

## Enhanced Biosorption of Cr(VI) Ions by Acid-treated Fermentation Waste Biomass

Yang Zhang\*, Haiying Shi, Wei Xu, Xuju Du, Xiuling Zhou, Kuiming Wang and Wei Feng

College of Life Science, Liaocheng University, Liaocheng, 252059, China.

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The waste biomass of  $\epsilon$ -Poly-L-lysine fermentation was investigated for hexavalent chromium [Cr (VI)] removal. The effect of pretreatment on the biosorption capacity of Cr (VI) ions onto fermentation waste biomass using several chemical agents were initially studied 1 mol/L HCl gave the maximum enhancement of the Cr (VI) uptake. The influence of solution pH, initial metal concentration, contact time and biomass dosage were studied. The biosorption process was affected markedly by the pH and initial metal concentration of the solution. Adsorption isotherms were modeled with the Langmuir and Freundlich equations and isotherm constants were calculated. Biosorption of Cr (VI) onto acid-treated waste biomass of *Kitasatospora* sp. MY 5-36 and *Streptomyces albulus* PD-1 followed the Langmuir isotherm model with the maximum biosorption capacity of 61.22 mg/g and 70.61 mg/g was achieved. The biosorption mechanisms have been investigated involving fourier transform infrared spectroscopic (FT-IR) and transmission electron microscopy and electron-dispersive X-ray (TEM-EDX) studies. The present investigation suggested that the two strains have great potential to act as a biosorbent for the removal of Cr (VI) from waste water, especially *S. albulus* PD-1 which was better than *K. sp.* MY 5-36 in terms of biosorption performance, efficiency, and cost reduction.

**Key words:** Biosorption; Hexavalent chromium; *Kitasatospora* sp. MY 5-36; *Streptomyces albulus* PD-1; FT-IR.

Heavy metals are discharged from various industries such as electroplating, corrosion inhibition, pigment manufacturing, leather tanning, ceramics, pyrotechnics, and wood preservation, among others. These pollutants are highly toxic and detrimental to animal and humans, including humans. Therefore, the removal of heavy metals ions from wastewater has received great attention in recent years. Chromate, which often exists in industrial effluents, is known to be a strong oxidizing agent and a potential carcinogen<sup>1,2</sup>. Chromium is one of the 13 metals found in the

contamination list proposed by the United States Environmental Protection Agency (USEPA)<sup>3</sup>. Therefore, the discharge of Cr (VI) on surface water is regulated to below 0.05 mg/L by the USEPA, whereas that of total Cr, including Cr (III), Cr (VI), and its other forms, is regulated to below 2 mg/L. Cr (VI) is approximately 100 times more toxic and 1000 times more mutagenic than Cr (III)<sup>4</sup>. Conventional methods for the treatment of chromate wastewater include precipitation under alkaline conditions, ion exchange, and adsorption<sup>5</sup>. However, these methods are expensive or inefficient for metal removal, especially at low metal concentrations of 1–100 mg/L and also result in the formation of secondary sources of environmental pollution<sup>7</sup>.

Biosorption based on native or pretreated

\* To whom all correspondence should be addressed.  
Tel.: 0635-8239910; Fax: 0635-8239910;  
E-mail: lcubiozy@163.com

biosorbents may provide versatile, efficient, and economical methods to overcome the problem of Cr (VI) reduction in low concentrations and offers a “natural” way of addressing environmental problems. Many bacteria and fungi, including *Escherichia*<sup>8</sup>, *Bacillus*<sup>9</sup>, *Desulfovibrio*<sup>10</sup>, *Deinococcus*<sup>11</sup>, *Pannonibacter*<sup>12</sup>, *Rhizopus*<sup>13</sup> and *Termitomyces*<sup>14</sup> are capable of reducing Cr (VI) to Cr (III), and cell-free extracts or purified proteins with chromate reductase activities have been reported by Desai *et al.*,<sup>15</sup> Sarangi and Krishnan<sup>16</sup>, and Thacker *et al.*<sup>17</sup>. However, several days or even weeks are generally needed for pure or mixed bacterial cultures to complete a reduction of less than 50 mg/L Cr (VI)<sup>11,18</sup>. In recent years, an increasing number of *actinomycetes* strains, especially *Streptomyces*, can be used as biosorbents for the removal of metal ions<sup>19-22</sup>. The objective of the present study is to investigate the biosorption potential of *Kitasatospora* sp. MY 5-36 and *Streptomyces albulus* PD-1 waste biomass which was obtained through polylysine fermentation in the removal of Cr (VI) from an aqueous solution. Research on the production of polylysine in China is newly emerging and has been rapidly developing. To the best of our knowledge, its annual production capacity is 1000 ton, which will produce more than 2000 ton of waste biomass that is increasing at the rate of 10% every year. Large amounts of waste biomass are generated, which are largely untapped. In an attempt to improve the biosorption capacity, the biomass was pretreated with different reagents. The effects of pH, initial concentration of chromium, biosorbent dose, and contact time on biosorption were investigated. Adsorption isotherm models were applied to fit the experimental data via experimental study and modeling simulation. Fourier transform infrared spectroscopy (FT-IR) and Transmission electron microscopy and electron-dispersive X-ray (TEM-EDX) were integrated to elucidate the interaction mechanism between Cr (VI) and the biosorbent.

