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# Uptake of Cr (VI) by *Sphingomonas paucimobilis* Biomass from Aqueous Solutions

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**The *Sphingomonas paucimobilis* biomass has been successfully utilized to degrade several persistent organic pollutants (POPs). However, few studies have been conducted to use it to remove heavy metals from aqueous solutions. In the present study, biosorption experiments for Cr (VI) were investigated using nonliving biomass of *S. paucimobilis* isolated from activated sludge, Lianyungang Dapu sewage treatment plant, China. The effects of several parameters including solution pH, contact time, and ionic strength, etc. on Cr (VI) uptake were studied. The biomass was characterized by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) and Fourier transform infrared spectrometer (FTIR). The applicability of the Langmuir and Freundlich models was tested. The correlation coefficients (*R*) of both models were greater than 0.95. The maximum adsorption capacities were found to be 28.5 mg/g for Cr (VI) at 20°C. The adsorption process was quick and found to follow the pseudo-second-order equation. The optimum adsorption was achieved at pH 2. The adsorption was also NaCl concentrations dependent.**

**Keywords** biosorption; Cr (VI); separation; *sphingomonas paucimobilis* biomass



## INTRODUCTION

Hexavalent chromium, Cr (VI) is a contaminant. Cr (VI) is highly mobile, posing hazards to humans as both a toxin and a suspected carcinogen (1). Conventional methods mainly consist of chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane separation, adsorption on activated carbon, and evaporation (2,3). However, these processes apart from being economically expensive have disadvantages such as high reagent and energy requirements, incomplete metal removal, and the generation of a large quantify of toxic waste sludge, which necessitates careful disposal in further steps (2). Recent attention has concentrated on biotechnological potential in metal removal processes (2,3). It is well documented that microbial biomass has been proven to be capable of removing heavy metal ions from aqueous solutions even when the cells have been killed. Moreover, it has been proposed that these materials could be used to decontaminate wastewaters from mining, refining, nuclear fuel processing, electroplating, and other industries and to concentrate metals. Presently, various microbial biomasses (*B. coagulans* (4), *B. megaterium* (4), *B. licheniformis* (5), *B. thuringiensis* (6), *Pseudomonas sp.* (7) have been investigated to remove Cr (VI) from aqueous solutions and promising results obtained.

The *S. paucimobilis* has been successfully utilized to degrade the phenoxy acid herbicide diclofop-methyl (8) and Polynuclear Aromatic Hydrocarbons (PAHs) including pyrene, benz[a]anthracene (B[a]A), chrysene, benzo[a] pyrene (B[a]P), benzo[b]fluoranthene (B[b]F), and dibenz [a,h]anthracene (DB[a,h]A) (9). However, few authors have attempted to use the *S. paucimobilis* biomass as biosorbent to remove heavy metal ions from aqueous solutions. In the present study, the *S. paucimobilis* biomass, isolated from activated sludge (Lianyungang Dapu sewage treatment plant, China) was used to remove Cr (VI) from aqueous solutions. The effects of several parameters including solution pH, contact time, and ionic strength, etc. on metal uptake were investigated. The adsorption mechanism was also discussed.

## MATERIALS AND METHODS

### Preparation of Biomass

The *S. paucimobilis* strain used was isolated from activated sludge (Lianyungang Dapu sewage treatment plant, China). Inocula from fresh slant were used to initiate preculture at 37°C. At late logarithmic phase of growth, inocula of 1 mL were transferred and allowed to grow in 50 ml volume of the growth culture medium which contained (in gram per liter) the following—beef extract, 2.5; peptone, 5; NaCl, 2.5; pH 7.2 – 7.4. The microorganism was maintained on solid medium obtained by adding 7 g agar to the above medium. Cells for the uptake studies were obtained by culturing in liquid medium at 37°C on an orbital shaker (150 rpm).

