BIOSORPTION OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS BY MODIFIED CHITOSAN BEADS

HẤP PHỤ SINH HỌC KIM LOẠI CADIMI (VI) TRONG NƯỚC BẰNG HẠT CHITOSAN BIẾN TÍNH

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ABSTRACT

The presence of heavy metals pollutants in the industrial effluents has become a serious problem for human beings and the environment. In this work, chitosan beads were crosslinked and modified by Saccharomyces cerevisiae (S. cerevisiae) and histidine to enhance its acid stability and mechanical strength and biosorption capacity. The ability of Chromium (VI) biosorption on chitosan beads modified with Saccharomyces cerevisiae and histidine using glutaraldehyde as a crosslinking agent (SC-HIS-CCB) was studied. Biosorption experiments were performed by varying solution pH (2.0-7.0) and the amount of biosorbent (0.5-5 g L^{-1}). The optimal pH was found to be 4.0. It has been found that the percentage removal efficiency of Cr (VI) increased as the biosorbent dose increased from 10 to 35 mg.g^{-1}.The agigation time is 30 min. The result shows that the modified chitosan beads could be used as an effective biosorbent for the removal of Cr (VI) from wastewater and contaminated water sources.

Keywords: *Biosorption; Cr (VI); Modified chitosan beads; Saccharomyces cerevisiae; Histidine.*

TÓM TẮT

Sự hiện diện của kim loại nặng trong nước thải công nghiệp hiện là một trong những vấn đề ảnh hưởng tới con người và môi trường. Trong nghiên cứu này, hatk chitosan được khâu mạch và gắn thêm nấm men S.C , histidine để tăng khả năng bên trong môi trường acid của chitosan cũng như hiệu quả hấp phụ sinh học. Khả năng hấp phụ cadimi (VI) trên hạt chitosan được biến tính bằng cách gắn thêm nấm men Saccharomyces cerevisiae và histidine sử dụng glutaraldehyde làm cầu nối (SC-HIS-CCB) được nghiên cứu. Thí nghiệm hấp phụ sinh học được khảo sát dưới các độ pH khác nhau (2.0-7.0) và lượng chất hấp phụ (0.5-5 gL^{-1}). pH tối ưu của quá trình là 4.0. Hiệu quả khử Cr (VI) tăng khi hàm lượng chất hấp phụ tăng từ 10 đến 35 mg g^{-1}. Thời gian hấp phụ tối ưu là 30 phút. Nghiên cứu cho thấy, hạt chitosan biến tính có hiệu quả tốt trong việc loại bỏ Cr (VI) trong nguồn nước bị ô nhiễm.

Từ khóa: *Hấp phụ sinh học; Cr (VI); hạt chitosan biến tính; Saccharomyces; Histidine.*

1. INTRODUCTION

The presence of heavy metals pollutants in the industrial effluents has become a serious problem for human beings and the environment [1-3]. Chromium (VI) is released into surface water from various industrial waste-water streams such as those from electroplating, leather tanning, wood preservation, pulp processing, steel manufacturing, etc...[4,5]. Meanwhile, the accumulation of chromium causes of serious

lung and kidney problems. Therefore, phenols and chromium are highly concerned to eliminate from the waste-water before discharging into the water streams [4,5]. Currently, chitosan has been reported as a notable biosorbent because of its low cost, plenitude and high selectivity toward pollutants including phenol and nickel [4, 6, 7]. In this work, chitosan beads were crosslinked and modified by *Saccharomyces cerevisiae* (*S. cerevisiae*) and histidine to enhance its acid stability and mechanical strength and biosorption capacity [5, 8].

The objective of this research is to investigate the chromium biosorption by chitosan beads modified with *S. cerevisiae* and histidine (SC-HIS-CCB) using glutaraldehyde as a crosslinking agent. Batch experiments were performed to evaluate effective parameters such as solution pH, contact time, amount of biosorbent.

2. MATERIALS AND METHODS

2.1 Chemicals

Chromium standard solution (1000 mg L^{-1}) was provided by Merck Co. Commercial chitosan with 85% degree of deacetylation and glutaraldehyde (25%) solution in water was achieved from Sigma Aldrich Co. Histidine amino acid was given by Alfa Aesar Co. All other reagents used in this study were analytical grade.

