PREPARATION OF CHITOSAN/POLY VINYL ALCOHOL HYDROGEL CROSSLINKED BY GLYOXAL TOWARDS APPLICATIONS IN THE REMOVAL OF COPPER (II) IONS FROM AQUEOUS SOLUTIONS

Bui Thi Thao Nguyen*, Nguyen Nhi Tru, Ha Thi Tram Anh,
Nguyen Thi Quynh Giao, Huynh Thi Ngoc Han
Ho Chi Minh City University of Technology - Vietnam National University Ho Chi Minh

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ABSTRACT

Recently, hydrogels have been utilized as effective adsorbents to remove heavy metal ions from aqueous solutions. In this study, the composite hydrogels based on chitosan and poly vinyl alcohol (PVA) crosslinked by glyoxal were conducted towards the application of removing copper ions from water. The specific functional groups of chitosan and PVA molecules were revealed by Infrared spectroscopy (FTIR). The swelling property of the composite was investigated and had the highest value of 850%. In addition, the ability of hydrogel to remove copper ions from aqueous solution was evaluated through the experiments supported by UV vis equipment. The Langmuir and Freundlich isotherm model could fit the data of the experiment. And the hydrogel with 10%wt glyoxal had maximum copper ion absorption with 183 $mg.g^{-1}$ at pH 7.

NGHIÊN CỨU CHẾ TẠO HYDROGEL TỪ CHITOSAN VÀ POLY VINYL ALCOHOL VỚI CHẤT ĐÓNG RẮN GLYOXAL HƯỚNG ĐẾN ỨNG DỤNG LOẠI BỎ ION ĐỒNG TRONG NƯỚC

Bùi Thị Thảo Nguyên*, Nguyễn Nhị Trự, Hà Thị Trâm Anh,
Nguyễn Thị Quỳnh Giao, Huỳnh Thị Ngọc Hân
Trường Đại học Bách khoa – Đại học Quốc gia Thành phố Hồ Chí Minh

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TỪ KHÓA

Composite hydrogel
Chitosan
PVA
Glyoxal
Ion đồng

TÓM TẮT

Gần đây, hydrogel được dùng phổ biến làm chất hấp phụ hiệu quả để loại bỏ các ion kim loại nặng khỏi dung dịch nước thải. Trong nghiên cứu này, các hydrogel được tổng hợp dựa trên chitosan và poly vinyl alcohol (PVA) được liên kết ngang bởi glyoxal đã được tiến hành theo hướng ứng dụng loại bỏ các ion đồng khỏi nước thải. Các nhóm chức đặc trưng của phân tử chitosan và PVA được khảo sát bằng quang phổ hồng ngoại (FTIR). Tính chất trương nở của composite cũng được nghiên cứu và đạt kết quả 850%. Ngoài ra, khả năng loại bỏ các ion đồng ra khỏi nước thải của hydrogel đã được đánh giá thông qua các thí nghiệm với thiết bị UV vis. Mô hình đẳng nhiệt Langmuir và Freundlich được sử dụng để đánh giá khả năng hấp phụ của hydrogel và dữ liệu của thí nghiệm khớp với mô hình. Hydrogel được tổng hợp với 10% glyoxal có khả năng hấp thụ ion đồng với độ hấp phụ 183 $mg.g^{-1}$ ở môi trường trung tính.

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* Corresponding author. *Email: btnguyen@hcmut.edu.vn*

1. Introduction

Nowadays, water pollution becomes a serious problem of mankind. Polluted water can also lead to numerous health conditions. Especially, the residue of heavy metals causes a poor impact on human health, leading to transmission of diseases such as cholera, diarrhea, and dysentery. Many methods of heavy metal treatment in wastewater have been studied and applied such as biochemical method, physicochemical method, chemical precipitation method, ion exchange, flotation, and electrochemical deposition. However, most of the above methods are expensive. Hydrogel technology is outstanding treatment methods with high adsorption efficiency, energy saving, and low operating costs based on the processes of adsorption of hydrogel [1].

