

Crosslinked hydrogel based on Polyvinyl alcohol/chitosan/glyoxal for the removal of Crom(VI) ions from aqueous solution

Bui Thi Thao Nguyen*, Nguyen Thi Quynh Giao, Nguyen Duc An, Nguyen Nhi Tru

ABSTRACT

This article describes an effective method to remove pollutants from wastewater using crosslinked hydrogels based on polyvinyl alcohol and chitosan. Glyoxal was used as the crosslinker for the hydrogels. The reaction between glyoxal and PVA as well as chitosan was conducted at 80°C for 90 minutes, contributing to the formation of the hydrogels which act as absorbents for removing Cr(VI) ions from the aqueous solution. The adsorption process was progressed at about 32°C and pH 7, in which the hydrogel samples were soaked in the Cr(VI) solution until the adsorption reached equilibrium state. The characterization of hydrogels was discovered with using various analytical techniques, including scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), UV-visible spectrophotometry (UV-Vis), and energy dispersive X-rays (EDX). The equilibrium adsorption isotherm analysis for Cr(VI) ions was researched by using Langmuir and Freundlich equilibrium isotherm models. The pseudo-first and pseudo-second-order kinetic models were studied for investigating adsorption kinetics. The microstructural surface of the hydrogel with the pores of 10 – 50 nm was revealed by SEM images. EDX analysis confirmed the existence of Cr(VI) ions on the hydrogel surface after adsorption. The adsorption capacity and removal efficiency were studied with the various initial concentrations of Cr(VI) solutions, from 10 - 50 (mg.L⁻¹). The maximum adsorption capacity was about 344 (mg.g⁻¹) and the removal efficiency was from 82.35 % to 89.99 %. About adsorption isotherm and kinetics, the experimental data were consistent with Langmuir isotherm model and agreed with the pseudo-second-order kinetics. These results showed the presence of the Cr(VI) ions monolayer on the hydrogels and existence of chemical interaction between metal ions and the hydrogels during the adsorption process. Therefore, the PVA/chitosan/glyoxal hydrogels could be effectively used as an application in removing Cr(VI) from wastewater.

Key words: Polyvinyl alcohol, chitosan, glyoxal, hydrogel, adsorption

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INTRODUCTION

Nowadays, water pollution has become an increasingly serious problem. Due to urbanization and industrialization, the contamination of the water is getting worse. Especially, the existence of heavy metal ions in wastewater endangers humans, animals, and ecosystems¹. Heavy metal ions are metallic elements and non-degradable materials. These take up the majority of inorganic pollutants and could cause toxicity at even low amounts in water. There are various ions such as Cu²⁺, Cr⁶⁺, Cd²⁺, Pb²⁺, Hg²⁺, and As⁵⁺². Chromium ion is a serious pollutant released from dye manufacturing, electroplating, textile industry, metal alloys manufacturing, leather tanning, dye, and mining³. There are two stable forms of chrome, including trivalent chrome (Cr(III)) and hexavalent chrome (Cr(VI)). The hexavalent chrome form is evaluated as more toxic for living organisms because of its mutagenic and carcinogenic characteristics⁴. Environmental contamination by Cr(VI) has become

a worldwide issue, requiring effective approaches to Cr(VI) elimination. There are various techniques to treat and eliminate Cr(VI) from wastewater, such as ion exchange, chemical precipitation, membrane separation, and physicochemical methods⁵. However, most of the methods have high costs and low treatment efficiency. In recent years, considerable studies have revealed that adsorption is a potential simple method by outstanding benefits, including low energy consumption, safety, cost saving, and nontoxicity⁶⁻⁸. Therefore, the study investigated the removing of Cr(VI) from aqueous solution by the adsorption. Recently, there have been several researches using materials from eco-friendly materials such as chitosan, cellulose, zeolite, and biocarbon for adsorbing Cr(VI)⁹. Bio-adsorbent based on chitosan/MoO₃ biocomposite removed hexavalent chromium ions effectively¹⁰. The activated biochar has a maximum Cr(VI) adsorption capacity of 28.019 mg.g⁻¹¹¹. Polyaniline/zeolite nanocomposite adsorbed Cr(VI)

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on its surface, obeying the Freundlich isotherm¹². Amongst adsorbents, hydrogels have become a potential material for the adsorption of chromium ions. These hydrogels could be prepared from chitosan, cellulose, and starch¹³⁻¹⁵.