The cells from the late-exponential growth phase were harvested by centrifugation (10,000 × g, 10 min) at room

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temperature and washed three times with deionized water in the absence of metabolizable substrate. The biomass was dried for 10 h at 60°C under reduced pressure. The product was ground in a mortar and pestle (10).

### SEM-EDX and FTIR Studies

The biomass was characterized with scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS). FT-IR analysis of the material used in this study was performed using a Fourier transform infrared spectrometer (WGH-30A, Tianjin, China). The biosorbent powders were blended with IR-grade KBr in an agate mortar and pressed into tablet. The spectra were recorded.

### Metal Uptake Experiments

The stock solution (1000 mg/L) was prepared by dissolving a known quantity of potassium dichromate in de-ionized water. For each isotherm, a series of flasks were prepared with known volumes of serial dilutions of standardized metal salt solutions. The pH was adjusted with 1 mol/L $HNO_3$ or NaOH using a PHS-3C pH meter using a combined glass electrode calibrated with buffers of pH 2, 4, and 7. Weighed quantities of the dried biomass were added, and the flasks were agitated at 150 rpm at 20°C. The biomass was removed by centrifugation and the supernatant was analyzed for metal concentrations.

Kinetic studies were carried out with an initial concentration of 40 mg/L and adsorbent concentration of 0.5 g/L at 20°C. After shaking, the solution samples were withdrawn at suitable time intervals. The effect of pH on the adsorption of metal ions was studied by varying the initial solution pH values (2 to 6) with an initial metal ion concentration of 40 mg/L. Sodium chloride was employed as a background electrolyte to investigate the effect of ionic strength on Cr (VI) uptake. Temperature control was provided by the water bath shaker unit.

All chemical reagents used in this study were analytical grade or better. All glassware was washed with 1 mol/L $HNO_3$ and rinsed thoroughly with deionized water prior to use. Solutions were made with deionized water purified by passage through a milli-Q water system. All experiments were performed in triplicate. Controls comprised of adsorbent in deionized water blank and adsorbent-free metal ions solutions.

### Metal Analysis

A colorimetric method, as described in the Standard Methods was used to determine the Cr (VI) concentrations (11). The purple-violet colored complex formed by the reaction of 1, 5- diphenylcarbazide with Cr (VI) in acidic solution was able to spectrophotometrically analyze at 540 nm using a model 722 UV-visible spectrophotometer (China Shanghai Third Component factory, Shanghai, China).

### Data Analysis

The amount sorbed by the biomass ($q_e$, mg/g) was calculated as follows

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where $V$ is the solution volume (L), $m$ is the amount of sorbent (g), and $C_0$ and $C_e$ (mg/L) are the initial and equilibrium metal concentrations, respectively.

## RESULTS AND DISCUSSION

### Effect of Solution pH on Cr (VI) Uptake

The effect of solution pH on the uptake of Cr (VI) from aqueous solutions was first investigated and is shown in Fig. 1. The pH of the solution influences uptake by its effect on the charge of the sorbing aqueous metal ion species and on the surface charge of the biomass. Figure 2 shows the pH dependence of the hydrolysis of Cr (VI). At an acidic media, the dominant species of Cr (VI) are charged negatively $HCrO_4^-$.

In gram-negative bacteria (*S. paucimobilis* is a gram-negative bacterium), the carboxylate and phosphate groups are primarily in the outer membrane lipopolysaccaride and amino groups are associated with the peptidoglycan or other proteins on the cell surface (12). Additionally, other functional groups include hydroxyl, sulfhydryl and others in the biomass (2).

Inspection of the data in Fig. 1 indicates that at pH 2 to 6, the lower the pH, the higher the Cr (VI) uptake. This might be ascribed to the electrostatic attraction between charged negatively Cr (VI) species (Fig. 2) and charged positively functional groups in the biomass. At $pH \leq 4$, many of the nitrogen-containing functional groups in the biomass would be quaternized, and the positive charges would attract the anions (10).