## MATERIALS AND METHODS

### Preparation of native and chemical treated biosorbents

The  $\epsilon$ -PL-producing mutant strain *K. sp.* MY 5-36 (CCTCC NO: M2011043) and *S. albulus*

PD-1 (CCTCC NO: M205012) was isolated from the soil<sup>23, 24</sup>. Waste biomass was obtained through polylysine fermentation (NanJing Shineking Biological Technology Company-China). After five days of fermentation, the waste biomass was harvested by centrifugation (8,000×g, 10 min), washed with deionized distilled water several times, and then dried in an oven at 80 °C for 24 h. The resulting dried waste biomass was stored in a desiccator and used for raw adsorbent. All the experiments were conducted at a constant temperature of 30 °C.

Several pretreatment techniques such as heat, acid or alkali treatment can be used to enhance the removal efficiency of metal ions by the biomass. The waste biomass of *K. sp.* MY 5-36 and *S. albulus* PD-1 was then treated using several chemical agents, 10 g of raw waste biomass was taken into flask which contacted with individual 1 mol/L solutions of HCl and NaOH or 0.1 mol/L CaCl<sub>2</sub>, ethylene diamine tetraacetic acid (EDTA) and dimethyl sulfoxide (DMSO) for 12 h at 30 °C. The biomass after each chemical pretreatment was washed with deionized water until the pH of the wash solution was approximately 4.5. The wet biomass was then dried in an oven at 80 °C for 24 h. The resulting dried waste biomass was stored in a desiccator and used for chemical treated adsorbent.

### Measurements of Chromium

A Cr (VI) stock solution (1000 mg/L) was prepared by dissolving 0.2829 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> salt (AR) in deionized distilled water. For biosorption experiments, concentrations ranging from 10–100 mg/L were prepared, and the pH was adjusted by adding 0.1 mol/L HCl or 0.1 mol/L NaOH. After the biosorption experiment solutions were centrifuged for 10 min at 8,000×g, the Cr (VI) concentration in the supernatant was determined colorimetrically using a spectrophotometer (Unico UV-2100, USA) at 540 nm after reaction with 1, 5-diphenylcarbazide (DPC)<sup>17</sup>.

The metal uptake was expressed as follows:  $q_e = \frac{C_0 - C_e}{X}$  (1)  
Removal efficiency was calculated by

where  $q_e$  is the equilibrium Cr (VI)

concentration on the biosorbent (mg/g dry cell),  $C_0$  and  $C_e$  are the initial and residual metal concentrations (mg/L), and  $X$  is the biomass concentration (g×cell/L).