Chitosan is prepared from N-deacetylation of chitin, which is the main component of the shells of shrimp, crabs, and insects. Therefore, chitosan is a natural, renewable, abundant, and inexpensive adsorbent. Due to polar groups, including hydroxyl group (-OH) and the amine group (-NH₂), chitosan easily interacts with contaminated metal ions in water sources for ion adsorption and exchange^{16,17}. As another adsorbent, polyvinyl alcohol (PVA) is a biopolymer possessing hydroxyl groups (-OH) which could interact with each other to create a hydrogel matrix¹⁸. Moreover, these hydroxyl functional groups also form hydrogen bonds with amine groups of chitosan, thus enhancing the mechanical properties of hydrogels based on PVA and chitosan. Many researchers are drawing from the advantages of the combination of PVA and chitosan^{19,20}.

In this study, glyoxal was used as the crosslinker for the hydrogels based on PVA and chitosan. The linkages are created from glyoxal and polar groups of polymer chains to form a network with PVA and chitosan, which contributes to enhancing the stability of the hydrogel structure. Hydrogels based on poly(vinyl alcohol), chitosan were synthesized and their properties were investigated by analytical methods such as FTIR, SEM, and UV-Vis, EDX. Moreover, the hydrogel was evaluated for Cr(VI) ion adsorption capacity. Langmuir and Freundlich's isotherm adsorption models were included in the research process to study the maximum adsorption capacity of hydrogels. The kinetics were researched with the pseudo-first and pseudo-second-order kinetic models.

MATERIALS AND METHODS

Materials

PVA (Mw = 125,000 g.mol⁻¹, 98-99 % hydrolyzed) and chitosan (Mw = 500,000 g.mol⁻¹, 82 % deacetylated) were obtained from Sigma Aldrich (Germany). Glyoxal was received from Wako Chemical Industries (Japan). All other chemicals, including acid hydrochloric, acetic acid, and potassium dichromate, were supplied from Guangdong Guanghua Sci-Tech Company (China).

Preparation of PVA/chitosan/glyoxal hydrogels

Firstly, chitosan powder was added to a 2 wt% aqueous solution of acetic acid and stirred overnight at

room temperature until a homogenized solution. In addition, PVA was dispersed in hot deionized water and stirred at 80°C about 90 minutes to achieve a solution. A mixture of chitosan and PVA solution was stirred for one hour at 60°C to form a homogeneous solution. Next, slowly add glyoxal into the solution. Continue stirring for one hour to homogenize the glyoxal with the solution. After that, pour the solution containing glyoxal into the Petri dish and place it in the oven for curing at 80°C for 90 minutes²¹⁻²³.

Adsorption Isotherms

The experiments of equilibrium adsorption were conducted with the initial concentration (C₀) of Cr(VI) solutions which varied in the range 10 - 50 mg.L⁻¹²⁴. The hydrogel samples were weighed and sank into Cr(VI) solutions which had different equilibrium concentrations at room temperature (about 32°C) and pH 7. In adsorption tests, the hydrogel and Cr(VI) solution were put in an erlen and stirred at room temperature. When the process reached the equilibrium, filtration was carried out to remove the samples, and the Cr(VI) solution concentrations (C) were determined through the relationship between the absorbance and concentration of colored solutions (ISO 18412 : 2005). The adsorption capacity q (mg.g⁻¹) and removal efficiency E (%) were achieved by the following equations⁶:

$$q = \frac{(c_0 - c)v}{m} \quad (1)$$

$$E = \frac{c_0 - c}{c_0} \times 100\% \quad (2)$$

Where C₀ and C (mg.L⁻¹) were the beginning and equilibrium concentrations of the Cr(VI) solution, respectively; V (L) was considered as the volume of the Cr(VI) solution, and m (g) was the weight of dried adsorbent hydrogel.

The adsorption was also studied with using Langmuir (3) and Freundlich isotherm (4) models⁹. These models investigated the interaction between adsorbents and Cr(VI) ions and predicted the adsorption mechanism of the adsorbent. The Langmuir isotherm model supposed that adsorbate linked on the adsorbent surfaces like monolayers, while the Freundlich isotherm model assumed that adsorbate concentrated at the surfaces like multilayers⁹.