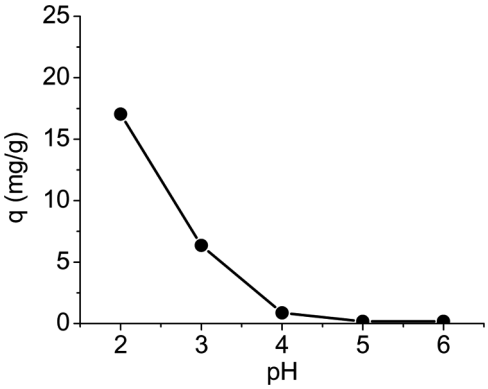



FIG. 1. The effect of initial solution pH on Cr (VI) uptake on *Sphingomonas paucimobilis* biomass (Initial concentration: 40 mg/L; contact time: 8 h; reaction temperature: 20°C; adsorbent concentration: 0.5 g/L).

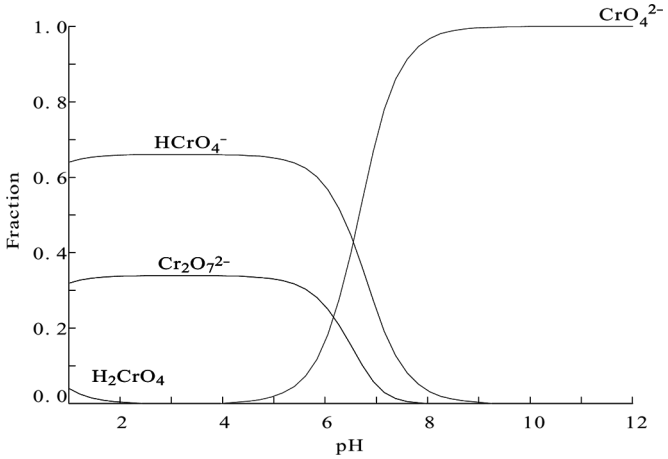



FIG. 2. Speciation of aqueous Cr (VI) as function of pH.

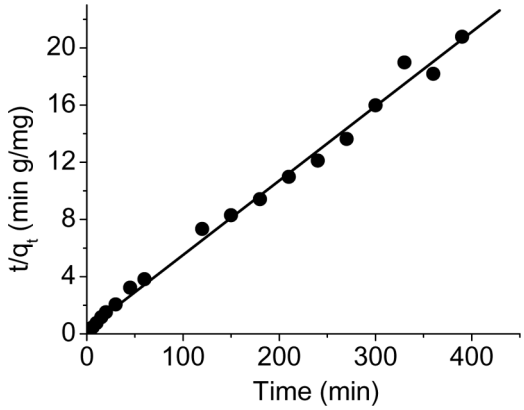



FIG. 4. Kinetic fitting by pseudo-second-order equation for uptake of Cr (VI) on *Sphingomonas paucimobilis* biomass.

## Kinetic Studies

The effect of contact time on the Cr (VI) uptake was studied and is shown in Fig. 3, which indicated that the adsorption process was fast. Nearly 70% of Cr (VI) for the adsorption capacities was reached within ca. 30 min. The initial rapid adsorption gives way to a relatively slow rate of approach to the equilibrium and saturation was reached after ca. 6 h. In many biosorption systems, most of the metal adsorption occurs within 5 to 15 min after solid-liquid contact (12).Based on these results, a 8-h contact time was used for the subsequent experiments.

In order to analyze the adsorption kinetics of Cr (VI) onto the *S. paucimobilis* biomass, the pseudo-second-order equation (13) was applied to the experimental data. This equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

