 \,\mu\text{m}$ . Cr(VI) decreased slowly and only 79.9% of it was removed from solution by straw of  $250 \,\mu\text{m} \le x \le 380 \,\mu\text{m}$  at time of 60 h. These results suggest that surface area of rice straw may play an important role in the Cr(VI) removal. Similar trend has been reported by Wong et al. in the removal of Cu and Pb using pretreated rice husk [18].



Fig. 4. Effect of straw particle size on Cr(VI) removal by rice straw (pH 2.0, 100 mg/l of Cr(VI) concentration, 10 g/l of biomass concentration, 47 °C). Straw of 250  $\mu$ m  $\leq x \leq$  380  $\mu$ m, 150  $\mu$ m  $\leq x \leq$  250  $\mu$ m and  $x \leq$  150  $\mu$ m were used in the Cr(VI) removal experiments.



Fig. 5. Time variation of Cr(VI) and Cr(III) concentrations and pH profiles (initial pH 2.0, 100 mg/l of Cr(VI) concentration, 10 g/l of biomass concentration,  $47 \,^{\circ}$ C).

### 3.5. Cr(VI) removal under standard conditions

In this study, Cr concentrations and pH profiles were evaluated to examine the Cr(VI) removal characteristics by rice straw and the results are presented in Fig. 5. Cr(VI) was completely removed from the solution. Meanwhile, Cr(III), which was not initially present, appeared in the solution, and increased to 69.25 mg/l at time of 48 h. These results indicated that some of the Cr(VI) was reduced to Cr(III) by contacted with rice straw. The solution pH increased from initial 2.0 to the final 2.77 after

Table 1 Effect of  $\mathrm{NO_3}^-$  and  $\mathrm{SO_4}^{2-}$  on Cr(VI) removal by rice straw



Fig. 6. Protons consumption in the process of Cr(VI) removal (initial pH 2.0, 100 mg/l of Cr(VI) concentration, 10 g/l of biomass concentration, 47  $^\circ$ C).

48 h of contact time. This increase is likely to be related to the removal of Cr(VI). The amount of proton that disappeared in the solution was proportional to the amount of removed Cr(VI); almost 4.5 mol of protons were consumed for the removal of 1 mol of Cr(VI) (Fig. 6). In addition, the pH value in the solution with rice straw increased much more in 0–36 h, followed by slow and slight increase. This also seems to be corresponding to the process of Cr(VI) removal (Fig. 5, most of Cr(VI) was removed in 0–36 h). Nakano et al. reported that a large amount of proton was consumed accompanied with the reduction of Cr(VI) in their recovery system utilizing condensed-tannin gels [10]. Daneshvar et al. also found a high efficiency for reduction of Cr(VI) to Cr(III) by soya cake at pH <1 and this is explained by the following reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$$

The consumption of  $H^+$  by Cr(VI) reduction diminished the amount of  $H^+$ , thus leading to the rise of pH [26]. As a consequence, it can be assumed that the increase of solution pH is correlative to the Cr(VI) removal activity by rice straw. Also, the straw degradation products and other reactions may contribute to the increase of pH, so further research work is necessary to find out the truth.

After complete Cr(VI) removal, the final Cr(III) concentration remained stable at 69.25 mg/l, indicating that 30.75 mg/l of total Cr was removed from the solution, which must be due to the adsorption by rice straw. Equilibrium was achieved in about

Time (h)	Cr(VI) removal (%)									
	Control sample <sup>a</sup>	+NO <sub>3</sub> <sup>-</sup> , 100 mg/l	+NO <sub>3</sub> <sup>-</sup> , 250 mg/l	+NO <sub>3</sub> <sup>-</sup> , 500 mg/l	$+SO_4^{2-}$ , 100 mg/l	$+SO_4^{2-}$ , 400 mg/l	+SO <sub>4</sub> <sup>2-</sup> , 800 mg/l			
3	37.8	19.1	15.5	10.1	30.8	32.0	32.5			
6	55.5	37.7	32.2	25.1	52.0	60.7	61.5			
9	67.7	56.2	50.3	46.8	69.9	76.8	78.3			
12	76.5	75.5	73.5	65.8	80.8	86.7	86.5			
24	92.0	83.4	80.5	73.9	93.8	96.4	96.4			
36	98.1	93.4	83.2	80.2	98.0	100	100			
48	100	96.4	87.1	83.8	100	100	100			
60	100	100	89.6	86.1	100	100	100			

<sup>a</sup> Control sample contained none of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. Initial Cr(VI) concentration was 100 mg/l.