#### Batch biosorption studies

Batch adsorption experiments focus usually on the study of factors influencing biosorption, which include solution pH, ionic strength, and biosorbent dosage. These factors are all important in the evaluation of biosorption potential. However, among these, the solution pH usually plays a major role in biosorption and seems to affect the solution chemistry of metals and the activity of the functional groups of the biomass<sup>25</sup>. The batch biosorption experiments were carried out in erlenmeyer flasks (500 ml), with every flask containing 150 ml of Cr (VI) solution. The effect of pH on Cr (VI) biosorption was studied and the pH of the solution was initially adjusted using either 0.1 mol/L HCl or 0.1 mol/L NaOH. Four different biosorbent include of *K. sp.* MY 5-36 raw waste biomass (KRWB), *S. albulus* PD-1 raw waste biomass (SRWB), *K. sp.* MY 5-36 acid-treated waste biomass (KAWB) and *S. albulus* PD-1 acid-treated waste biomass (SAWB) were added to the solution and shaken on a temperature controlled shaker. Unless otherwise stated, the standard conditions for the biosorption experiments included an initial pH of 2.0, agitation at 120 rpm, and a waste biomass dosage of 1 g/L. After the solutions were agitated for a given period and at a given pH, measurement samples were centrifuged at 8,000×g for 10 min to remove the biomass. The residual Cr (VI) ions in the supernatant were analyzed, as described in Section 2.3. The Cr (VI) removal capacities of the KAWB and SAWB were studied in batches under initial Cr (VI) concentrations (10, 50, and 100 mg/L) and contact times (5–420 min) at 30 °C. The influences of biosorbent dose were also studied, different waste biomass densities (0.5, 1, 1.5, 2, 2.5, and 3 g/L) of the KAWB and SAWB were added into 150 ml of the solution having 50 mg/L of Cr (VI) in 500 ml flasks.

#### Equilibrium and dynamics biosorption studies

The biosorbent was suspended in Cr (VI) solutions with initial concentrations ranging from 1 to 100 mg/L and agitated for 12 h. All biosorption experiments were conducted under optimum conditions, as determined by Section 2.3. The

Langmuir and Freundlich isotherm models were applied successfully to many biosorption processes to examine the relationship between sorbed and aqueous concentration at equilibrium<sup>19</sup>. The Langmuir model assumes that a monomolecular layer is formed when biosorption takes place without any interaction between the adsorbed molecules. The Langmuir adsorption isotherm is given by the following equation<sup>26</sup>:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (3)$$

To determine whether the adsorption for a Langmuir-type adsorption process is favorable or not, a dimensionless separation factor is defined as follows:

$$R_L = \frac{1}{1 + b C_i} \quad (4)$$

Where  $C_i$  is the highest Cr (VI) concentration (mg/L). If  $R_L > 1$ , the adsorption process is unfavorable; if  $R_L = 1$ , the adsorption process is linear; if  $0 < R_L < 1$ , the adsorption process is favorable; and if  $R_L = 0$ , the isotherm is irreversible.

The Freundlich model of metal biosorption is expressed by the following equation<sup>27</sup>:

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where  $K_F$  gives a measure of the adsorbent capacity (mg/g), and  $n$  gives the intensity of adsorption ( $1 < n$ ).

#### FT-IR analysis

To locate the distribution of Cr (VI) on waste biomass, FT-IR analyses were conducted. FT-IR spectroscopy was used to identify the chemical groups present in the waste biomass. The *K. sp.* MY 5-36 and *S. albulus* PD-1 of the natural and Cr (VI) loaded samples were analyzed by FT-IR spectroscopy (Thermo AVATAR360 USA). The biomass was oven-dried at 60 °C and mixed with KBr at a ratio of 1:100. The mixture was compressed into translucent sample disks and was analyzed immediately with a spectrophotometer in the range of 4000–400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The background was subtracted automatically from the sample spectra.

### Transmission electron microscopy and energy dispersive X-ray analysis (TEM-EDX)

A transmission electron microscope (HRTEM JEM 2010, Japan) equipped with energy dispersive X-ray analysis (EDX) was used for the observation of *K. sp.* MY 5-36 and *S. albulus* PD-1 before and after treatment with a 50 mg/L initial Cr (VI) concentration, the incubate time is 6 and 12 h. The samples before and after chromium uptake for transmission electron microscopy were prepared as described earlier<sup>28</sup>.

## RESULTS AND DISCUSSION

### FT-IR spectroscopic study

To confirm the differences between functional groups in relation to Cr (VI) biosorption of the two strains, FT-IR study was conducted. The FT-IR analysis of natural and Cr (VI)-loaded *K. sp.* MY 5-36 and *S. albulus* PD-1 biomass is shown in Figure 1. The FT-IR spectra of metal-

