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Synthesis and study of adsorption for ion Cu(II) from aqueous solution by chitosan beads

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ABSTRACT

Chitosan beads were synthesized by sodium lauryl ether sulfate (SLES) gelation process and alkaline treatment. The characterization and morphology of chitosan beads were investigated by Fourier-transform infrared spectroscopy technique (FT-IR), optical microscope and scanning electron microscope technique (SEM). The influence of NaOH concentration, pH, reaction time and adsorption isotherm was studied. Langmuir and Freundlich adsorption models were applied to describe isothermal lines. The alkalization process enhanced significantly Cu(II) adsorption capacity of CS/SLES/NaOH to 4489,6 mg/g. The results showed that chitosan beads would be a promising material to remove heavy metals in wastewater.

Introduction

The growth of world economy results in generation of a large amount of toxic heavy metals, leading to a great pressure on the environment [1,2]. Several methods of heavy metal removal have been reported, of which, the adsorption method has been paid much attention due to its economic value, ease of application and high efficiency [3].

Chitosan – a natural polymer material, which is widely used for adsorption, is the deacetylation form of chitin and exists in nature with variety of special properties, such as non-toxic, biocompatible and biodegradable [4,5]. The structure of chitosan contains a large amount of amino and hydroxyl groups that can adsorb dyes, metal ions, and proteins. However, pure chitosan has a high cost, poor chemical stability, gelation at low pH [6], which has limited its application in adsorption. For improvement of mechanical strength and adsorption as well as remedy of disadvantages of chitosan, we will study the use of chitosan beads by surfactant gelation process.

This paper aimed to synthesize chitosan beads which were synthesized by dropping chitosan into SLES (sodium lauryl ether sulfate) and then treated into alkaline environment (NaOH). CS/SLES/NaOH beads formed and applied to adsorb of ions Cu(II) from aqueous solution.

Experimental

Chitosan (CS) (fine powder, ivory color, 97% of acetylation, Thien Nguyen Company, Vietnam), acetic acid > 99,5% (d = 1,05 g/ml), $Cu(NO_3)_2.3H_2O$ (crystalline form), KH_2PO_4 > 99,5% (crystalline form), 4-(2-pyridylazo)-resorcin (PAR), NaOH > 96%, H_2SO_4 95-98%, sodium lauryl ether sulfate SLES (gel form, ivory color, China).

FT-IR spectra of the samples were recorded by FT-IR Prestige-21 spectrophotometer (Shimadzu, Japan) in

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the wavenumber range of 4000-400 cm^{-1}. The optical microscopic images of chitosan beads were taken by optical microscope (Olympus, Japan). The general morphology of the beads was characterized by the scanning electron microscope (SEM, Hitachi S–4800, Japan). Absorbance of Cu(II) solution was determined by Biochrom S60 Spectrophotometer (England).

Synthesis of chitosan beads [7,8]:

Chitosan solution: Stir completely 1,5 g chitosan in 80 mL of solution of acetic acid 0,2 N overnight. Transfer the mixture into 100 mL volumetric flask and make up to the volume with distilled water. Then leave solution undisturbed for 6 hours to make sure that the homogeneous mixture is obtained.

SLES solution: Stir completely 25 g SLES in 500mL of distilled water in 4 hours. Transfer the mixture into 1000 mL volumetric flask and make up to the volume with distilled water. Leave the solution undisturbed for 2 hours to make sure that the homogeneous mixture is obtained.

Synthesis of CS/SLES beads: Slowly drop chitosan solution into 20mL of SLES solution. CS/SLES beads were formed and kept in SLES solution for 15 minutes. Rinse and store CS/SLES beads in distilled water.

Synthesis of CS/SLES/NaOH beads: Add 20 beads of CS/SLES to NaOH solution. Concentration of NaOH solution varies from 0.006 N to 0.04 N. CS/SLES/NaOH beads were formed and kept in NaOH solution for 4 hours at 25°C. Rinse CS/SLES/NaOH beads in thoroughly with distilled water until no foam remains and store in distilled water.

Concentration of Cu(II) in solution was determined by optical absorption method. PAR reagent complexed with Cu (II) at pH = 6.5 [9]. The calibration curve for determining the concentration of Cu(II) with PAR at $\lambda_{max} = 510$ nm was constructed as:

Abs = (0.496 $\pm$ 0.006) x C with R^2 = 0.999.