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

$$\ln q = \frac{1}{n} \cdot \ln C + \ln K \quad (4)$$

Where q_{∞} (mg.g^{-1}) was the maximum adsorption capacity, b ($\text{L.m}^{-1}.\text{g}^{-1}$) and K (mg.g^{-1}) were Langmuir and Freundlich constants respectively, relating to the adsorption energy of adsorbent material, and $1/n$ was the Freundlich coefficient.

The dimensionless equilibrium parameter, R_L , indicating the chemical affinity between the adsorbent and the adsorbate, was determined as follows³:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

The values of R_L could be good when R_L was less than 1.

Kinetic study

The pseudo-first-order (6) and pseudo-second-order (7) models were utilized for examining the experimental data and evaluating the kinetic mechanism of adsorption^{5,11}, which were described by following equations

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (6)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where q_e (mg.g^{-1}) and q_t (mg.g^{-1}) were the adsorption capacity at equilibrium state and after the period of time, respectively; k_1 (min^{-1}) and k_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$) were the rate constants of first-order and second-order adsorption, respectively.

For kinetics, 0.05 g PVA/chitosan/glyoxal was prepared to adsorb Cr(VI) ions from 50 mL solution at the beginning concentration of 17 mg.L^{-1} and pH 7.

Characterization methods

The functional groups of hydrogels were examined by FT-IR/NIR instrument (PerkinElmer Frontier, America). The scan rate and speed were 4000 – 4500 cm^{-1} and 0.2 mm/s, respectively. The morphology of hydrogels was observed by SEM system (Hitachi S-4800, Japan). The absorbance of Cr(VI) solution was determined by UV-Vis spectrophotometer (UV/UV-NIR Horiba Dual-FL, Japan) based on reading the absorbance value at the wavelength of 540 nm. The existence of chemical elements of the hydrogel was confirmed by EDX (JSM-IT 200 JeOL, Japan).

RESULTS AND DISCUSSION

Characterization of the PVA/chitosan/glyoxal hydrogel

To study the interaction between chitosan and PVA in the hydrogel, the FTIR spectra of PVA, chitosan, and PVA/chitosan/glyoxal were described in Figure 1.