48 h under standard condition, thereafter it remained almost unchanged with respect to time.

# 3.6. Effect of $NO_3^-$ on Cr(VI) removal

As shown in Fig. 5, the presence of Cr(III) in the solution indicates that rice straw has the ability to reduce Cr(VI) to Cr(III). While many studies have reported that NO<sub>3</sub><sup>-</sup> can compete with Cr(VI) for accepting electrons [2,27,28], the objective of this part is to investigate the effect of NO<sub>3</sub><sup>-</sup> on Cr(VI) reduction by rice straw. The removal of Cr(VI) in the experiment with different NO<sub>3</sub><sup>-</sup> concentrations (100-500 mg/l) is presented in Table 1. In the 100 mg/l NO<sub>3</sub><sup>-</sup> experiment, the complete Cr(VI) removal took 60 h, which was 12 h longer than that of the control sample. In contrast, Cr(VI) decreased slowly in the presence of high  $NO_3^-$  concentration (250–500 mg/l), and were not removed completely in both of these two samples at time of 60 h. The redox potential of  $NO_3^{-}/N_2$  in an aquatic system is very similar to that of Cr(VI)/Cr(III), thus the presence of dissolved  $NO_3^-$  could influence the reduction of Cr(VI). This study revealed that the presence of NO<sub>3</sub><sup>-</sup> in rice straw solution did retard Cr(VI) reduction to Cr(III). However, Zhang and William Franken Berger indicated that organic materials released from rice straw could promote bacterial immobilization of  $NO_3^{-1}$  [21], thus leading to a complete Cr(VI) removal at 60 h in the 100 mg/l NO<sub>3</sub><sup>-</sup> experiment in our study. This may indicate that rice straw is a strong natural reducing agent that can be used in the Cr(VI) reduction to Cr(III).

# 3.7. Effect of $SO_4^{2-}$ on Cr(VI) removal

SO<sub>4</sub><sup>2-</sup> has also been reported an anion which could influence the reduction of Cr(VI) [29,30], thus the removal of Cr(VI) in the rice straw solution with different  $SO_4^{2-}$  concentrations (100-800 mg/l) was investigated and the results are presented in Table 1. In the high level of  $SO_4^{2-}$  (400–800 mg/l) experiments, Cr(VI) was completely removed from the solution at time of 36 h, while in the low level of  $SO_4^{2-}$  (100 mg/l) experiment, it took 48 h. The results indicated that a relatively high level of  $SO_4^{2-}$  did promote the reduction of Cr(VI) to Cr(III), the reason of which is likely because  $SO_4^{2-}$  does not serve as a competitive electron acceptor in Cr(VI) reduction by rice straw. Additionally,  $SO_4^{2-}$  can serve as an electron acceptor for microbial oxidation of organic materials, and its reduction product,  $S^{2-}$  can serve as an electron donor for microbial respiration [21]. Therefore, Cr(VI) reduction by rice straw could be promoted by a relatively high level of  $SO_4^{2-}$ .