Adsorption capacity of the chitosan beads was then calculated according to the following equation:

$$q_e = \frac{(C_o - C_e) \times V}{w}$$

Where q_e (mg/g) is the adsorption capacity of CS/SLES/NaOH beads, V (mL) is the volume of the used Cu(II) solution, w (g) is the weight of the used beads, C_o (mg/l) is the initial Cu(II) concentration, C_e (mg/l) is the equilibrium Cu(II) concentration

Results and discussion

Characterization of CS/SLES/NaOH beads

In the figure 1, the optical microscopic image showed that CS/SLES/NaOH beads had core-shell structure.

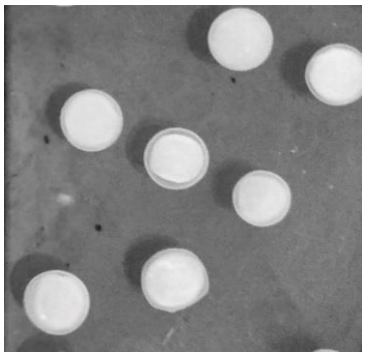
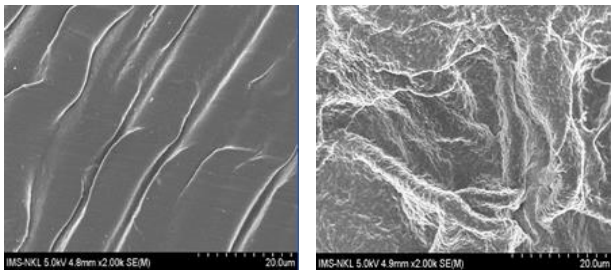


Figure 1: Optical microscopic image of CS/SLES/NaOH



a- CS/SLES b- CS/SLES/NaOH

Figure 2: SEM images of CS/SLES and CS/SLES/NaOH beads

The SEM images of CS/SLES/NaOH (figure 2b) showed that the intermembrane space increased much after alkaline treatment with NaOH. It suggested that NaOH solution would enhance the Cu(II) adsorption capacity CS/SLES beads.

FT-IR spectra of CS/SLES and CS/SLES/NaOH beads were shown in Figure 3. The FT-IR spectrum of CS/SLES showed an absorption peak at 3419 cm^{-1} (O–H group), 2920 cm^{-1} and 2854 cm^{-1} (C–H group), 1639 cm^{-1} (group C=O), 1519 cm^{-1} and 1452 cm^{-1} (C–O–S group), 1203 cm^{-1} (group S=O), 1084 cm^{-1} (C-O group), 777 cm^{-1} (S-O group). Clearly, the presence of SLES molecules was determined at a number of peaks in the spectrum at 1519 cm^{-1}, 1452 cm^{-1}, 1203 cm^{-1}, 777 cm^{-1} attributed to the hydrophilic head of SLES molecule [10].

Subsequently, after processing with NaOH, the disappearance of these peaks showed that SLES molecules could have been extracted from CS/SLES beads through an anion exchange process.

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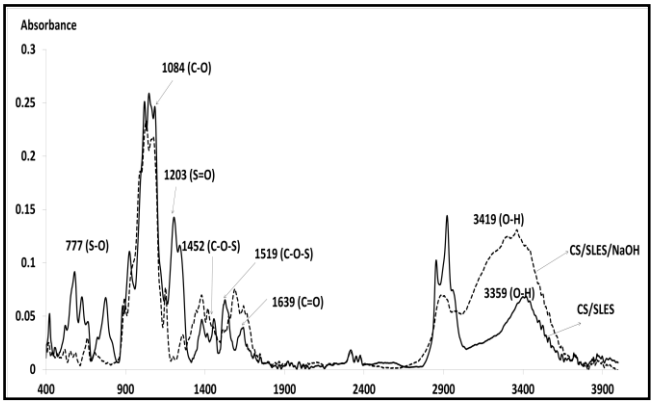

Figure 3: FTIR spectra of CS/SLES and NaOH-extracted beads (CS/SLES/NaOH)

CS/SLES/NaOH beads were dried on the paper towel. Then these beads were weighed exactly and converted to dry weight after oven drying at 105 °C in order to determine the swelling level of beads. The moisture of CS/SLES/NaOH beads was in range from 97.3 to 98.3% (table 1).