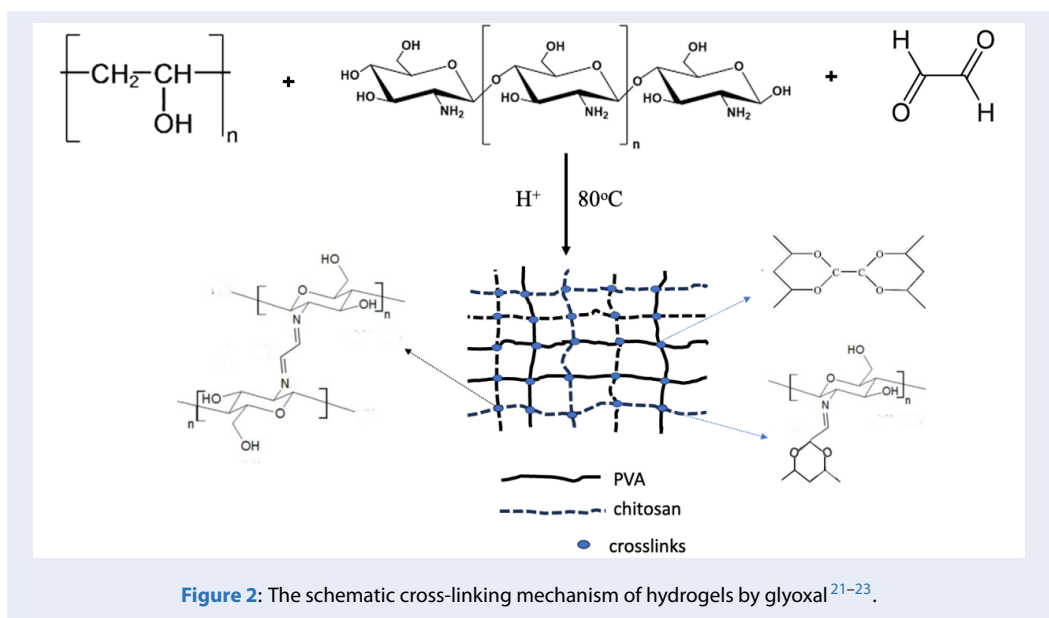
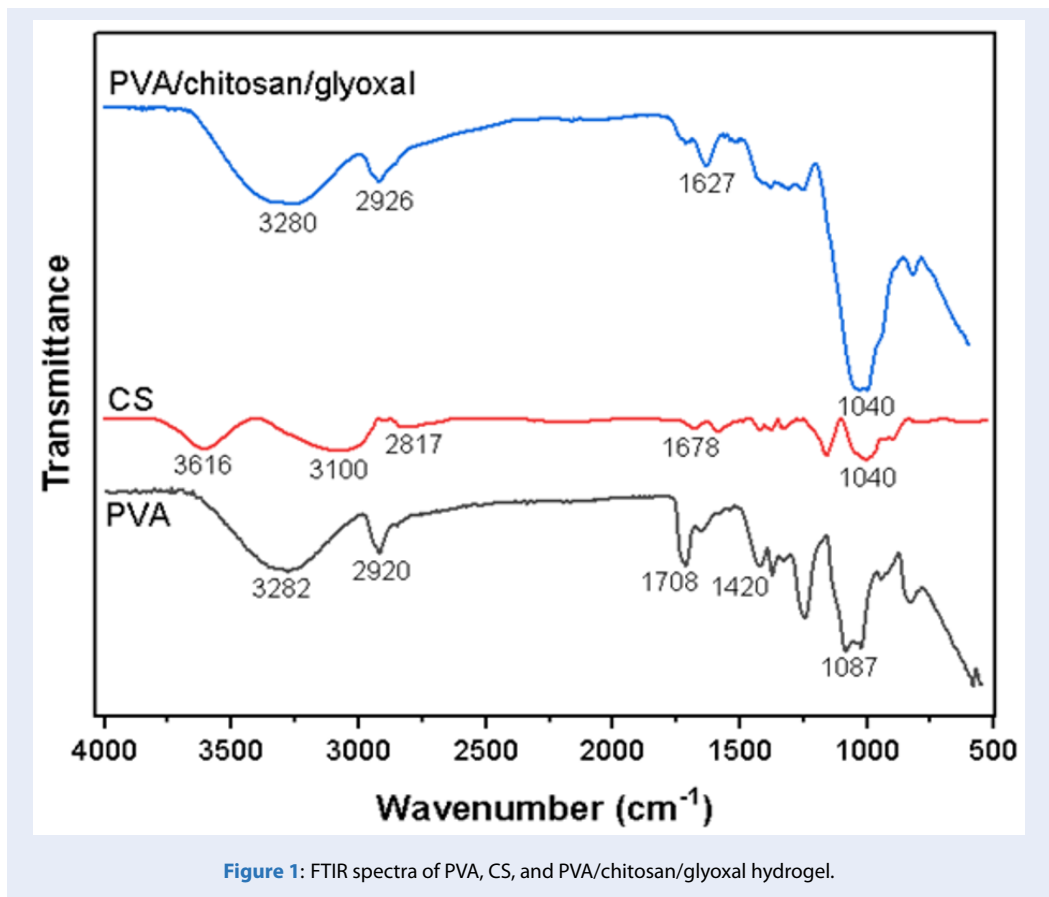
From the FTIR spectrum of PVA, the broad band at 3282 cm^{-1} referred the stretch of OH groups. The strong peaks appeared at 2920 cm^{-1} and 1420 cm^{-1} reflected CH stretching and CH_2 bending respectively. The peak observed at 1708 cm^{-1} described the C=O stretching, presenting the existence of acetate groups of PVA because of the hydrolyzation level of the PVA. The peak showed at 1087 cm^{-1} reflected the C-O stretching in PVA¹⁸.

For the FTIR spectrum of chitosan, the absorption peak around 3616 cm^{-1} could be assigned for -OH stretching vibration. The absorption band around 3100 cm^{-1} indicated the stretching vibration of - NH_2 . The peak at 2817 cm^{-1} referred to the CH_2 stretching. The peak appeared at 1678 cm^{-1} reflected the stretch of C=O due to deacetylation. The absorption band around 1040 cm^{-1} was characterized for C-O stretching²⁵.