Among bio-adsorbent materials, chitosan is a natural, non-toxic, hydrophilic, biocompatible, and biodegradable agent. Moreover, chitosan is a kind of cheap raw material with high metal adsorption capacity. Being another adsorbent material, poly vinyl alcohol (PVA) is a water-soluble polymer with functional chemical groups which can interact with other polymers to form hydrogel. PVA hydrogel possesses numerous advantages such as biodegradation, biocompatible, and high degree of swelling in water [2], [3]. In PVA - chitosan (PVA/CS) hydrogel crosslinked with glyoxal, PVA contributes to increase mechanical property and swelling behavior. In addition, glyoxal crosslinker is used to link polymer chains, contributing to enhancing hydrogel strength by forming network from PVA and chitosan molecules [4], [5]. Consequently, polymer hydrogels based on PVA and chitosan are candidates for a range of application in environmental fields, especially water treatment based on adsorption properties of PVA and chitosan through various scientific researches [6], [7].

In this study, the hydrogels based on PVA and chitosan were synthesized and investigated their properties. Particularly, the effect of curing agent on the hydrogel properties was researched in order to produce the hydrogel with high applicability of wastewater treatment. Moreover, other analytical methods were used to evaluate hydrogel properties, including infrared spectroscopy (FTIR) and UV-vis spectroscopy.

2. Materials and Methods

2.1. Materials

PVA (average M_w = 205 000 g.mol^{-1}, 98-99% hydrolyzed) and chitosan (average M_w = 5000 g/mol) were purchased from Sigma Aldrich (Germany). Glyoxal was obtained from Wako Chemical Industries, Japan. Other chemicals with 99% purity were distributed by Guangdong Guanghua Sci-Tech Company (China).

2.2. Preparation of PVA-chitosan hydrogel composite

Firstly, PVA solution 8 wt% and chitosan solution 5 wt% were prepared respectively by adding PVA into distilled water and chitosan into acetic acid solution 0.5 M. Next, PVA and chitosan solution were poured sequentially into reaction flask. The experiment was conducted at 60^{o}C with a stirring time of 180 minutes to get homogenous mixture. After that, glyoxal was put into the reacted solution. The solution was continually stirred to get homogenous dispersion at constant temperature 60 ^{o}C.

Then proper weight of the mixture was put in glass Petri dish, followed by being cured at 80^{o}C for 90 minutes in an oven. After that, the sample was dried at 60^{o}C and stored in a desiccator.

The weight percentage of chitosan in the composite hydrogel was 30 wt% and the weight percentage of glyoxal was investigated with 10, 15 and 20 wt% and the samples were named as S10, S15, S20 respectively.

2.3. Measurements

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of PVA and lignin molecules were investigated by Frontier FT-IR/NIR instrument model at Institute of Applied Materials Science, Ho Chi Minh City, Vietnam. The scan range is 4000-450 cm $^{-1}$, the scan speed is 0.2 mm/s.

2.3.2. Swelling behavior test

The composite hydrogel samples were dried and weighed (W_o), then were put into distilled water for 24 h to equilibrium swelling weight (W_s) for removing soluble parts from the hydrogel. Next, the hydrogel was dried at 60^{o}C in an oven.

Then, the samples were cut into 2 x 2 cm piece and weighed (W_e). Next, the dried samples were soaked in distilled water at 33^{o}C. After that, the samples shall be removed from the water one at a time, all surface water was wiped off with a dry cloth, then weighed (W_s) immediately (ASTM D 570 – 98). The formulations of calculating the water uptake (swelling ratio) was shown below [8]:

$$\text{Water uptake (swelling ratio \_ SR \%)} = [(W_s - W_e)/W_e] \times 100 \quad (1)$$

2.3.3. Adsorption experiments

a) Adsorption calculation

The adsorption equilibrium experiments were conducted with the initial concentration (C_o) of Cu (II) ranged from 30 to 220 mg.L^{-1}. Hydrogel was weighed and soaked in Cu (II) solutions with different initial concentration under stirring at room temperature for 24 h. After adsorption process, the Cu (II) concentrations (C) were determined through the relationship between the absorbance and concentration of colored solutions. The absorbance of $CuSO_4$ solution was determined at a wavelength of 635 nm by UV-Vis spectrophotometer (UV/UV-NIR Horiba Dual-FL). The amount of adsorption q (mg.g^{-1}) was calculated using the equation (2) below [9], [10]:

$$q = \frac{(C_o - C).V}{m} \quad (2)$$

Where C_0 and C (mg.L^{-1}) were the initial and equilibrium concentration of the copper solution, and V (L) is the volume of the Cu(II) solution, and m (g) is the weight of the dried adsorbent hydrogel.