Table 1: The swelling level of beads

	A wet bead (g)	A dry bead (g)	Moisture (%)
CS/SLES/ NaOH 0.006N	0.0180	5.10^{-4}	97.3
CS/SLES/ NaOH 0.007 N	0.0194	5.10^{-4}	97.5
CS/SLES/ NaOH 0.008 N	0.0286	5.10^{-4}	98.3
CS/SLES/ NaOH 0.009N	0.0291	6.10^{-4}	98.0
CS/SLES/ NaOH 0.010N	0.0294	7.10^{-4}	97.7

Adsorption of Cu(II) from aqueous onto CS/CLES/NaOH

In the first experiment, the CS/CLES beads were used to adsorb Cu(II) ions in the solution. The Cu(II) adsorption capacity of CS/CLES beads was almost 0.0 mg/g. It could be explained that there was an electrostatic interaction between SLES molecules and chitosan groups. The interaction can obstruct Cu(II) ions to approach chitosan surface. In fact, in FTIR spectrum, there were a large peaks of C–O–S bonds and almost no signs of N–O–S bonds.

Next, adsorption of Cu(II) from aqueous onto CS/CLES/NaOH were investigated and the result was shown in figure 4 below. The results showed that the adsorption happened very quickly in the first fifteen mins. As adsorption time increased, the slope of the graph decreased. The reason was that in the early time, the surface area of the adsorbent material was larger, then gradually decreased over time to saturation. The absorption reached equilibrium after about 120 mins, at which the adsorption capacity of CS/CLES/NaOH was 3754,1 mg/g. CS/SLES/NaOH beads were formed after almost SLES molecules had been extracted. This could lead to increase the adsorption surface area.

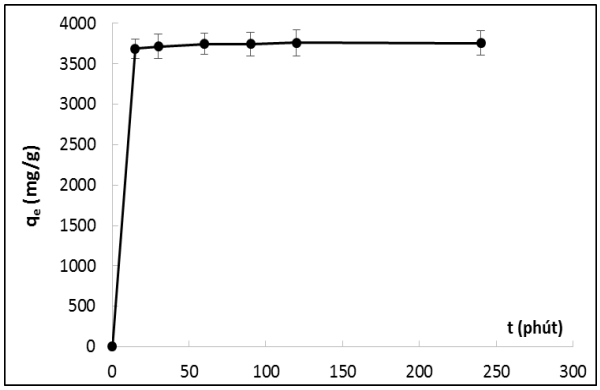

Figure 4: Cu(II) adsorption capacity of CS/SLES/NaOH after different intervals of time

Effect of NaOH concentrations on the adsorption process of ion Cu(II)

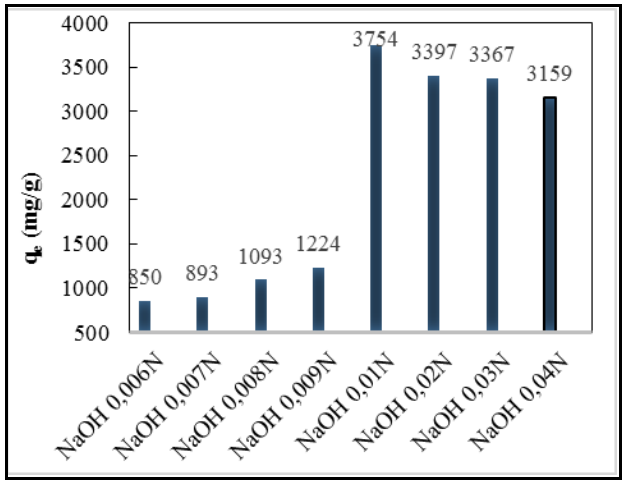

Figure 5: Cu(II) adsorption capacity of CS/SLES/NaOH after 120 mins with different concentrations of NaOH

The concentration of NaOH solution for CS/SLES treatment varied from 0.006N to 0.04 N to investigate the effect of NaOH concentrations on the adsorption process of ion Cu(II). The results in figure 5 showed that after 120 mins, Cu(II) adsorption capacity CS/SLES beads after treatment with 0,01N NaOH solution was higher than that of other CS/SLES/NaOH beads. Therefore, the optimum NaOH concentration was 0.01N.