In the term of PVA/chitosan/glyoxal FTIR, due to the interaction of PVA and chitosan, the peak corresponding to OH stretching of chitosan and PVA shifted to 3280 cm^{-1} . In addition, the peak around 1040 cm^{-1} being attributed to C-O stretching increased its intensity due to appearing the cross-linkage between glyoxal and PVA. The peak obtained at 1627 cm^{-1} showed the presence of C=N group from the interaction of glyoxal with chitosan. The hydrogel became the network (Figure 2) as the consequence of the reaction between glyoxal with PVA and chitosan, which could be considered in previous research²¹⁻²³.

The SEM images are presented in Figure 3, illustrating the microstructural surface of the hydrogel. The SEM micrographs showed the pores of 10 – 50 mm distributed across the surface. The unevenly sized pores appeared with highly dense density, being created from the linkage between glyoxal and polymer chains of PVA and chitosan. The micropores formed a porous structure like 3D dimension space from the inside to the outside of the hydrogel. The result promised to provide the good water swelling ability of the hydrogel.

EDX analysis was carried out to confirm the formation of Cr(VI) ions on the hydrogel after adsorption. Figure 4a showed that Cr(VI) ions were not found on the surface of the hydrogel before adsorption. According to the EDX results for the hydrogel after adsorption in Figure 4b, the existence of Cr(VI) ions could be observed by the peaks at 0.57, 5.41, and 5.95 keV in EDX spectrum.



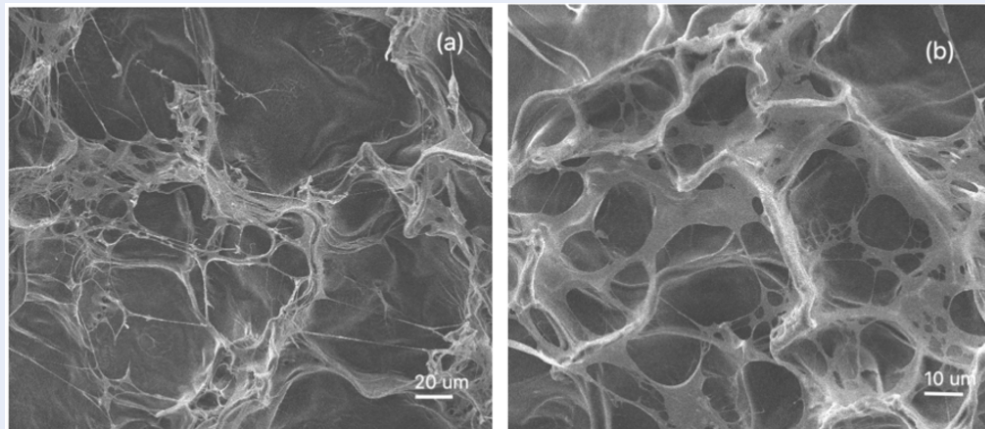


Figure 3: SEM images (a, b) of PVA/chitosan/glyoxal hydrogel with different magnification

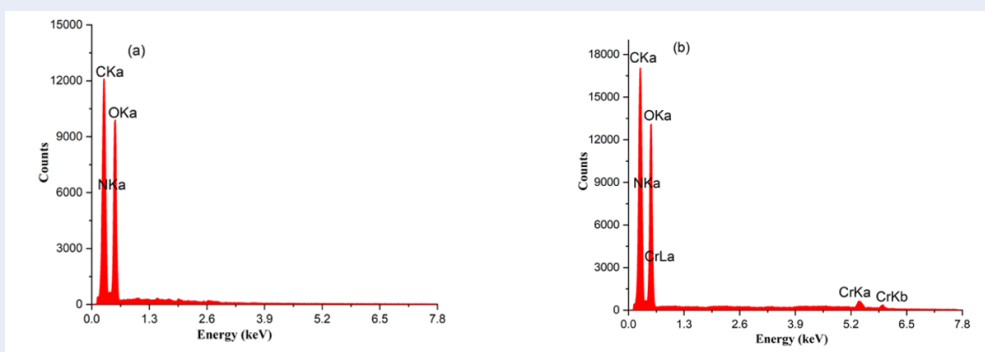


Figure 4: EDX patterns of PVA/chitosan/glyoxal hydrogel before (a) and after adsorption (b)