unloaded and loaded forms of the two biosorbents in the range of 400–4000  $\text{cm}^{-1}$  were taken, and the possible functional groups participating in the biosorption process were analyzed. As shown in Figure 1, the FT-IR spectra of natural *K. sp.* MY 5-36 and *S. albulus* PD-1 biomass showed broad and strong bonds at 3434.65  $\text{cm}^{-1}$  and 3400.46  $\text{cm}^{-1}$ , respectively, indicating the presence of bounded hydroxyl (-OH), amine (-NH) groups or presence of  $\text{H}_2\text{O}$  molecules. The broad and strong bands were at 1635.36  $\text{cm}^{-1}$  (MY 5-36), 1650  $\text{cm}^{-1}$  (PD-1) (mainly C=O stretch), 1529.29  $\text{cm}^{-1}$  (MY 5-36), 1540  $\text{cm}^{-1}$  (PD-1) (mainly -NH, -CN stretch), 1392.37  $\text{cm}^{-1}$  (MY 5-36), and 1380  $\text{cm}^{-1}$  (PD-1) (mainly C-N stretch)<sup>29</sup>.

The moderately strong bonds at 1070.31  $\text{cm}^{-1}$  for *K. sp.* MY 5-36 biomass and 1070.57  $\text{cm}^{-1}$  for *S. albulus* PD-1 biomass can be attributed to the C-O stretching of alcohols and carboxylic acids or the C-N stretching vibration of an amide bond. Particular absorption bands for an aromatic

**Table 1.** Langmuir and Freundlich models parameters for Cr (VI) sorption on various biomasses of *K. MY* and *S. albulus*

Model Parameters	Biomass			
	KAWB	SAWB	KRWB	SRWB
Langmuir model				
$q_{\text{max}}$ (mg/g)	61.22	70.61	51.85	58.34
$b$ (L/g)	0.07	0.15	0.07	0.09
$R^2$	0.984	0.976	0.975	0.986
Freundlich model				
$K_f$ (L/g)	5.95	11.28	5.64	7.86
$n$	1.72	1.88	1.86	1.93
$R^2$	0.974	0.985	0.987	0.988

**Table 2.** Comparison of the biosorption capacity of different biosorbents

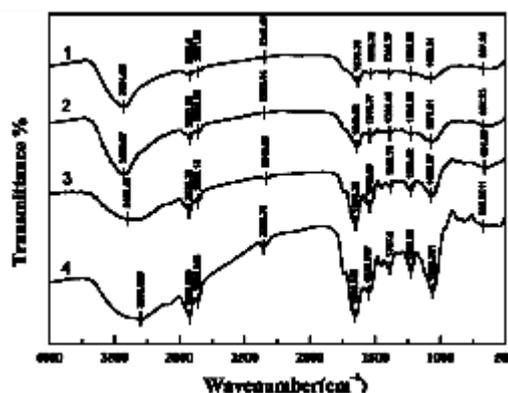
Biosorbent	$q_{\text{max}}$ (mg/g)	Reference
<i>Streptomyces rimosus</i>	26.7	[19]
<i>Pseudomonas sp.</i>	95	[32]
<i>Staphylococcus xylosus</i>	143	[32]
<i>Zoogloea ramigera</i>	2	[33]
<i>Bacillus licheniformis</i>	69.4	[34]
<i>Bacillus thuringiensis</i>	83.3	[35]
<i>Aeromonas caviae</i>	284.4	[36]
<i>Saccharomyces cerevisiae</i>	32.6	[37]
<i>Penicillium purpurogenum</i>	36.5	[38]
<i>Streptomyces albulus</i>	70.61	This study
<i>Kitasatospora</i>	61.22	This study

structure were also obtained at 667.26  $\text{cm}^{-1}$  (MY 5-36) and 661.23  $\text{cm}^{-1}$  (PD-1)<sup>20</sup>. Compared with those of the natural biomass, the FT-IR spectra of *K. sp.* MY 5-36 biomass loaded with Cr (VI) did not change significantly. However, the peaks indicating C=O and -CN stretches were shifted to 1640.62 and 1390.46  $\text{cm}^{-1}$  for the Cr (VI)-loaded *K. sp.* MY 5-36 strain. This phenomenon is more evident in the spectra of *S. albulus* PD-1. At 1800 to 600  $\text{cm}^{-1}$ , the adsorption intensity of the *S. albulus* PD-1 biomass increased significantly after treatment with 50 mg/L of initial Cr (VI) concentration. Furthermore, an increase in adsorption intensity occurred at 1650.32 and 1070.57  $\text{cm}^{-1}$ , and these peaks were shifted to 1653.74 and 1058.78  $\text{cm}^{-1}$ .