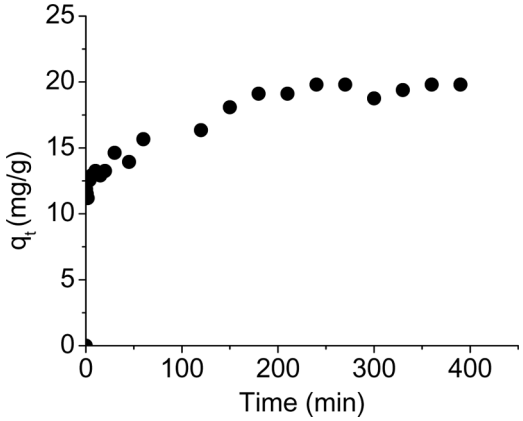



FIG. 3. Effect of contact time on the uptake of Cr (VI) by *Sphingomonas paucimobilis* biomass (Initial concentration: 40 mg/L; pH: 2; reaction temperature: 20°C; adsorbent concentration: 0.5 g/L).

where $q_e$ and $q_t$ (mg/g) are the amounts of the adsorbed adsorbate onto the adsorbent at equilibrium and at time $t$ (min), respectively, $k_2$ (g/(mg min)) the rate constant of pseudo-second-order equation.

The fitting results are shown in Fig. 4 and the related parameters acquired are summarized in Table 1. The high correlation coefficients for a pseudo-second-order equation implied that the adsorption of Cr (VI) on *S. paucimobilis* biomass was a pseudo-second-order reaction.

## Adsorption Isotherm

The most commonly used equations (i.e., the Langmuir isotherm (14) and the Freundlich isotherm (15) were applied to the isotherm data. These two equations are generally written

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{3}$$

$$q_e = K_f C_e^{1/n} \tag{4}$$

where $q_m$ is the maximum uptake (mg/g), $b$ the Langmuir constant (L/mg), $K_f$ ([(mg/g)/(mg/L)$^{1/n}$]) and $n$ (dimensionless) are the Freundlich empirical constants. Nonlinear regressions using a least-squares fitting program (Origin 7.0, OriginLab Corp., Northampton, MA) were conducted to acquire the best estimated of all constants.

Cr (VI) isotherm for *S. paucimobilis* biomass and fitting results are shown in Fig. 5 and Table 2. The correlation

TABLE 1
Parameters of pseudo-second-order equation for *S. paucimobilis* biomass

| | $q_e$ (mg/g) | $k_2$ ($\times 10^{-3}$ mg/g · min) | $R$ |
|---|---|---|---|
| Cr (VI) | 19.23 | 8.455 | 0.9972 |

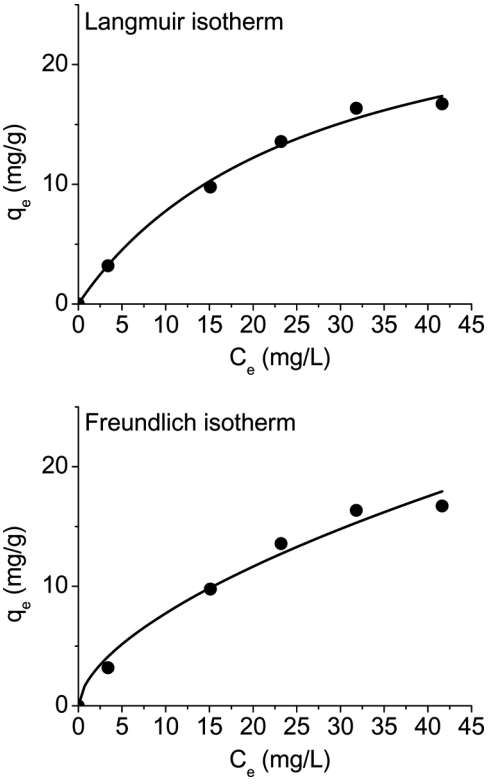



FIG. 5. Cr (VI) adsorption isotherm on *Sphingomonas paucimobilis* biomass with the results fitted to the Langmuir and Freundlich isotherms (Contact time: 8 h; pH: 2; reaction temperature: 20°C; adsorbent concentration: 0.5 g/L).

coefficients of both models were greater than 0.99, which indicates that both models adequately described the experimental data of the adsorption of Cr (VI). The maximum uptake capacity ($q_m$) for Cr (VI) of *S. paucimobilis* biomass at 20°C is comparable to those reported in the literature (4).