Adsorption isotherms

The equilibrium adsorption had been investigated by isotherm models, including Langmuir and Freundlich models. The equilibrium concentrations of the Cr(VI) solution (C) were obtained at the equilibrium state. The data was showed in Table 1 and Figure 5. The Figure 5a presented the relationship between q and C according to Langmuir model. The Figure 5b showed the relationship between lnq and lnC according to Freundlich model. According to Langmuir model, the maximum adsorption capacity of Cr(VI) ions (q_{∞}) penetrated into the hydrogel were derived by Langmuir model was about 344 (mg.g^{-1}). The q_{∞} for Cr(VI) on PVA/chitosan/glyoxal hydrogel was compared with those of various adsorbents from previous research (Table 2). From the Figure 5a and Figure 5b, it was found that the Langmuir curve fitted the experimental parameters and the correlation coefficients (R^2) of the linear graph for Langmuir isotherm model were closer to 1.0 than that of

Freundlich isotherm, demonstrating that Langmuir model presented properly the Cr(VI) adsorption by hydrogel adsorbents, illustrating the monolayer adsorption of Cr(VI) ions on the hydrogel^{26,27}.

Influence of initial concentrations and adsorption time on the adsorption process.

The influence of initial concentrations on the equilibrium adsorption capacity and removal efficiency of the hydrogel were shown in Figure 6a. The beginning concentrations were in the range 10 -50 (mg.L^{-1}). Table 2 showed the initial concentrations of this work and previous study. The capacity of Cr(VI) ions inserting to hydrogel structure was determined by the formula (1) at the equilibrium state. We saw that the adsorption capacity increased linearly when the initial concentrations of Cr(VI) achieved higher value. When initial concentrations increased from 10 (mg.L^{-1}) to 50 (mg.L^{-1}), the amount of Cr(VI) ions increased from 53.99 (mg.g^{-1}) to 262.04 (mg.g^{-1})

Table 1: The parameters of langmuir and freundlich isotherm models.

Langmuir Isotherm				Freundlich Isotherm		
$q_{\infty}(\text{mg.g}^{-1})$	$b(\text{L.m}^{-1}.\text{g}^{-1})$	R^2	R_L	$1/n$	K	R^2
344.828	0.193	0.9916	$0.119 \div 0.340$	0.6503	6.0146	0.9651

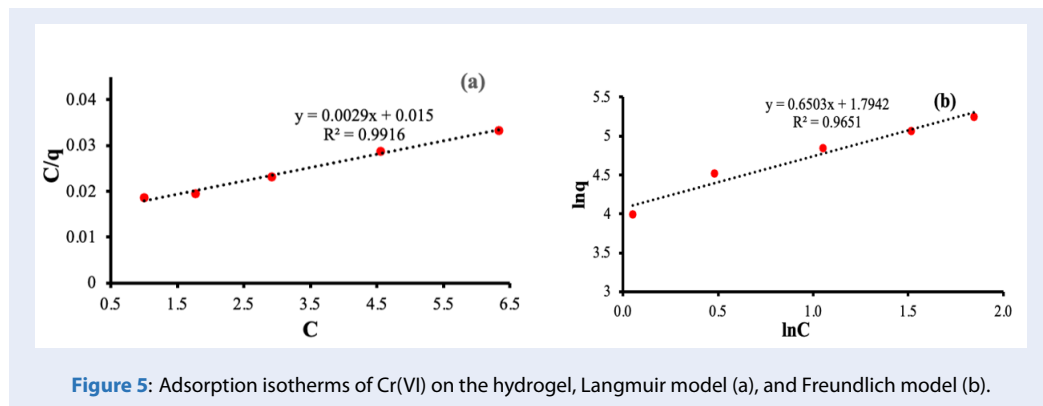


Figure 5: Adsorption isotherms of Cr(VI) on the hydrogel, Langmuir model (a), and Freundlich model (b).

and the removal efficiency was from 89.99 % to 82.35 %. These results revealed that the Cr(VI) ion adsorption depended on the removing of Cr(VI) ions from the solution to the surfaces of the hydrogels. With increasing initial and equilibrium concentrations of Cr(VI) solution, the amount of Cr(VI) ions which penetrated on the surfaces of the hydrogel increased to equilibrium²⁶.