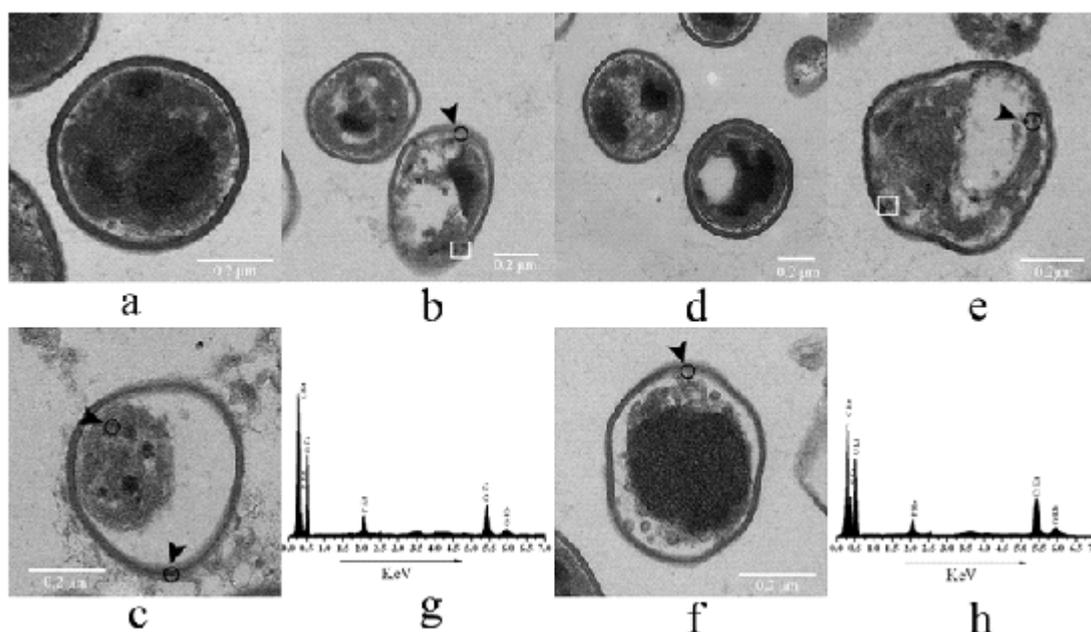
Comparing the FT-IR spectra of the two strains, the FT-IR spectra of *S. albus* PD-1 showed more changes than those of *K. sp.* MY 5-36. In the case of *S. albus* PD-1, the spectral analysis before and after metal binding indicated that carbonyl (C=O), amino (-NH), carboxyl (-COOH), and aromatic (-C<sub>6</sub>H<sub>5</sub>) groups might participate in the Cr (VI) biosorption process. Similar FT-IR results were achieved in the report of Li *et al.*<sup>20</sup> and Yuan *et al.*<sup>22</sup> on cadmium and zinc biosorption by *Streptomyces* strains.

Transmission electron microscopic study and energy dispersive X-ray analysis (TEM-EDX) Furthermore, to understand the morphology and mechanism of the biosorbent and Cr (VI) interactions before and after metal binding can help to enhance the process performance. Accumulation and quantification of chromium within *K. sp.* MY 5-36 and *S. albus* PD-1 was performed by Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray (EDX) analysis. Figure 2b and 2e show the typical TEM micrographs of *K. sp.* MY 5-36 and *S. albus* PD-1 cells following the contact of the biomass with Cr (VI). The images exhibit dense electron granules on the cell wall whereas in the control cells, these

are absent (Figure 2a, 2d). Elemental analysis as provided by EDX showed that the electron dense granules are composed of chromium. EDX spectra taken in spot profile mode record the signals of oxygen, nitrogen and carbon (Figure 2g, 2h) likely to be present in polysaccharides and proteins on the cell wall of the biomass.