A mathematically equivalent form of the Langmuir equation (Eq. (3)) is the Scatchard equation:

$$\frac{q_e}{C_e} = -q_e b + q_m b \tag{5}$$

When the plot of $q_e/C_e$ versus $q_e$ yields a straight line, the intercept yields $q_m b$, whereas the slope of the line is $b$. The

TABLE 2
Isotherm parameters of Cr (VI) for *S. paucimobilis* biomass

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $q_m$ (mg/g) | $b$ (L/mg) | $R$ | $K_f$ [(mg/g)/(mg/L)$^{1/n}$] | $n$ (−) | $R$ |
| Cr (VI) | 28.5 | 0.0374 | 0.9967 | 1.99 | 1.69 | 0.9915 |

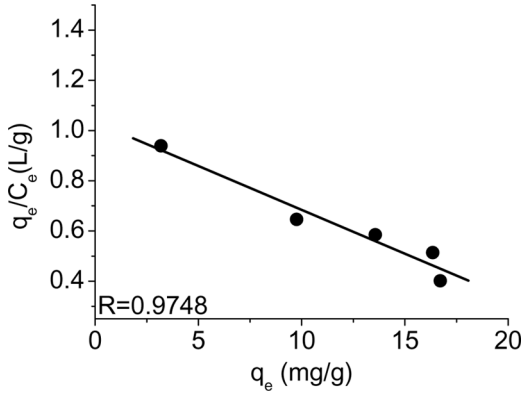



FIG. 6. Scatchard plot of Cr (VI) adsorption by *Sphingomonas paucimobilis* biomass.

shape of Scatchard curve provides information related to the nature of the interaction between the ligand and its receptor (16,17). For purposes of the present discussion, the ligands are the functional groups in the biomass, whereas the receptors are Cr (VI) ions in aqueous solutions.

The result for Scatchard plot of Cr (VI) is shown in Fig. 6. The linear plot of $q_e/C_e$ versus $q_e$ for Cr (VI) uptake on *S. paucimobilis* biomass indicates that the interactions between Cr (VI) and the ligands binding sites in the biomass were independent.

## Effect of NaCl as a Background Electrolyte on Cr (VI) Uptake

The effect of NaCl as a background electrolyte on Cr (VI) uptake by *S. paucimobilis* biomass is illustrated in Fig. 7. The results show that the uptake of Cr (VI) on *S. paucimobilis* biomass decreased with increasing NaCl

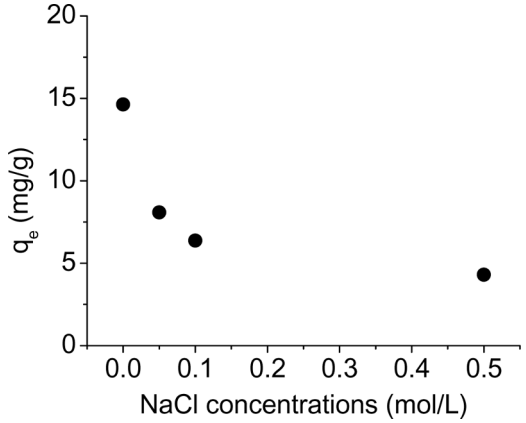



FIG. 7. Effect of NaCl as electrolyte on the Cr (VI) uptake by *Sphingomonas paucimobilis* biomass (Contact time: 8 h; pH: 2; reaction temperature: 20°C; adsorbent concentration: 0.5 g/L; initial concentration: 40 mg/L).

