

Biosorption of chromium by the spores of *Aspergillus niger*

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Abstract—Quite a number of reports are available on metal binding capacity of different groups of microorganisms. However, reports on the fungal spores are quite inadequate. In the present study the effect of *Aspergillus niger* spores dosage, initial solution pH and adsorption temperature on the uptake of Cr (VI) by spores of *A. niger* from aqueous solution were investigated. Batch experiments were carried out in order to model and optimize the biosorption process. The influence of three parameters on the uptake of Cr (VI) was described. Optimum Cr (VI) uptake of 99.9 mg/g Cr (VI) biomass was achieved at pH 2, biomass dosage of 2g/L and 30°C. The biosorption mechanism was also investigated by using Fourier transfer infrared (FT-IR) and Scanning electron microscope (SEM) analysis of biomass and Cr (VI) loaded biomass.

Keywords—Biosorption; Chromium; *Aspergillus niger*; Spores.

INTRODUCTION

Uncontrolled discharge to the environment of wastewater containing heavy metal to the environment can be harmful to human, animals, plants and ecosystems [1]. Current treatment process, for metal containing wastewater are reported to exhibit reduce efficiency at low concentration. Increasing interest is observed in the application of biological materials for heavy metal removal from diluted, large volume solutions. Biosorption has become a method of choice as compared with traditional method such as precipitation, adsorption, coagulation, etc. as it is economically and environmentally more viable [2, 3].

Chromium is one of the major contaminant in the wastewaters of dyes and pigments, film and photography,

galvanometric and electric, plating and electroplating, leather and mining industries [3]. This has led to the concern over the environmental effects of chromium present in surface wastewater and groundwater. Chromium removal using *Aspergillus niger* fungal biomass has been investigated by some researchers [4, 5]. Park et al. [6] reported that the removal efficiency of total chromium decreased in the following order for biosorbent used in the study: *S. cerevisiae* (44.2%) > *P. chrysogenum* (40.3%) > *A. niger* (29.3%) > *R. oryzae* (23.5%). Fungus *A. niger* is reported to have less affinity to Cr (VI) compared to other fungal biomass, *R. nigricans*, *R. arrhizus*, and *A. oryzae* [4]. Fungi of Mucorales family (*Mucor rouxii* or *R. arrhizus*) were found to possess more chitinous than *A. niger* [7]. However, spores of the *A. niger* biomass to improve the biosorption capacity has not yet been investigated. Spores of *A. niger* has potential been used for sorption of chromium from industrial wastewater. Therefore, this present work focuses on the aspect of chromium biosorption by *A. niger* spores.

MATERIALS AND METHODS

A. Biosorbent preparation

A Strain of fungal of *A. niger* used in this study obtained from maize straw. The strain was grown in Czapek's medium and maintained in nutrient agar at 4 °C. The composition of growth medium was (grams per liter): sucrose (local market), 30; NaNO₃ (Kermel), 3; KH₂PO₄ (Kermel), 1; MgSO₄ (Kermel), 0.5; KCl (Kermel), 0.5; FeSO₄ (Kermel), 0.01; agar, 20. The medium was sterilized by autoclaving at pressure of 1.5 atm and

temperature of 121 °C for 20 min. The pH of the growth medium was adjusted to 5.0 by using 0.5 NH₂SO₄. Spores from established culture (6 to 7 days old) incubated on growth media agar at 30 °C was used as biosorbent.

B. Chromium solution and analysis

Stock chromium solution of 1000mg/L was prepared by dissolving 2.828 g of potassium dichromate in 1 L of deionized water. The working chromium solution (100mg/L) was prepared by diluting the stock chromium solution. The total chromium concentration in the solution was determined by atomic absorption spectroscopy using a (Persee TAS-990) atomic absorption spectrometer [8].

C. Metal uptake (q)

Uptake of metal ions was calculated from a metal mass balance yielding:

$$q = \frac{V(C_i - C_f)}{m} \quad (1)$$

where q is mg metal ions per g dry biosorbent; V is the reaction volume (l), C_i and C_f are the initial and residual metal concentrations (mg/L), respectively, and m is the amount of dry biosorbent (g).

D. Effect of adsorbent weight

To study the effect of dosage of *A.niger* spores, the adsorbent doses range from 2 g/L–10 g/L, with increments of 0.5 g/L. The sample were shaken 3h at 150 rpm at room temperature (22 ± 2 °C).

E. Effect of pH

The effect of pH on the biosorption of chromium was investigated by contacting the spores biomass (2 g/L) in the pH range of 2.0–5.0, with increments of 1. The pH was kept constant during the study. The samples were shaken 3 h at 150 rpm at room temperature (22 ± 2 °C).

F. Effect of temperature

The effect of temperature on the biosorption of chromium was investigated by contacting the spores biomass (g/L) in the temperature range of 5 °C–35 °C, with increments of 5 °C.

G. FT-IR analysis of biosorbent

For the Fourier transform infrared spectroscopy (FT-IR) study, samples of 1 mg of the strained cells before and after the metal biosorption, respectively, were obtained with 300 mg of KBr to prepare translucent sample disks [9]. Infrared spectra were recorded using a Lambda FTIR7600 spectrometer.