**Fig. 1.** FT-IR spectrum of *K. sp.* MY 5-36 and *S. albus* PD-1 biosorbents loaded with and without Cr (VI). (1: natural *K. sp.* MY 5-36; 2: Cr (VI)-loaded *K. sp.* MY 5-36; 3: Natural *S. albus* PD-1; 4: Cr (VI)-loaded *S. albus* PD-1)



**Fig. 2.** TEM micrographs of *K. sp.* MY 5-36 (a, b, c) and *S. albus* PD-1 (d, e, f). (a, d control cell without Cr (VI) treatment; b, e waste biomass treated with 50 mg/L Cr (VI) at pH 2 for 6 h; c, f waste biomass treated with 50 mg/L Cr (VI) at pH 2 for 12 h) EDX spectra of chromium adsorbed biomass of *K. sp.* MY 5-36 (g) and *S. albus* PD-1 (h). EDX spectra were recorded from the square marked area

The arrows in the micrographs indicate the location of the metal ion. Micrographs of the post adsorbed biomass (Figure 2b, 2e) show the presence of chromium on the cell wall, periplasmic space, and cytoplasmic membrane. The appearance and distribution of chromium in both the cell wall and the cytoplasm of the biomass indicate that chromate ions are adsorbed initially on the cell wall and then accumulated in the cytoplasm<sup>14</sup>. This can occur through the electrostatic interaction between the chromate ions and the positively charged functional groups of the cell wall. The micrographs also exhibit that the adsorption of chromium on cell induces cytoplasmic aggregation (Figure 2c, 2f) of spheroplast with respect to the control cell.

#### Pretreatment

In order to determine the optimal

pretreatment for the biomass, Cr (VI) biosorption onto biosorbents from an aqueous solution was carried out with a pH ranging from 1.5 to 6.0, which was adjusted by adding 0.1 mol/L HCl or 0.1 mol/L NaOH. As shown in figure 3 the raw biomass of *K. sp.* MY 5-36 and *S. albulus* PD-1 exhibited a uptake of 27.60 mg/g and 34.7 mg/g at pH 2.0, a 228 % and 154 % increase over at pH 6.0. For the two strains, Cr (VI) biosorption capacity uptake decreased with an increase in pH from 2.0 to 6.0.

Treatment of waste biomass with different chemical agents resulted in significant change in the uptake of Cr (VI). The pretreatment of *K. sp.* MY 5-36 and *S. albulus* PD-1 with NaOH, CaCl<sub>2</sub> and DMSO resulted in a decreased Cr (VI) biosorption capacity, while 1 mol/L NaOH pretreatment decreased the biosorption capacity to the greatest extent (22.83 mg/g and 26.15 mg/g)

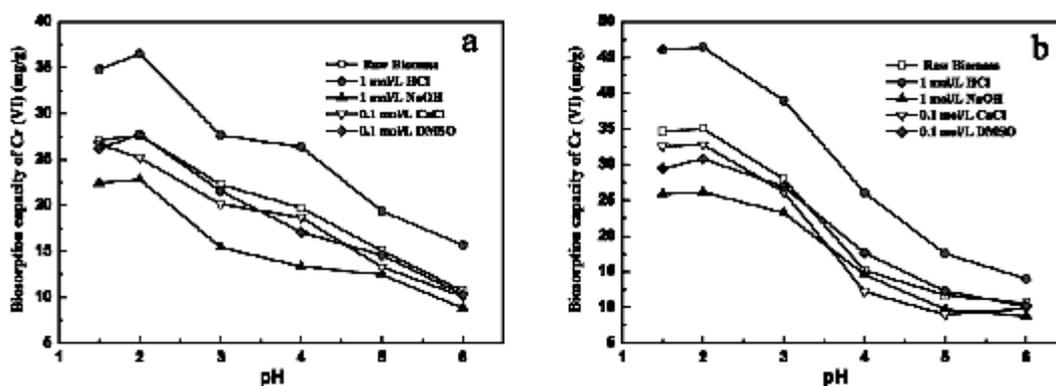


Fig. 3 .Effect of pretreatment and pH on biosorption of Cr (VI) by *K. sp.* MY 5-36 and *S. albulus* PD-1. (Initial Cr (VI) concentration: 50 mg/L; biosorbent dose: 1 g/L temperature: 30 °C; agitation speed: 120 rpm/min)

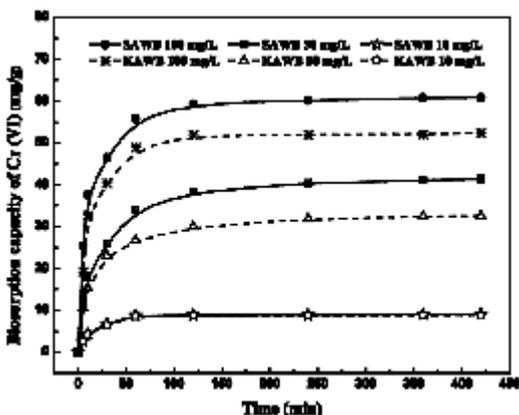


Fig. 4. Effect of initial Cr (VI) concentration on Cr (VI) biosorption by KAWB and SAWB. (biosorbent dose: 1 g/L; Temperature: 30 °C; agitation speed: 120 rpm/min)

