NGHIÊN CỨU CÂN BẰNG HẤP PHỤ KẼM BẰNG CHITOSAN BIẾN TÍNH DẠNG VẢY

ADSORPTION EQUILIBRIUM STUDIES OF ZINC(II) BY MODIFED CHITOSAN FLAKES

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TÓM TẮT

Nghiên cứu hấp phụ Zn(II) bằng chitosan khâu mạch glutaraldehyde ghép với axít xitric **(**C-Gch) được thực hiện bằng phương pháp gián đoạn. Ảnh hưởng của các tham số như pH, thời gian tiếp xúc, liều lượng chất hấp phụ và nồng độ của các ion đã được xác định. Dung lượng hấp phụ cực đại của Zn(II) ở pH 5 thu được là 82,5 mg Zn(II)/g C-Gch sau 420 phút tiếp xúc. Mô hình hấp phụ đẳng nhiệt Langmuir, Freundlich, Tempkin và Redlich-Peterson được sử dụng để mô tả cân bằng hấp phụ. Các phương trình phân tích sai số được dùng để đánh giá các dữ liệu nghiên cứu cân bằng hấp phụ. Các mô hình nghiên cứu đều mô tả tốt quá trình hấp phụ của C-Gch.

Từ khóa: Kẽm (II), chitosan biến tính, đẳng nhiệt hấp phụ

ABSTRACT

Investigation of Zn(II) adsorption by the chitosan grafted with citric acid via crosslinking with glutraldehyde (C-Gch) was conduced by bath method. Effect of parameters such as pH, contact time, adsorbent dosage and other metal cations was determined. The maximum adsorption capacity of Zn(II) at pH 5 was found to be 82,5 mg Zn(II) /g C-Gch after 420 min of contact time.The equilibrium data were analyzed using Langmuir, Freundlich, Tempkin and Redlich-Peterson isotherm models. The equilibrium data were analysed using different error analysis equations. The models were found to be describing the data of C-Gch.

*Keyword: Zinc (II), modifed chitosan, adsorption isotherm***.**

1. **Introduction**

In recent years, adsorption method has been shown that it is an economical and effective method for removing metal ions from water[1]. Recently, the search for new and innovative technology to remove toxic heavy metal ions from diluted wastewater has focused on the removal of heavy metal by various low-cost material[2]. Among the many low cost absorbents identified, chitosan, poly(1→4)-2-acetamido-2-deoxy-β-D-glucan which is prepared from chitin is one of the highest sorption capacity absorbent for the several metal ions. Chitin is a natural polymer extracted from the sells of crustaceans such as prawns, crabs, krill, insects and shrimps[2, 3]. Chitosan has high potential in the adsorption of metal ions because they possess a number of different functional groups such as hydroxyls and amines. So, the metal ions can bind either by chemical or physical adsorption. Furthermore physical and chemical modifications of chitosan have been made to enhance the resistance of chitosan against acid, alkali, mechanical strength and chemical stability, improve the selectivities and the capacity of absorption for metal ions[3]. Different kinds of cross-linking agents such as glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether have been used in cross-linking reaction of chitosan[3]. Although cross-linking increases the chemical stability of the biosorbents in such acidic solutions but cross-linking has been found decreases the adsorption capacity of chitosan[3, 4]. In order to increase adsorption capacity of cross-linked chitosan, we have synthesized a new material from cross-linked chitosan by the reaction of cross-linked chitosan with citric acid. This is a new research direction to increase the adsorption ability of cross-linked chitosan on zinc ions.

In this work, cross-linking chitosan (Gch) was synthesized by the reaction of chitosan with glutaraldehyde. Glutaraldehyde cross linking occurs through a Schiff's base reaction between aldehyde ends of the cross linking agent and amine moieties of chitosan to form imines functions[5]. Cross-linked chitosan grafted citric acid (C-Gch) was synthesized by the reaction between Cross-linked chitosan and citric acid. The effects of pH, initial Zn(II) concentration, dose of C-Gch and the contact time on copper removal from aqueous solution by C-Gch have been investigated using bath method.

2. *Material and methods*

The flakes of raw chitosan (0.2-0.45 mm) with 87% degree of deacetylation and molecular weight of $10^5 - 10^6$ was supplied from VINAGAMA centre. Glutaraldehyde, citric acid, zinc and the other reagents were supplied from Merck Company. All solutions were prepared with doubly distilled water. Cross-linked chitosan was prepared by adding 50g of chitosan flakes to a beaker containing 750ml of 2,5%(v/v) glutaraldehyde solution[4]. The mixture was agitated for 12 hours at 250 rpm and then rinsed several times with distilled water. An obtained orange solid was dried at room temperature . After that, 30 g of CCTS and 120 ml of 2 % (w/v) citric acid solution were added to a beaker. Then, the beaker was agitated for 1 h at 250 rpm. The mixture was kept at 60^0C for 24 hours, washed with deionizer water and dried in air. To each 50 ml solution of Zn(II) and 0,1 g C-Gch were added in 150 ml Erlenmeyer flasks. The mixture was agitated in an incubated orbital shaker at the desired temperature for predetermined time intervals.