# 3.8. Effect of modifications on carboxyl groups

Several chemical pretreatments were performed to examine the role of carboxyl groups present on the biomass and to discuss their function on the adsorption of chromium by rice straw. Fig. 7 shows the removal of Cr(VI) using TARS and ERS. The results indicated that TARS greatly increased the Cr(VI) removal rate and decreased the time demanded for complete Cr(VI) removal from 48 to 24 h, compared with the control



Fig. 7. Effect of chemical pretreatments on Cr(VI) removal by rice straw (pH 2.0, 100 mg/l of Cr(VI) concentration, 10 g/l of biomass concentration,  $47 \degree$ C).

sample. While in the case of ERS, Cr(VI) concentration in the solution decreased slowly especially at the beginning and was not completely removed from the solution until 60h of contact time. Many previous studies have already indicated that the biosorptive removal of metal ions mainly depends on the chemical mechanism via reaction with specific groups such as carboxylic ligands associated with the cell wall of the biomass [9,31]. Wong et al. reported that the presence of carboxyl groups in tartaric acid modified rice husk (TARH) was primarily responsible for the sorption of Cu and Pb [18]. In contrast, Cr(VI) behaves as an oxo-anion  $(CrO_4^{2-} \text{ or } Cr_2O_7^{2-})$  in aqueous solution and may not bind to a negatively charged functional group such as carboxyl because of the repulsion of charges [31]. Therefore, the promotion of the TARS on Cr(VI) removal in our study may indicate that the reduction process really exists and the reduction product, Cr(III), is adsorbed on the carboxyl groups located on the surface of the biomass, and because of the enhancement of Cr(III) binding on the increased carboxyl groups, Cr(VI) removal is promoted. Gardea-Torresdey et al. reported that Cr(VI) could be bound to an oat byproduct, which could catalyze the reduction of Cr(VI) to Cr(III), and Cr(III) was subsequently adsorbed by available carboxyl groups [1]. Nakano et al. also found that the carboxyl groups produced by the oxidation of tannin molecules were responsible for more binding sites for the reduced Cr(III) [10]. Contrarily, esterification of the carboxyl groups decreased the Cr(VI) removal rate by rice straw, especially the initial removal rate. Donghee Park et al. suggested that the carboxyl groups also took part in Cr(VI) biosorption at acidic pH and claimed the esterification treatment on the carboxyl groups could reduce the amount of positively charged sites for Cr(VI) complexation, thus leading to the decrease of the Cr(VI) removal rate [9]. Furthermore, Wong et al. found that the esterified tartaric acid modified rice husk decreased 74% and 80% of Cu and Pb uptake, respectively, thus confirming that the carboxyl groups are essential in the sorption of metal ions [18]. As a consequence, it can be assumed that carboxyl groups present on the biomass may have influence on both Cr(VI) and Cr(III) adsorption. Additionally, we found that Cr(VI) could also be completely removed from the solution by ERS. This implies that carboxyl groups may not be fully responsible for the removal of Cr(VI) by rice straw, although they were H. Gao et al. / Journal of Hazardous Materials 150 (2008) 446-452

Comparison of chromium sorption isotherm constants derived from previous literature with this study on chromium adsorption in aqueous solutions											
Material	Langmuir isotherm constants			Freundlich isotherm constants			Reference				
	$\overline{Q_{\max} (mg/g)}$	b (l/mg)	$R^2$	K	1/n	R <sup>2</sup>					
Sawdust	_	_	_	1.482	0.0374	0.9375	[12]				
Rice husk	_	_	_	0.057	0.6387	0.9389	[12]				
Coirpith	_	_	-	0.159	0.5442	0.9988	[12]				
Soya cake	0.28	0.623	_	0.14	0.20	_	[26]				
Raw rice bran	_	_	-	0.069	0.9901	0.9857	[33]				
Rice straw	3.15	0.498	0.9919	1.397	0.2486	0.9461	Present study				



Fig. 8. Langmuir isotherm of chromium-rice straw system at  $27 \,^{\circ}$ C (pH 2.0, 40 mg/l of Cr(VI) concentration, initial biomass concentration in the solution was adjusted to 5, 10, 15, 20 and 25 g/l).

proved to have effect on biosorption of both Cr(VI) and Cr(III) species.

# 3.9. Isotherm studies

Table 2

Experimental isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application and for the predictive modeling procedures for analysis and design of sorption systems. The Langmuir and Freundlich isotherms are most frequently used to represent the data of sorption from solution [32]. In this study, the adsorption equilibrium of chromium onto rice straw particles was modeled using the Langmuir and Freundlich isotherms at different adsorbent doses.