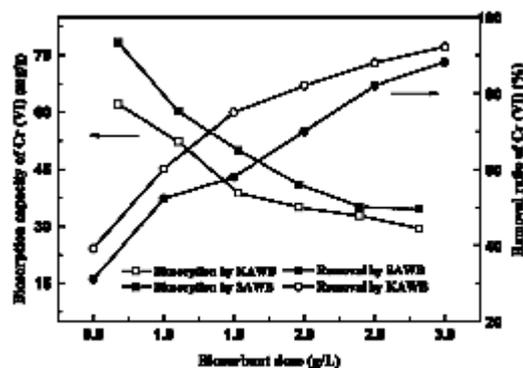


Fig. 5. Effect of biosorbent dose on biosorption capacity and removal efficiency of Cr (VI) by KAWB and SAWB. (Initial Cr (VI) concentration: 50 mg/L; Temperature: 30 °C; agitation speed: 120 rpm/min)

at pH 2. In contrary, the adsorption capacity of acid-treated waste biomass for Cr(VI) was greatly improved as compared with that of raw waste biomass. Two strains pretreated with HCl performed well and exhibited highest Cr(VI) uptakes (35.83 mg/g and 46.37 mg/g) at pH 2. Apart from the opening up of new binding sites or the removal of ions blocking the sites, the performance of mineral acids may also be attributed to the structural modification of biomass and the protonation of the functional groups responsible for biosorption. So acid-treated waste biomass of *K. sp.* MY 5-36 and *S. albulus* PD-1 by 1 mol/L HCl was utilized in further experiments.

At present, the optimum conditions for Cr(VI) biosorption were determined as a pH of 2.0, agitation at 120 rpm, 30 °C and a dose of 1 g/L waste biomass; all the following biosorption experiments were conducted under these conditions.

#### Effect of initial concentration and contact times on biosorption

The initial concentration is an important driving force to overcome all mass transfer resistances of Cr(VI) between the aqueous and solid phases. The initial concentration of Cr(VI) in the solution influenced remarkably the equilibrium uptake of Cr(VI), as seen clearly in Figure 4. As shown in Figure 4, the biomass biosorption capacity of Cr(VI) increased at varying initial concentrations (10, 50 and 100 mg/L) of Cr(VI) in an aqueous solution. The Cr(VI) biosorption process of KAWB and SAWB exhibited similar trends. The equilibrium biosorption capability of KAWB was always lower than that of SAWB, and the difference seemed to increase with an increase in initial concentration. The highest biosorption capacity was achieved at the highest initial Cr(VI) concentration, where the equilibrium biosorption capacity for KAWB biomass was 52.06 mg/g. Meanwhile, SAWB cells were able to uptake 61.12 mg Cr(VI) for each gram of dry cells.

The effect of contact time on the biosorption equilibrium of KAWB and SAWB at initial concentrations of 10, 50, and 100 mg/L are represented in Figure 4. The Cr(VI) uptake was high and very fast during the first 5–60 min. Equilibrium was attained after 120 min. The fastest stage of biosorption can be dependent principally on the surface nature of the cells, which is

substantially related to the composition of proteins and carbohydrates and the charge density of the cell surface<sup>30</sup>. Groups with higher affinities are freshly occupied, so removal was high and fast during the initial contact time.

#### Effect of the biomass dose on Cr(VI) adsorption

The biosorbent dose was also an important parameter affecting biosorption capacity and removal efficiency. It determines the potential of a biosorbent to remove Cr(VI) at a given initial concentration. The experiments were carried out by varying the KAWB and SAWB concentrations from 0.5 to 3 g/L (Figure 5). As shown in Figure 5, the biosorption capacity decrease gradually with an increase in biosorbent concentration. With an increase in the concentration of biosorbents, more binding sites were available and thus the biosorption efficiency increased. The results also demonstrate that the Cr(VI) removal ratio decreased as the biosorbent concentration increased. The decrease in the removal ratio may be due to the splitting effect of the concentration gradient between the sorbate and the sorbent with an increase in biomass concentration, causing a decrease in the amount of Cr(VI) adsorbed onto each unit weight of biomass. A similar trend of a decrease in biosorption capacity with an increase in biosorbent dosage has been reported by many researchers<sup>20, 31</sup>.