Batch adsorption experiments were conducted to determine the effect of pH, contact time, adsorbent dose and co-ions on the adsorption of Zn(II) by C-Gch. For investigation of effect of pH, 0.1g C-Gch was added into flasks containing 50 ml of 20 mg/l Zn(II) solution. pH of the solution was adjusted from 1 to 7 by either diluted HNO_3 or NaOH solution. The mixtures were shaken for 300 min at room temperature (29 ± 1^0C). The effect of the contact time was studied by variation of shaking time while maintained concentration of Zn(II), pH, adsorbent dose constant. Effects of adsorbent dose, co-ions were determined in the same manner as experiments mentioned above by varying the dose or concentration of co-ions while kept other parameters constant. Adsorption isotherm was investigated by varying the concentration of Zn(II) in the range of 20 to 200 mg/l of Zn(II).

The solutions affter adsorption were filtered and the filtrates were analyzed for Zn(II) by polar graphic analysis. The removal efficiency (%) and adsorption capacity of Zn(II) was determined by relationship:

$$P(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

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

where P is adsorption percentage (%), q_e is adsorption capacity (mg/g), C_0 is the initial Zn(II) concentration (mg/l), C_e is the final or equilibrated Zn(II) concentration (ppm), V is the volume of the Zn(II) solution (*l*) and *m* is the weight of the adsorbent (*g*).

3. Result and discussion

3.1. Effect of contact time

The effect of contact time on the adsorption of Zn(II) was studied under conditions: 0.1g of adsorbent, pH 5.0, room temperature, 20 and 40 mg/L Zn(II). The adsorption experiment were carried out for contact times ranging from 10 to 480 min. The results obtained are shown in *Fig. 1*.

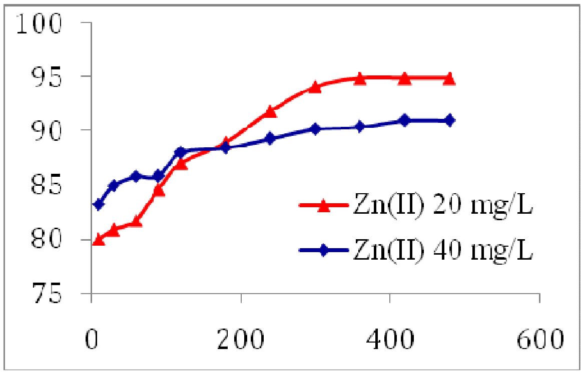

Fig.1: Effect of contact time

It was found that the adsorption percentage of Z(II) increased with increasing contact time and reached equilibrium after 420 min. This time was suggested to apply for next experiments.

3.2. Effect of solution pH

pH is an important factor for the adsorption process. Because pH of solution controlled the charge of the adsorbent surface and existence of Zn(II) ions in the solution. The relation of adsorption percentage and pH was given in *Fig.2*. The results shown that the Zn((II) adsorption percentage (%) by C-Gch was strongly depended on pH. The adsorption percentage increased with increasing pH and reached the maximum value at pH 5 - 6 and then reduced slowly with pH further increase. The low adsorption capacity at pH less 4 is probably because hydrolyzed ions Zn(II) have to compete with H^+ ions, which protonation of negative charge sites on the adsorbent surface.

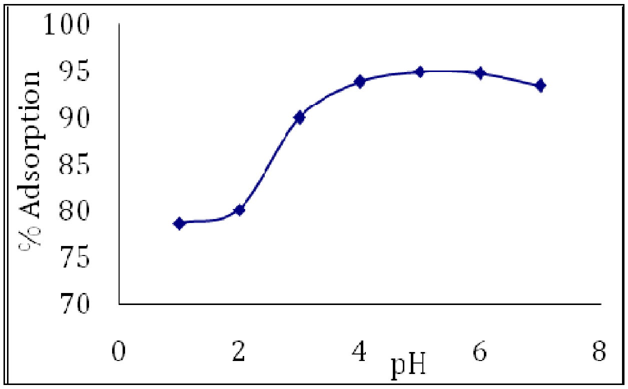

Fig.2: Effect of pH

3.4. Effect of dose

Fig.3 shown the effect of adsorbent dose on the adsorption of Zn(II) by C-Gch. The Zn(II) adsorption percentage increased with increasing of C-Gch dose. This phenomenon relates to the number of available adsorption sites in the adsorbent surface.