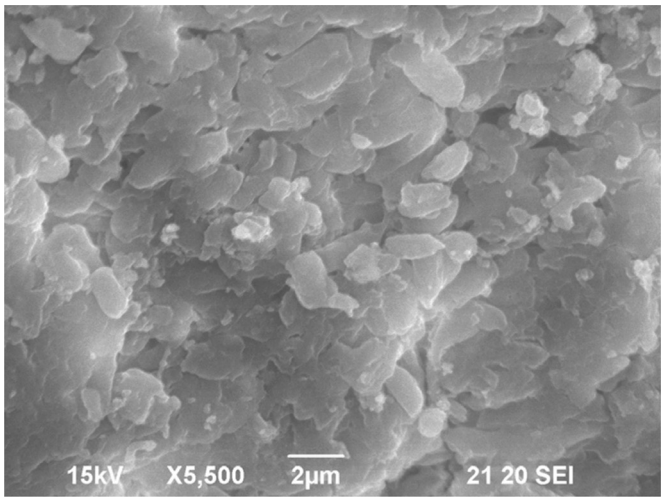
concentration from 0.05 to 0.5 mol/L The decline in Cr (VI) uptake due to the addition of NaCl might be attributed to the competitive effects (18).

## SED-EDX and FTIR Analysis

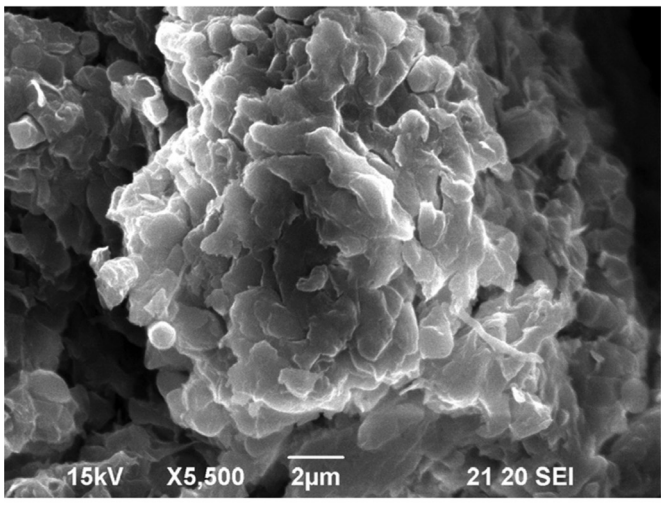
The biomass surface, before and after reacting with Cr (VI) in aqueous solution, was characterized using SEM-EDS (Figs. 8 and 9). The un-reacted surfaces contained elements of C, O, P, S, K, and Ca. After reaction, the surfaces contained element Cr.

Figure 10 shows the infrared spectra of the raw biomass. The broad peak at around 3344 $cm^{-1}$ in the raw biomass was attributed to O-H and/or N-H stretching vibration. The bands at 2980 and 2944 $cm^{-1}$ represented contribution from $CH_3$ and $CH_2$ stretching, respectively. The band at 1650 $cm^{-1}$ was indicative of C=O chelate stretching of carboxyl groups (19).The absorption bands at 1650, 1540, and 1397 $cm^{-1}$ was attributed to the amide (C=O stretching), amide (N-H bending), and amide (C-N) bands of the amide bond of protein peptide bonds, respectively (19,20). The peak at 1450 $cm^{-1}$ was assigned to the asymmetric bending of the $CH_3$ of the acetyl moiety. The absorption band at 1050 was assigned to the C-N stretching vibration of the protein fractions (21).

The infrared spectra of the Cr (VI) -loaded biomass (data not shown) were almost similar to that of the raw biomass. The changes of these absorption peaks before and after Cr (VI) adsorption were difficult to be discriminated.