Langmuir and Freundlich models are described by the following equations:

$$\frac{1}{q} = \frac{1}{Q_{\max}} + \frac{1}{Q_{\max}bC_e}$$
(2)

$$\log q = \left(\frac{1}{n}\right) \log C_{\rm e} + \log K \tag{3}$$

where  $C_e$  is the concentration of the chromium solution at equilibrium (mg/l), q the amount of chromium sorbed at equilibrium (mg/g),  $Q_{\text{max}}$  the maximum sorption capacity of the chromiumrice straw system, b the constant related to the binding energy of the sorption system and K, 1/n are the constants which are considered to be the relative indicators of adsorption capacity and adsorption intensity [17].



Fig. 9. Freundlich isotherm of chromium-rice straw system at  $27 \,^{\circ}$ C (pH 2.0, 40 mg/l of Cr(VI) concentration, initial biomass concentration in the solution was adjusted to 5, 10, 15, 20 and 25 g/l).

The Langmuir and Freundlich isotherms plots for rice straw are shown in Figs. 8 and 9. Comparatively the obtained  $R^2$  values are more satisfactory for Langmuir model. Using the slope and the intercept of this line, *b* and  $Q_{\text{max}}$  were found to be:

$$Q_{\rm max} = 3.15 \,{\rm mg/g}, \qquad b = 0.498.$$

Assuming  $C_0 = 40 \text{ mg/l Cr}$ ,  $R_L = 0.048$  was calculated from the relation:

$$R_{\rm L} = \frac{1}{1 + bC_0}.$$
 (4)

Since the obtained  $R_L$  is in the range of 0 and 1, the adsorption of chromium on rice straw is favorable [26].

The basic assumption of Langmuir model is based on monolayer coverage of the adsorbate on the surface of adsorbent and which is an indication of the fact that the sorption of chromium onto the rice straw generates monolayer formation.

Comparison of Langmuir and Freundlich isotherm constants with literature data (Table 2) shows that rice straw, an abundant low cost biomaterial which had high chromium uptake capacity (3.15 mg Cr/g) should be seriously considered for the disposal of chromium from water and wastewater.

# 4. Conclusion

Various parameters were evaluated on the Cr(VI) removal by rice straw—a new kind of antidote of Cr(VI). The optimal initial pH was 2.0 and the Cr(VI) removal rate increased with decreased Cr(VI) concentration and straw particle size and with increased temperature. Equilibrium was achieved in about 48 h under stan-

dard conditions. The increase of the solution pH suggested that protons were needed for Cr(VI) removal by rice straw. A relatively high NO<sub>3</sub><sup>-</sup> concentration notably restrained the Cr(VI) reduction. However, high SO<sub>4</sub><sup>2-</sup> level supported it. The studies on the effect of chemical pretreatments indicated that carboxyl groups present on the biomass took part in the Cr(VI) removal and could influence the removal rate via a biosorptive mechanism. Isotherm studies showed that the sorption of chromium onto the rice straw generates monolayer formation. Although it was clarified that Cr(VI) could be reduced to Cr(III) by rice straw, very little is known about the Cr(VI) reduction mechanism. Therefore, studies are needed to investigate this further.

Rice straw has been shown to be a potentially useful material for the removal of chromium from aqueous solution in our study. There are three advantages in using rice straw to remediate Cr(VI)-contaminated wastewaters. The first is that rice straw, which is often burned as waste, is abundant in South China and available at a much lower cost. Secondly, rice straw has a relatively high disposal capacity of chromium, which reaches to 3.15 mg Cr/g. Additionally, using rice straw in the Cr(VI) removal does not need continuous nutrient supply and the straw cells are not subjected to constraints of physiological factors such as Cr(VI) toxicity.

Therefore, rice straw may be a new kind of low-cost material which could convert Cr(VI) to the less toxic and more stable Cr(III) and could be used economically in the field to treat Cr(VI)-contaminated wastewaters.

#### Acknowledgements

This research was supported by the National Natural Science Foundation of Hunan (No. 04JJ3010) and the Doctoral Foundation of Ministry of Education of China (No. 20050532009).

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