2.2 Preparation of biosorbent

The process to prepare the biosorbents well followed the previous studies [9]. Chitosan beads (CB) were prepared using chitosan powder (6 g) dissolved in 240 mL of 7% acetic acid. The slurry was degassed under vacuum, and dropped into 200 mL of an alkali coagulating solution (H_2O:methanol:NaOH = 4:5:1, w/w/w) to prepare highly swollen spherical beads with an average diameter of 3.5 mm by KDS pump. The beads were collected and thoroughly washed with distilled water.

The crosslinking process was carried out by adding wet chitosan beads (200 mL in volume) into a glass beaker containing glutaraldehyde solution (the molar ratio between CHO groups of glutaraldehyde and amine groups of chitosan was fixed at 1:2). The materials were then mixed and agitated for 16 h, 200 rpm. The resulting crosslinked chitosan (CCB) was washed several times with distilled water to remove the residual of glutaraldehyde.

The immobilization of histidine on CCB was achieved using the same procedure as described previously. After washing with 1.5 mol L^{-1} of sodium carbonate solution, the beads were placed in a recipient and 10% (w/v) solution of histidine in 1.5 mol L^{-1} of sodium carbonate solution added. The mixture was agitated at 60^{o}C for 24 h. After this time, the beads (HIS-CCB) were washed until excess of non-immobilized histidine was washed out.

The HIS-CCB was suspended in 0.05 mol L^{-1} phosphate buffer solution (pH 7.0) and was kept at room temperature for 4 h. The *S. cerevisiae* powder (1 g) was then added and the mixture was agitated at 200 rpm for 16 h. The beads (SC-HIS-CCB) were then washed several times with distilled water.

2.3 Biosorption studies

Biosorption experiments were performed by batch equilibration method. Stock solution containing 1000 mg L^{-1} was prepared. Batch biosorption experiments in duplicate were carried out by mixing 2 g L^{-1} of biosorbent with 100 mL solution. The contents were shaken thoroughly using an orbital shaker incubator (LM-570RD) at a speed of 200 rpm at 303 K. The solution was then filtered and residual chromium concentration was detected by Atomic Absorption Spectrophotometer. The pH measurements were carried out with

Horiba pH meter. The effect of agitation time was conducted at 303 K and under a stirring rate of 200 rpm with 2 g L^{-1} of biosorbent. The effect of pH on the biosorption of Cr (VI) was studied in a pH range of 2.0-7.0 by adding appropriate buffers.

The amount of adsorbed chromium (VI) was calculated according to the following equation:

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

wherein, q_e is the amount of Cr(VI) adsorbed on SC-HIS-CCB (mg g^{-1}), C_0 and C_e are the Cr(VI) concentrations in the solution initially and at equilibrium (mg L^{-1}), respectively, V is the volume of the solution (L), and m is the mass of biosorbent used (g).

3. RESULTS AND DISCUSSION

3.1 Effect of pH on the biosorption capacity

The biosorption of phenol and nickel (II) on SC-HIS-CCB was dependent on the pH of solution. The effect of initial pH on the biosorption of SC-HIS-CCB could be found in Fig. 1. In the other hand, the optimum pH of the biosorption of Cr (VI) was found at pH 4.0. The capacity of biosorbent increased with the increase of pH in medium. As the pH was lowered, the overall surface charge on the beads became positive, which would inhibit the approach of positively charged metal cation [10].

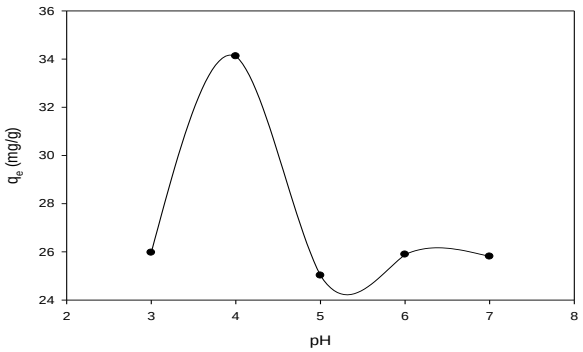

Figure 1. *Effect of pH on the biosorption of Cr (VI) on SC-HIS-CCB at 303 K and an initial Cr (VI) concentration of 50 mg L^{-1}*