b) Equilibrium Isotherms Study

To evaluate Cu (II) absorbing ability of the hydrogel, the adsorption process with various initial concentrations was investigated with Langmuir isotherm (3) and Freundlich isotherm (4) models [11].

$$\frac{C}{q} = \frac{C}{q_\infty} + \frac{1}{bq_\infty} \quad (3)$$

$$lnq = \frac{1}{n} lnC + lnK. \quad (4)$$

where q_∞(mg.g^{-1}) was the maximum adsorption capacity, k (L.mg^{-1}) was a Langmuir constant related to the adsorption energy, K (mg.g^{-1}) was a Freundlich constants related to absorption capacity of adsorbent material, and 1/n was the Freundlich coefficient relative heterogeneity.

3. Results and discussion

3.1. Investigating characteristic functional groups of the composites

The FTIR spectrum of PVA was shown in Figure 1. It can be seen that the absorption peak at 3282 cm^{-1} was specific for hydroxyl group. The sharp peak at 2919 cm^{-1} was related to the prolonged vibration of the –CH_2 group. Peaks 1720 and 1085 cm^{-1} referred C = O and C - O stretching from the acetate group remaining from PVA. Absorption peaks from 1423 cm^{-1} revealed C–H bending of the $–CH_2$ group. Peaks 835 cm^{-1} reflected C-C stretching vibration.

Similar peaks were discovered for the crosslinked PVA - chitosan samples. Due to the interaction between groups of both chitosan and PVA, the peak referring to the vibration of hydroxyl groups was 3689 cm^{-1} whereas the peak was 3282 cm^{-1} in PVA sample. In addition, a new peak located at 3319 cm^{-1} appeared in chitosan-PVA hydrogel due to the NH_2 vibration of chitosan.

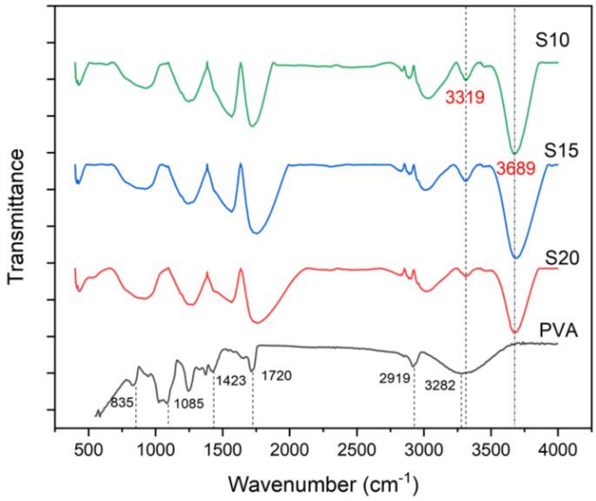

Figure 1. *FTIR spectra of PVA and crosslinked PVA-chitosan*

3.2. Investigating swelling behavior

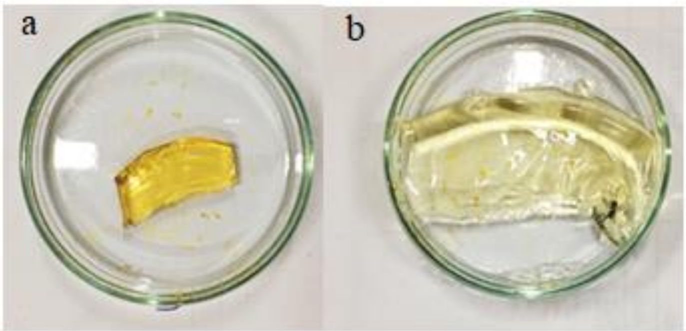

Figure 2. *The shape of the hydrogel before (a) and after (b) swelling test*

Within swelling test, the hydrogel absorbed water and increased the hydrogel volume (Figure 2). The hydrogel became light brown compared to original sample.