The experiment was conducted by soaking 0.05 g PVA/chitosan/glyoxal into 50 mL Cr(VI) ions solution with the beginning concentration of 17 mg.L⁻¹. The effect of adsorption time on the adsorption process was observed (Figure 6b). The result showed that the removal efficiency of Cr(VI) increased when the experimental time increased and reached the equilibrium after adsorption time attained 600 minutes. The removal efficiency was about 89 % for the initial concentration of 17 mg.L⁻¹ as the adsorption reached the equilibrium.

Kinetic models

Pseudo-first-order and pseudo-second-order kinetics were used for determining the experimental data. The two models are depicted in Figure 7. The results of kinetic parameters of Cr(VI) ions adsorption are presented in Table 3. According to the first-order kinetic model, the k_1 constant was calculated from the graph of $\ln(q_e - q_t)$ versus t . According to the second-order model, the k_2 constant was also derived from the graph of t/q_t versus t . The R^2 correlation coefficient pseudo-second-order model was

0.9993, showing a good compatibility between experiment data and the pseudo-second-order model. The pseudo-first-order model did not fit well with the data. The first-order kinetic was used in the case of reversible reaction with the equilibrium state while the second-order kinetic referred to chemical adsorption with limited rate. Cr(VI) ions adsorption on the PVA/chitosan/hydrogel could obey the pseudo-second-order kinetic model. Therefore, it could predict that the chemical adsorption occurred between Cr(VI) ions and the hydrogel³⁰.

CONCLUSIONS

In the current study, the hydrogels based on PVA, and chitosan were synthesized by using glyoxal crosslinker. The adsorption process was investigated by conducting a batch experimental procedure. The parameters of adsorption isotherms were achieved from the experiment of adsorbing Cr(VI) from the aqueous solution, which was conducted at 32°C and pH 7. The maximum adsorption capacity was obtained at about 344 mg.g⁻¹. The experimental data had good consistency with the Langmuir isotherm, revealing the existence of Cr(VI) monolayer on the hydrogel surfaces. Moreover, the kinetic data agreed very well with the pseudo-second-order kinetics, demonstrating that the mechanism of adsorption is mainly related to chemical interactions between metal cations and PVA/chitosan/glyoxal hydrogels. In conclusion, the hydrogels can be used for the application relating to removing Cr(VI) ions from aqueous solution.

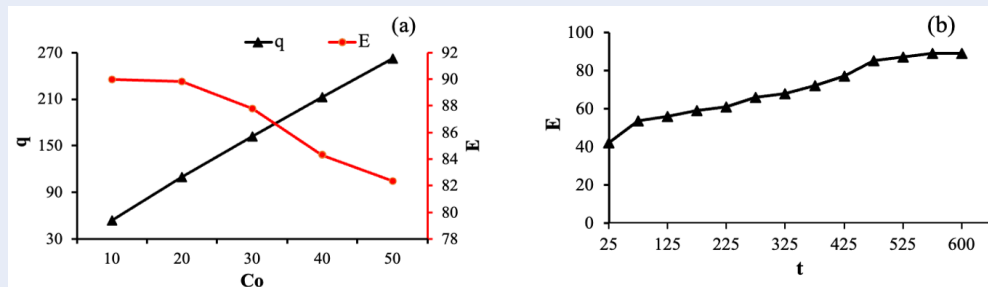


Figure 6: The effect of the beginning concentrations (a) and adsorption time (b) on the adsorption amount and the removal efficiency.

Table 2: Maximum adsorption capacity of cr(vi) on PVA/chitosan/glyoxal and other adsorbents

Adsorbents	Maximum adsorption capacity (mg.g ⁻¹)	Initial concentrations (mg.L ⁻¹)	References
Fe ₃ O ₄ /chitosan	162	10-100	26
Cellulose/chitosan	197	20-240	25
Fluorescent chitosan	228	20-120	15
Fluorescent carbon dots/nanocellulose/chitosan	294	1-50	13
Activated carbon	28	10-50	11
Chitosan@MoO ₃	128	0.5-200	10
lignosulfonate-modified graphene	1743	50-400	28
Polyethylenimine/lignin	657	50-400	29
PVA/chitosan/glyoxal	344	10-50	This work

Table 3: Kinetic studies, k₁ and k₂ were first-order and second-order rate constants, R² was correlation coefficient.