#### Modeling of adsorption isotherms

On the basis of the above analysis, the optimal pH values in the isotherm experiments on the Cr(VI) removal of biosorbents were controlled

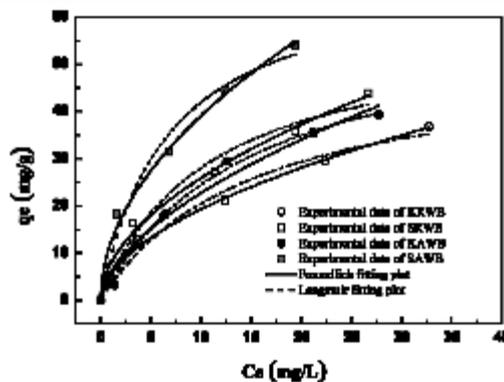


Fig. 6. Langmuir and Freundlich fitting plots of biosorption of Cr(VI) onto KRWB, SRWB, KAWB, and SAWB. (Symbols: experimental data; lines: model prediction)

at 2.0, and the initial Cr (VI) concentrations in the sorption isotherm experiments were controlled at 5–80 mg/L. To examine the relationship between sorption and aqueous concentration at equilibrium, various sorption isotherm models are widely employed for fitting with the data. The Langmuir and Freundlich adsorption models are used to describe the KAWB and SAWB Cr (VI) sorption phenomena. The non-linearized Langmuir and Freundlich adsorption isotherms of Cr (VI) are presented in Figure 6. The constants and the correlation coefficient ( $R^2$ ) are given in Table 1. In view of the results presented in Table 1, the adsorption data for the raw and acid-treated biomass fitted well with the Freundlich isotherm. The Freundlich isotherm is originally empirical in nature.  $K_F$ , one of the Freundlich constants, has been used as a relative measure of adsorption capacity, the magnitude of  $K_F$  (Table 1) was found to be maximum for the SAWB after treatment with acid and minimum for KRWB.

From the Langmuir adsorption constant  $q_{max}$  value, it was observed that the equilibrium capacity for Cr (VI) of the strain *S. albulus* PD-1 appeared to be significantly higher than that of the strain *K. sp.* MY 5-36, acid-treated biomass has slightly better adsorbing capacity for Cr(VI) than raw biomass. Strain *S. albulus* PD-1 had a Cr (VI) uptake of up to 58.34 mg/g and 70.61 mg/g by raw and acid-treated biomass, whereas the maximum biosorption of strain *K. sp.* MY 5-36 only reached up to 51.58 mg/g and 61.22 mg/g by raw and acid-treated biomass. The adsorption data of raw biomass was found to be fitting more to the Freundlich model than the Langmuir and indicated a  $R^2 > 0.97$ . However, the adsorption data of acid-treated biomass has been found to be fitting to both the models.

The Freundlich constant ( $1 < n < 10$ ) and the Langmuir separation factor ( $0 < R_L < 1$ ) indicated that it is a favorable adsorbent for Cr (VI) removal. All the data showed that *S. albulus* PD-1 is more suitable and applicable for Cr (VI) removal.

#### Compare with other adsorbents

Compares maximum adsorption capacities obtained in this study with various biosorbents reported in the literature are given in Table 2. The biosorption capacity of acid-treated biomass of *K. sp.* MY 5-36 and *S. albulus* PD-1 is same order of magnitude or greater than that of the majority of

other biosorbents reported<sup>19,25,32-38</sup>. The differences in sorption capabilities of individual biological materials may be due to the presence of different functional groups on the cell wall.

## CONCLUSIONS

As the fermentation industry wastes, waste biomass of *K. sp.* MY 5-36 and *S. albulus* PD-1 are generated in huge quantities over a short period of time. The raw and pretreated waste biomass is studied for the removal of Cr (VI) from aqueous solutions, and the biosorption performance is investigated. Acidic pretreatment enhanced the biosorption capacity of both strains. The biosorption process depends significantly on the pH and initial metal concentration of the solution. Overall, the present study shows that the two strains have great potential for use as biosorbents in the removal of Cr (VI) from wastewaters.

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