Considering various samples with glyoxal ratio separately, from Figure 3, the S10 hydrogel had about 850% swelling ratio (SR) which is the highest water absorption and swelling capacity compared to other hydrogels. Whereas the S15 hydrogel sample showed lower water swelling results about 550% SR. It could be explained that the higher glyoxal ratio contributed to increasing the crosslinking density, which reduced the -OH group content in the sample, leading to a decrease in the water swelling capacity of S15. And S20 sample with the highest glyoxal content possessed the lowest water swelling about 400% SR. Compared to chitosan/Poly (Vinyl Alcohol) blended films with degree of swelling for the blended films about 1047% and poly (vinyl alcohol) and chitosan hydrogel prepared by UV irradiation with swelling ratio about 350% in some previous research [12], [13], the crosslinked PVA chitosan hydrogels had remarkable swelling degree ranging from 400% to 850%.

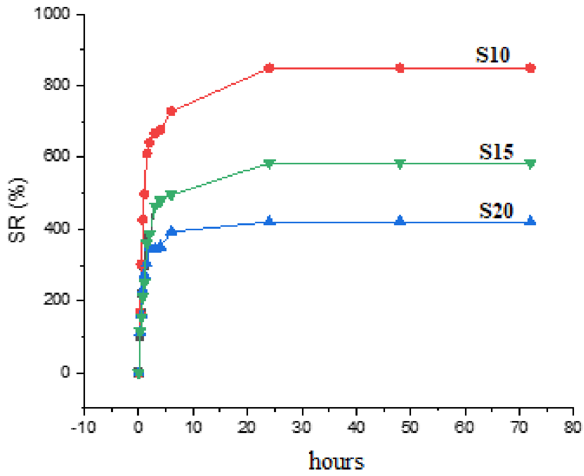

Figure 3. *Swelling ratio of the hydrogel samples*

3.3. Cu (II) isothermal adsorption

The equilibrium isotherm is used to investigate the properties of the adsorbent [10], [11]. In this study, the Cu (II) adsorption isotherms of PVA/chitosan hydrogel were measured at 30°C and pH 7, which were presented in Figure 5.

From table 1, the Cu (II) ions inserted to hydrogel increased linearly with the initial concentrations of Cu (II) increasing. When initial concentration was from 30 ($mg.l^{-1}$) to 220 ($mg.l^{-1}$), the amount of Cu(II) ions adsorbed increased from 19.429 ($mg.g^{-1}$) to 92.841 ($mg.g^{-1}$) (Table 1).

Table 1. *The adsorption amount q of S10 hydrogel*

C_o ($mg.l^{-1}$)	C ($mg.l^{-1}$)	*q* ($mg.g^{-1}$)
220	176.674	92.841
170	133.002	79.281
120	89.634	65.070
90	66.356	50.666
60	42.643	37.194
30	20.933	19.429

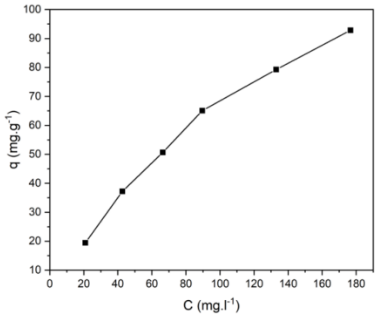

Figure 4. *The effect of equilibrium Cu (II) ion concentration on the adsorption amount of S10 hydrogel*

It could be seen from Figure 4 that the Cu (II) ion adsorption depended on the moving of Cu (II) ions from the solution to the surfaces of the hydrogels. At increasing initial concentrations of Cu (II) solution, the adsorption on the surfaces of the hydrogel increased to equilibrium [9]. The equilibrium adsorption had been investigated by isotherm models, including Langmuir and Freundlich.

Figure 5a presented the relationship between lnq and lnC, following Freundlich model. Figure 5b illustrated the relationship between q and C, following Langmuir model. The parameters were revealed in Table 2.