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Effect of pH

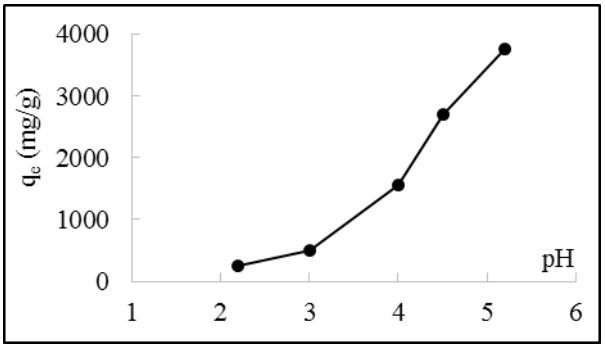

Figure 6: Effect of pH on the adsorption process of ion Cu(II) onto CS/SLES/NaOH

pH of the solution played an important role in the adsorption process and much affected the adsorption. The highest adsorption capacity q_e was 3754.1 at pH = 5.2. When the pH was lower, the adsorption capacity of Cu(II) decreased. This was explained in the following: in neutral or base, the amino groups of chitosan interacted with Cu(II) ions by electrostatic attraction, so that Cu(II) adsorbed onto the surface of the material and removed from the solution. At low pH, the amino group of chitosan would be protonated – NH_3^+, which was not favorable for the adsorption of Cu(II). At pH=5.3 (higher than 5.2), the blue precipitate of Cu(II) hydroxide was observed in the experiment. This value was in agreement with the threotical value of pH when hydroxide $Cu(OH)_2$ precipitated from the Cu(II) 0.01 M solution and the solubility product K_{sp} of copper(II) hydroxide was $4{,}8\times10^{-20}$ [11]. Thus, an optimum pH of about 5.2 was chosen for the further experiments.

Isotherm adsorption line

The adsorption isotherms were studied by varying the initial concentration of Cu (II) with fixed dose of CS/SLES/NaOH beads. To investigate the sorption isotherms, two models, Langmuir and Freundlich isotherm equations were applied. The Langmuir isotherm equation in a linear form can be expressed as [12]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}.K_L} + \frac{C_e}{q_{\max}}$$

Where:

C_e (mg/l) is the equilibrium liquid phase concentration of Cu(II) (mg/L); q_e (mg/g) is the amount of Cu(II) adsorbed per unit weight of CS/SLES/NaOH beads at equilibrium; $q_{\max}$ (mg/g) is the maximum amount of Cu(II) (per unit weight of the CS/SLES/NaOH beads) capable of forming complete monolayer coverage on the surface at the high equilibrium concentration; K_L is the Langmuir constant.

The Freundlich isotherm equation in a linear form is [13]:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

Where:

K_F (mg/l) is the predicted indicator of adsorption capacity and 1/n of the adsorption intensity. A linear form of the Freundlich equation yields the constants K_F and 1/n.

Base on experiments, the isotherm equation in the form of the Langmuir and Freundlich were represented in figure 7, figure 8 and table 2.