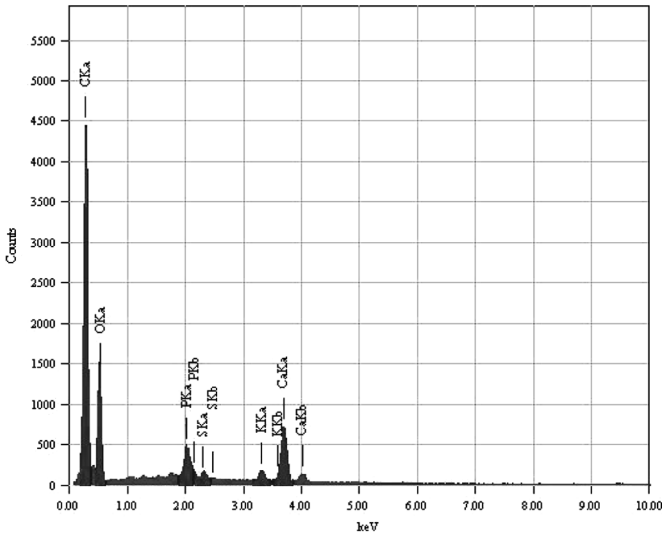



(a) Biomass before reaction with Cr (VI)

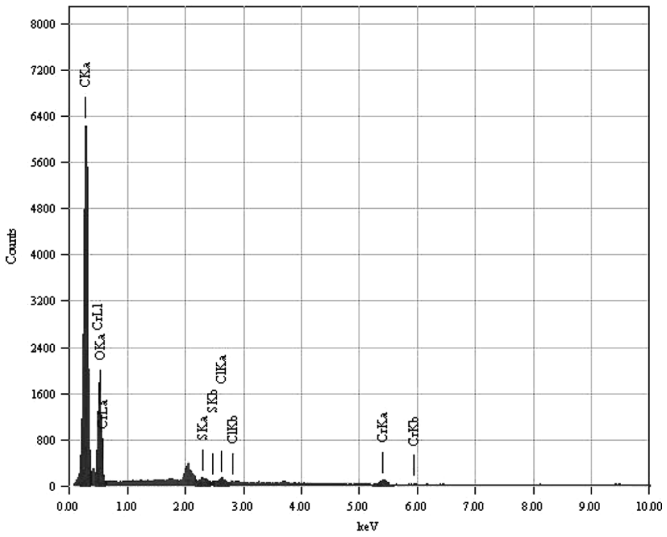



(b) Biomass after reaction with Cr (VI)

FIG. 8. Scanning electron micrographs of the surfaces before and after reaction with Cr (VI).




(a) Biomass before reaction with Cr (VI)




(b) Biomass after reaction with Cr (VI)

FIG. 9. EDS spectra before and after reaction with Cr (VI) (the peak of Cl was from HCl used for pH adjustment).

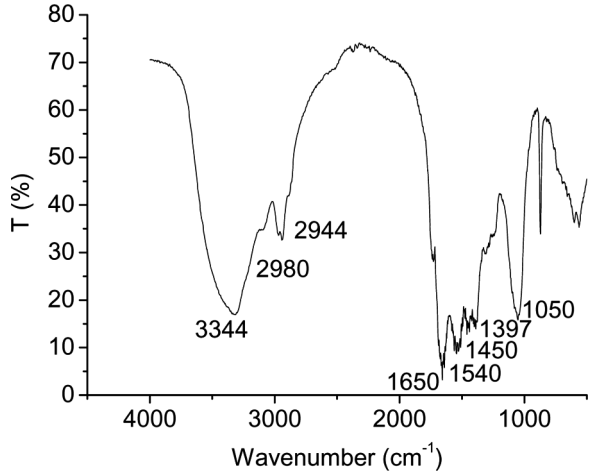



FIG. 10. Infrared spectra of the raw biomass.

## CONCLUSIONS

The nonliving biomass of *S. paucimobilis* isolated from activated sludge was applied to remove Cr (VI) from aqueous solutions. The following conclusions were drawn:

1. The adsorption was strongly pH-dependent. The lower the pH, the higher the Cr (VI) removal.
2. The Cr (VI) adsorption was sharply dependent on NaCl concentrations, indicating that Cr (VI) removal *S. paucimobilis* biomass was principally by electrostatic interactions.
3. The adsorption process for Cr (VI) was found to follow the pseudo-second-order equation. The Cr (VI) equilibrium data followed the Langmuir and the Freundlich isotherm very well.
4. The *S. paucimobilis* biomass could serve as bioadsorbent to remove Cr (VI) from industrial effluents.

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