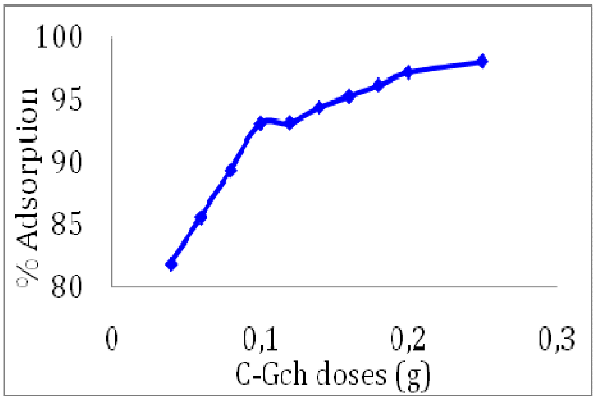

Fig.3: Effect of dose

3.5. Effect of other metal cations

The effect of cations including Cu(II) , Pb(II) , and Cd(II) on the adsorption of Zn(II) onto C-Gch was investigated using 50 ml of Zn(II) 20 mg/L, pH 5 at room temperature and 420 min of contact time. The results obtained are shown in *Fig.4*. It can be seen that the adsorption percentage of Zn(II) was reduced with increasing concentrations of cations, particularly ion Cu^{2+} ion. In the presence of Cu^{2+} with concentration ranging from 0 to 200 mg/l, the adsorption percentage of Zn(II) reduced from to 98.5% to 18% while the adsorption percentage of Zn(II) reduced to 73.2% and 62.8% in the presence of Cd(II) and Pb(II) respectively. The effect of metal ions on the adsorption of Zn(II) can be arranged in the order as following Cu(II) > Pb(II) > Cd(II)

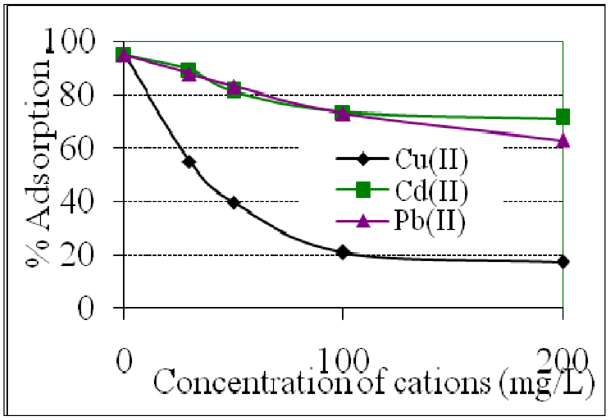

Fig.4: Effect of cations

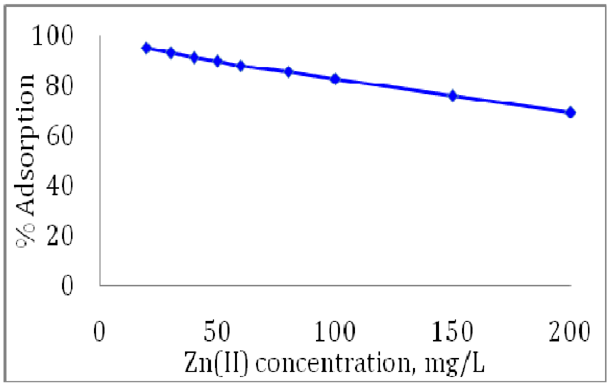

Fig.5: Effect of initial concentration on the adsorption Zn(II)

3.6. Effect of initial Zn(II) concentration

The effect of the initial Zn(II) concentration on the adsorption capacity was studied by variation of initial Zn(II) concentration ranging from 20 to 200 mg/L. The results obtained are shown in *Fig.5*. It is remarkable that the adsorption percentage of Zn(II) decreased with increasing the initial Zn(II) concentration. This phenomenon can be explained by fitting the amount of adsorbent dose while more amount of Zn(II) was added into the system.

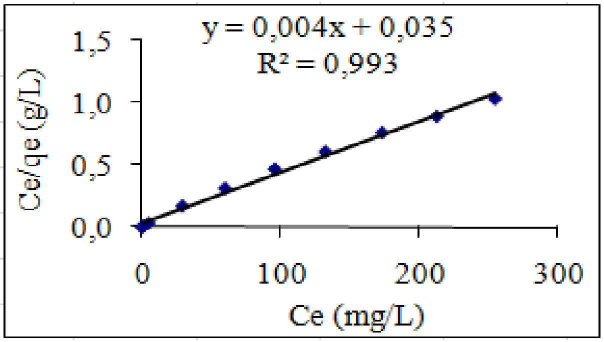

Fig.6: Adsorption isotherms of U(VI) on CCTS-citric, linearized according to the Langmuir equation