3.2 Effect of biosorbent dose on the biosorption capacity

One of the most important parameters that strongly affected the biosorption capacity was the dose of biosorbent. The removal efficiency (%) and biosorption capacity (mg g^{-1}) is shown in Fig. 2 Cr (VI). As seen in Fig. 2, the amount of Cr (VI) adsorbed increased with increasing of biosorbent dose from 0.5 to 5 g L^{-1} from 10 to 35 mg g^{-1}. However, the uptake capacity of solutes per unit mass of biosorbent (mg g^{-1}) decreased with the increase of amount of adsorbent. These results can be explained by the increased adsorbent dose leading to the saturation of adsorption sites on the surface of adsorbent, therefore, no further adsorption occured [11].

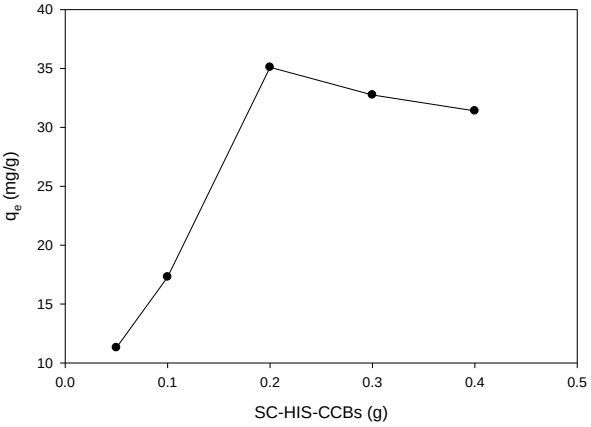

Figure 2. *Effect of dose of biosorbent on the biosorption of Cr (VI) on SC-HIS-CCB at pH 4.0, 303 K, and an initial chromium concentration of 50 mg L^{-1}*

3.3 Effect of agitation time on the biosorption capacity

The effect of agitation time on the biosorption of Cr (VI) l at different initial concentrations on the SC-HIS-CCBs is illustrated in Figure 3. A rapid biosorption occured within the first 10 mins. The biosorption equilibrium was completely obtained after 30 min. Therefore, 30 min of contact time should be chosen as the optimal contact time.

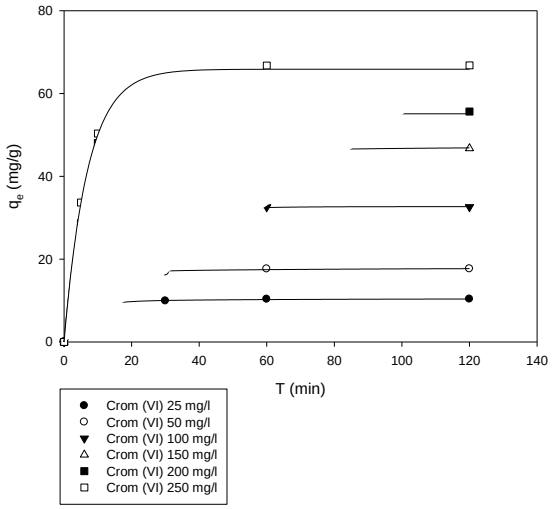

Figure 3. *Effect of contact time on the biosorption of Cr (VI) on the SC-HIS-CCBs at pH 4.0, 303 K, and different initial Cr (VI) concentrations*

4. CONCLUSION

In this study, the ability of Cr (VI) biosorption on chitosan beads modified with *Saccharomyces cerevisiae* and histidine (SC-HIS-CCB) using glutaraldehyde as a crosslinking agent was investigated. The optimal pH value for biosorption was 4.0. The increase in dose of biosorbent led to the increasing of percentage removal efficiency. The amount of Cr (VI) adsorbed increased with increasing of biosorbent dose from 0.5 to 5 g L^{-1} from 10 to 35 mg g^{-1}. However, the adsorption capacity decreased with increasing adsorbent dose. 30 min of contact time was found to be the optimal contact time. Because this biosorbent was of low cost; its utility could be economical and viewed as a part of a feasible waste management strategy.

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