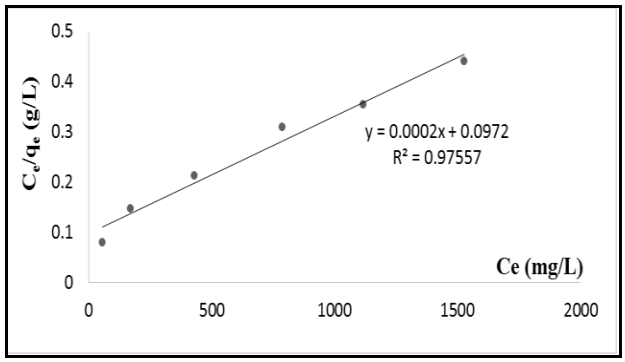

Figure 7: Relationship of C_e/q_e and C_e in Langmuir isotherm

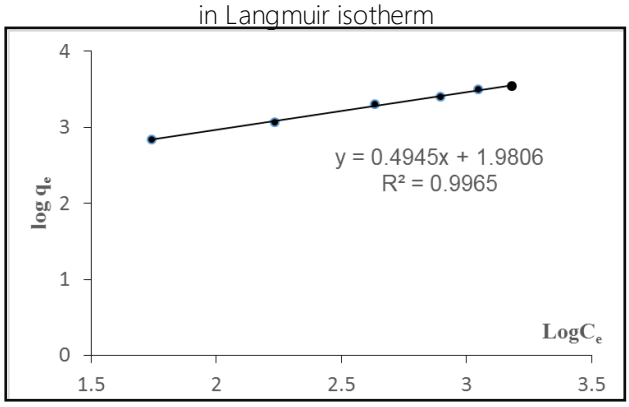

Figure 8: Relationship of $Logq_e$ and $LogC_e$ in Freundlich isotherm

Table 2: The parameters corresponding to the two isotherm models

Isotherm models	Langmuir			Freundlich		
Parameters	K_L (l/mg)	q_{max} (mg/g)	R^2	K_F (l/mg)	n	R^2
Value	0.002	4489.6	0.976	106.4	2.09	0.996

Adsorption kinetics

The results showed that value of correlation coefficient R^2 of the second-order adsorption kinetic model (R^2 = 0,9999) was greater than the first-order ones (R^2 = 0.9000). Therefore, the Cu(II) adsorption of

CS/SLES/NaOH beads was more suitable for the second-order kinetic model.

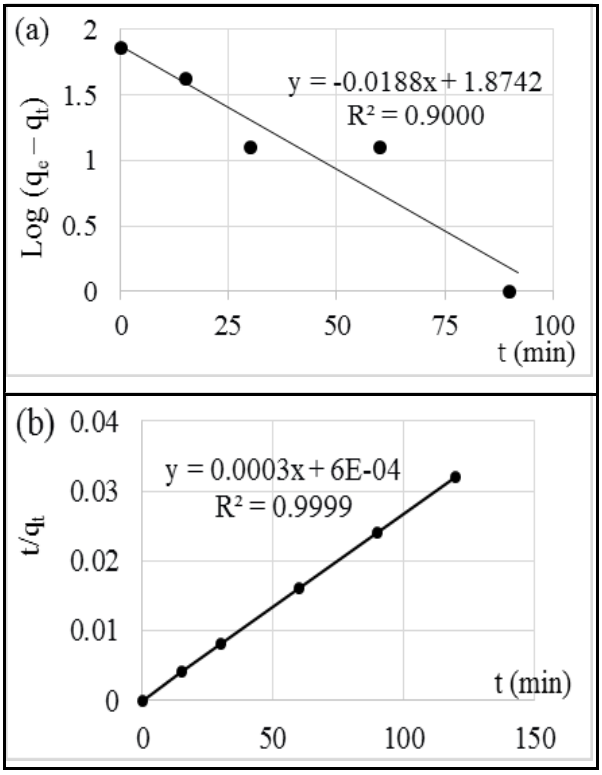

Figure 7: First-order order kinetic plot (A) and second-order kinetic plot (B) for the sorption of Cu(II) on CS/SLES/NaOH beads.

Table 3: The parameters corresponding to the two adsorption kinetics models of Cu(II) adsorption on CS/SLES/NaOH beads.

C_o (mg/l)	$q_{e,exp}$ (mg/g)	First-order model		Second-order model	
		$q_{e.cal}$ (mg/g)	R^2	$q_{e.cal}$ (mg/g)	R^2
2500	3760	74.8	0.900	3762.2	0.990

In addition, when comparing the adsorption capacity value at the time of equilibrium (q_e) according to the model and experiment, it can be seen that the adsorption capacity according to the second-order kinetic model was closer to experiment value $q_{e\ exp}$ (q_{e2} = 3762.2 mg/g $\approx \boldsymbol{q_{e\ exp}}$ = 3760 mg/g).

Conclusion

The study results showed that CS/SLES/NaOH beads formed from SLES with concentration of 25 g/L and NaOH with concentration of 0.01N have the highest adsorption capacity for Cu(II) ions. SEM measurement demonstrated that extremely increased intermembrane space of CS/SLES/NaOH beads leading to enhance the Cu(II) adsorption capacity. Freundlich equation fitted well the adsorption isotherm data. The maximum adsorption capacity of CS/SLES/NaOH at pH = 5,2 and the equilibrium time of 120 mins was 4489.6 mg/g. The pseudo second-order kinetics model agreed very well with the dynamic behavior of Cu(II) adsorption. For achieved results, CS/SLES/NaOH may be used as a promising new adsorbent for heavy metal removal from aqueous solutions.

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