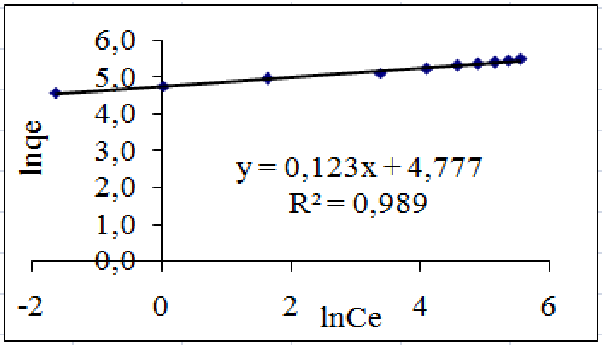

Fig.7: Adsorption isotherms of Zn(II) on CCTS-citric, linearized according to the Freundlich equation

3.7 Adsorption isotherm

The adsorption isotherm is the most important information, which indicates how the adsorbent molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state**[7]**. The experimental adsorption data were fitted the Langmuir, Freundlich Tempkin and Redlich-Peterson isotherm equations.

The linear forms of Langmuir and Freundlich models are presented as following equations **[4-13, 17-20]**:

The Langmuir equation:

$$C_e / q_e = 1 / klq_m + C_e / q_m \qquad (1)$$

The Freundlich equation:

$$\ln q_e = \ln k_f + 1/n \log C_e \qquad (2)$$

where q_e is amount of Zn(II) adsorbed per unit weight of the adsorbent at equilibrium concentration (mg/g), C_e is the final concentration in the solution (mg/l), q_m is the maximum adsorption capacity of Zn(II) (mg/g), K_l and K_f are the Langmuir and Freundlich constants, respectively, 1/n is Freundlich coefficient. The parameters of Langmuir and Freundlich equations obtained were given in Table 1. High K_L values indicate high adsorption affinity. From the Langmuir equation, the maximum adsorption capacity for Zn(II) was found to be 102.4 mg/g.

The magnitude of K_F showed a high Zn(II) adsorptive capacity of C-Gch from aqueous solution studied. Table 1 also indicated that $0 < 1/n_F < 1$, indicating that Zn(II) is favourably adsorbed by C-Gch at all studied parameters.

Tempkin isotherm, assumes that the heat of adsorption decreases linearly with the coverage due to adsorbent-adsorbate interaction[13]. The Tempkin isotherm has generally been applied in the following linear form[13].

$$q_e = B\ln A + B\ln C \qquad (3)$$

$$B = RT/b \quad (4)$$

where A (L/g) is Tempkin isotherm constant,

b (J/mol) is a constant related to heat of sorption, R is the gas constant (8.314 J/mol K) and T the absolute temperature (K). A plot of q_e versus lnCe enables the determination of the isotherm constants A, b from the slope and intercept. The data are listed in Table 1.

Redlich- Peterson isotherm (R- P) contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms into a single equation. The general isotherm equation can be described as follows [8]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}} \qquad (5)$$

where K_R (L/g) and a_R (L/mg) are R-P isotherm constants and g is the exponent. The exponent, g, lies between 0 and 1. There are two limiting behaviors; Langmuir form for $g = 1$ and Henry's law for $g = 0$. The values of b_R lies between 0 and 1 (Table 1) indicate favorable adsorption.

4. Conclusions

From the results obtained, it could be concluded that CCTS-citric is an effective adsorbent for Zn(II) adsorptio. The Zn(II) adsorption percentage by CCTS-citric was strongly dependent on contact time, pH, dose of adsorbent, cations and initial Zn(II) concentration.

The adsorption capacity of Zn(II) on C-Gch increases with an increasing of contact time and reaches adsorption equilibrium within 420 min, The adsorption percentage increased with increasing pH to a maximum value (pH 5 - 6) and then declines slowly with further increase in pH. The adsorption percentage Zn(II) decreased with increasing concentration of Cu(II), Pb(II) and Cd(II) ions. With the low value of RMSE and χ^2 , it could be concluded that four models can be used for describing the adsorption process of Zn(II).

Table 1: Parameters of isotherms for Zn(II) adsorption

Isotherm modes	Parameters			RMSE	χ^2
Langmuir	q_m (mg/g)	K_L (L/mg)		2,95	3,70
	82,54	0,07			
Freundlich	K_F (L^n/g)	$1/n_F$		1,39	0,52
	10,67	0,46			
Temkin	K_T (L/g)	b_T (J/mol)		4,88	8,97
	1,12	171,69			
Redlich- Peterson	K_R (L/g)	a_R (L/mg)	b_R	1,06	0,67
	10,87	0,50	0,69		

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