H. Scanning electron microscope (SEM)

SEM was used to study the outer surface, microporosity and pore size of the non-viable *A.niger* spores. The samples were dried and viewed by

microscope (Hitachi—S4800). Finally, the SEM images were analyzed at 25000 magnifications.

RESULTS AND DISCUSSION

A. Effect of adsorbent weight

The effect of adsorbent weight (g/L) on the adsorption efficiency is shown on Fig .1. Adsorption experiments were carried out at different biosorbent doses ranging from 2 g/L to 10 g/L in chromium solution. It was observed as a general trend that there is an increase of the removal of heavy metal ions with increase in adsorbent weight .The maximum removal of the most heavy metal ions was attained at an adsorbent dose of 2 g/L with no further significant increase in the removal of heavy metal ions at higher biosorbent concentration tested was observed.

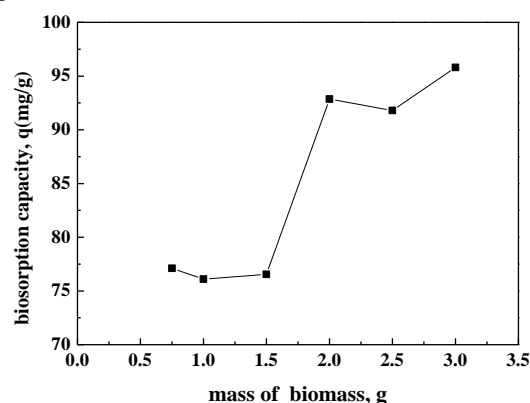


Figure 1. The effect of mass of biomass on biosorption of chromium

B. Effect of pH

The highest chromium removal efficiency was observed at pH 2.0, and removal efficiency decreased with an increase in pH (Fig .2). A similar trend has been reported for a variety of biosorbents[10]. As the pH is lowered, the surface of the spores of *A.niger* with positive charge, which will provide strong affinity to the negative charge Cr (VI) complex ions in the solution. Hence, biosorption increase with an increase in the acidity of the solution. But as the pH increase, the concentration of OH ions increase and overall charge on the surface of spores will be negative. This cause a hindrance to the biosorption of negatively charged chromium ions such as Cr₂O₇²⁻, CrO₄²⁻ resulting in a decrease of biosorption of chromium at higher pH levels [11, 12]. Hence, it can be concluded that electrostatic attraction plays an important role in this biosorption process.

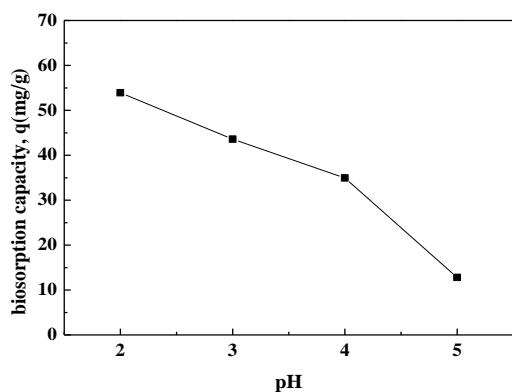


Figure 2. The effect of pH on biosorption of chromium

C. Effect of temperature

The results on effect of temperature indicated that the maximum uptake of Cr (VI) was observed at 30. The increase in temperature increased the Cr (VI) biosorption rate.

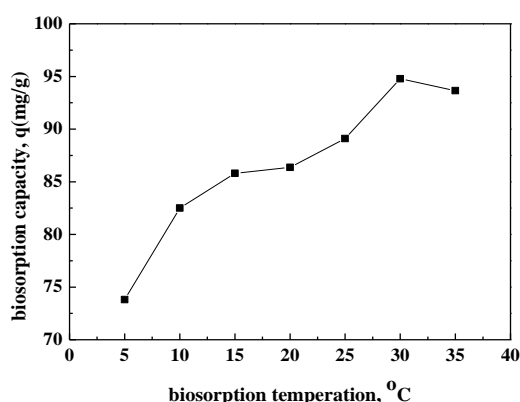


Figure 3. The effect of mass of biomass on biosorption of chromium

D. Biosorption mechanism: The FT-IR analysis

The infrared spectra of autoclaved biomass, and biomass loaded with chromium are shown in Fig .4. The figure shows a number of absorption peaks, which indicates the complex structure of the examined biomass. The IR spectrum of *A.niger* spores biomasses with chromium was similar to the IR spectrum of the autoclaved biomass. It didn't show any characteristic omission or addition of peaks, indicating the structure of the biomass with chromium didn't change. The FT-IR bands show five major IR absorption bands: broad amines and amides band (N-H stretching), amide(C=O) stretching band, amides (N-H bending), carbonyl group (-CO) stretching band and fingerprint band. The most remarkable difference between the two spectra is at intensity of 3000–3600 cm-1 representing amines and amides band (-NH) group stretching, and at intensity of 1600–1700cm-1 representing amide (-C=O) stretching. The intensity of

amino and amide bands of Cr (VI) sorbed biomass was much greater than the biomass without chromium.