According to Table 2, the correlation coefficients (R^2) of the linear form for Langmuir model were much closer to 1.0 than that of Freundlich models (Figure 5). According to Langmuir model, the maximum Cu (II) uptakes of the hydrogel were drawn from Langmuir model as shown in Table 2. From the Figure 5b, it was found that the Langmuir curve fitted the experimental parameters. Langmuir curve proved that Langmuir model described properly the Cu

(II) adsorption by hydrogel adsorbents, revealing the monolayer adsorption of Cu (II) ions on the surface of the hydrogel. Compared to polyvinyl alcohol/chitosan/graphene oxide hydrogel with maximum Cu (II) adsorption capacities about 162 $mg.g^{-1}$ [14] and cross-linked chitosan-PVA spherical hydrogel with maximum adsorption capacity for Cu(II) about 62.1 $mg.g^{-1}$ [15], the PVA/chitosan hydrogel sample had the Cu (II) adsorption capacity varying from 19.429 ($mg.g^{-1}$) to 92.841 ($mg.g^{-1}$) (Table 1) and the maximum adsorption capacity with 183.486 ($mg.g^{-1}$) (Table 2) according to Langmuir Isotherm.

Table 2. *The isotherm parameters of Langmuir and Freundlich models*

Langmuir Isotherm				Freundlich Isotherm		
$q_\infty (mg.g^{-1})$	*b (l/mg)*	R^2	R_L	*1/n*	*K*	R^2
183.486	0.00583	0.99236	0.438	0.73131	2.264	0.98754

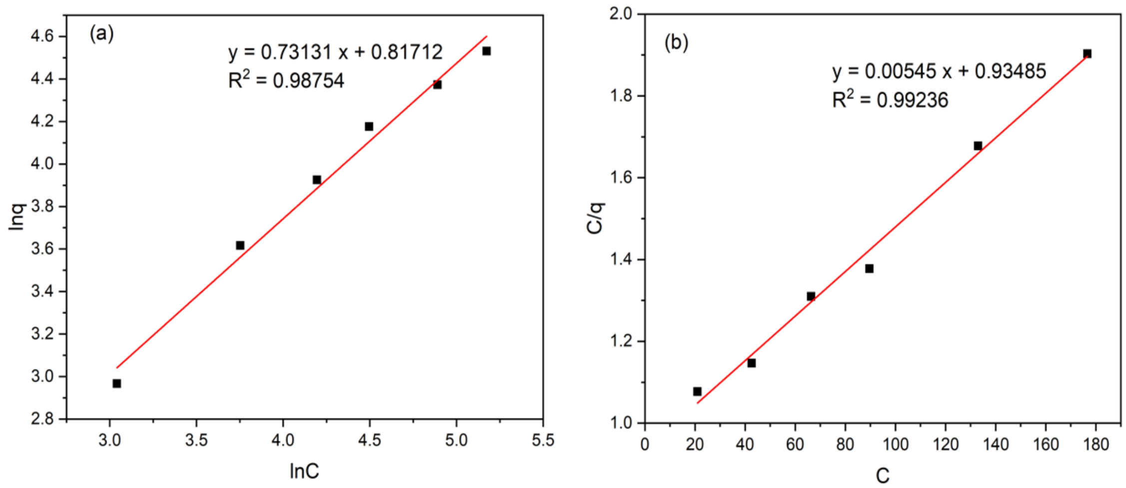

Figure 5. *Adsorption isotherms of Cu (II) on the hydrogel, (a) Freundlich model and (b) Langmuir model*

A dimensionless separation coefficient, R_L, which helped to further discovery on adsorption process based on Langmuir model, can be calculated from the equation (5) below [11]:

$$R_L = \frac{1}{1+bC_o} \quad (5)$$

The favorable value of R_L was about ($0 < R_L < 1$), which gave a good indication on affinity between the adsorbent and the adsorbate. According to the Table 2, the R_L value for the hydrogel was smaller than 1.0, showing a good adsorption for Cu (II) ions.

4. Conclusion

In this study, the hydrogel based on PVA and chitosan was fabricated successfully. The FTIR spectra showed that the hydrogel had functional groups of PVA and chitosan. By investigating the effect of the glyoxal crosslinker content to the water swelling behavior of the hydrogel, the adsorbents showed the highest swelling ratio about 850% when using 10% glyoxal. In the copper ion adsorption experiment, the Langmuir and Freundlich isotherm models were using to evaluate the copper ion adsorption capacity. The maximum copper ion adsorption of the hydrogel was 183.486 mg/g. This reveals that the hydrogel based on PVA and chitosan could remove copper ion from the wastewater with the high adsorption capacity.

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