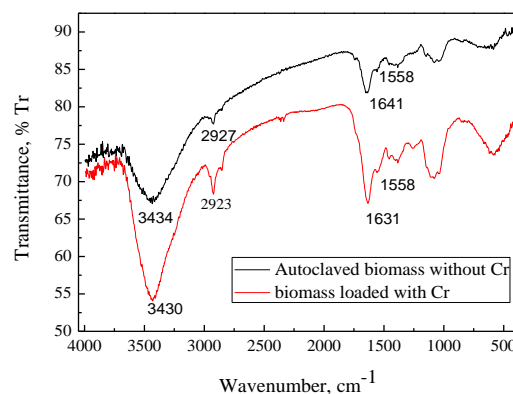


Figure 4. IR spectrum of autoclaved biomass without Cr (VI), biomass loaded with Cr (VI)

E. Scanning electron microscope (SEM) analysis

Fig .5 show scanning electron microscope (SEM) observation of surface morphology for autoclaved biomass and biomass loaded with chromium. The surface morphology of autoclaved biomass and biomass loaded with chromium may exhibit microstructure porosity. Autoclaved biomass(Fig .5a) display smooth surface morphology and much accessible space within glucan-chitin skeleton, hence allowing more heavy metal ions chelation at the surface [13, 14]. It can be seen that the space and pores of biomass loaded with chromium obviously decreased (Fig .5b). These *A. niger* spores with clean surface and high porosity may have application as biosorbent for heavy metal removal from wastewater effluents.

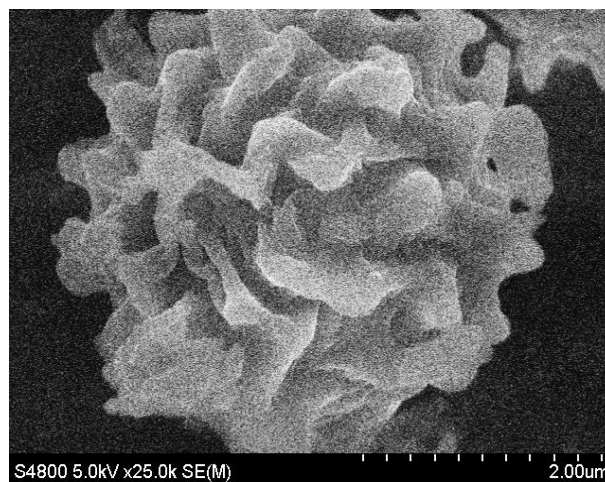


Figure 5a. Autoclaved spores of *A. niger*

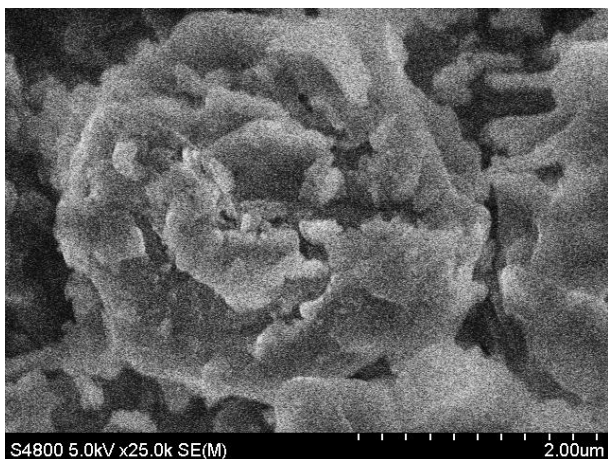


Figure 5b. Spores of *A. niger* loaded with chromium Scanning electron microscope (SEM) of spores with and without Cr(VI)

CONCLUSION

A. niger spores is suited for removing Cr(VI) from aqueous solution due to its high capacity of biosorption. The initial solution pH, biomass dosage and temperature significantly influence Cr (VI) uptake while maximum adsorption was found to be at pH 2, 2.0 g/L and 30, respectively. The uptake capacity of Cr (VI) increased with decrease in pH and increase in temperature. The maximum uptake capacity by *A. niger* biomass was obtained at 99.9 mg Cr (VI)/ g biomass. The present study indicates that spores of *A. niger* could be used as an efficient biosorbent for removal of Cr (VI) from wastewater. In the study, the biomass was justified on the basis of the Fourier transfer infrared (FT-IR) analysis. The interaction of *A. niger* spores biomass with Cr (VI) was characterized using FT-IR spectra. The FT-IR analysis implied that the interaction between chromium and N-containing bioligands on the cell surface of *A. niger* spores. Studies conducted using synthetic metal ions solution, revealed the practical application of the *A. niger* spores biomass as a potential biosorbent for sequestration of Cr (VI) from industrial effluents as well as from contaminated groundwater.

ACKNOWLEDGMENTS:

The study was funded by a research grant to the first author by the Science and Technology Department of Heilongjiang Province (Grant number GC13C304)

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