Pseudo-first-order model		Pseudo-second-order model	
k ₁ (min ⁻¹)	R ²	k ₂ (g.mg ⁻¹ .min ⁻¹)	R ²
0.0129	0.7555	0.0016	0.9993

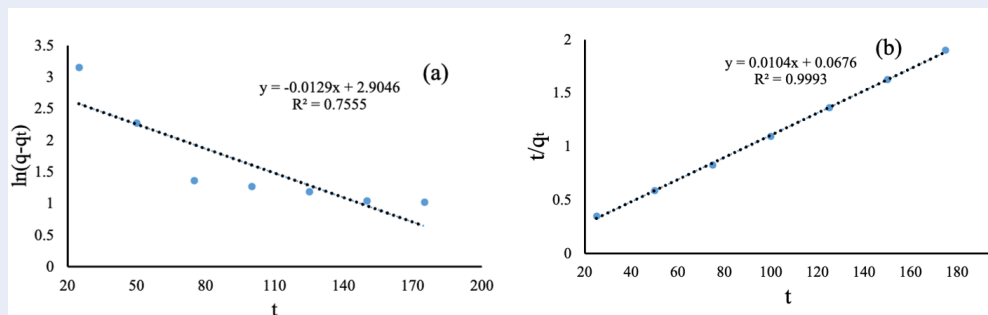


Figure 7: Kinetic studies for pseudo-first-order adsorption (a), and pseudo-second-order adsorption (b).

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CONFLICT OF INTEREST

The authors have no conflict of interest to declare.

AUTHORS' CONTRIBUTIONS

Nguyen Duc An: Investigation. Nguyen Thi Quynh Giao: Formal analysis, writing draft. Bui Thi Thao Nguyen: Organizing research and completing the manuscript. Nguyen Nhi Tru: Supervision.

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Tổng hợp hydrogel liên kết ngang từ Polyvinyl alcohol/chitosan/glyoxal có khả năng loại bỏ Crom(VI) khỏi môi trường nước

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TÓM TẮT

Nghiên cứu này trình bày một phương pháp hiệu quả để loại bỏ các chất ô nhiễm khỏi nước thải trên cơ sở sử dụng hydrogel từ polyvinyl alcohol và chitosan. Trong đó, glyoxal được sử dụng làm chất liên kết ngang cho hydrogel. Hydrogel được hình thành từ phản ứng giữa glyoxal với PVA cũng như chitosan ở nhiệt độ 80°C trong thời gian 90 phút được khảo sát khả năng loại bỏ ion Cr(VI) ra khỏi môi trường nước theo cơ chế hấp phụ. Quá trình nghiên cứu hấp phụ được tiến hành ở nhiệt độ khoảng 32°C và pH 7 với các mẫu hydrogel được ngâm trong dung dịch Cr(VI) cho đến khi quá trình hấp phụ đạt trạng thái cân bằng. Các tính chất của hydrogel được khảo sát bằng các phương pháp phân tích khác nhau, bao gồm kính hiển vi điện tử quét (SEM), quang phổ hồng ngoại biến đổi Fourier (FTIR), phép đo quang phổ (UV-Vis) và phổ tán xạ năng lượng tia X (EDX). Phân tích đẳng nhiệt hấp phụ được nghiên cứu bằng cách sử dụng mô hình đẳng nhiệt cân bằng Langmuir và Freundlich. Các mô hình động học giả bậc nhất và giả bậc hai được dùng để nghiên cứu động học hấp phụ. Bề mặt vi cấu trúc của hydrogel với các lỗ xốp 10 – 50 nm được thể hiện qua ảnh SEM. Phân tích EDX xác nhận sự tồn tại của ion Cr(VI) trên bề mặt hydrogel sau khi hấp phụ. Dung lượng hấp phụ và hiệu suất hấp phụ được khảo sát với các nồng độ ban đầu của dung dịch Cr(VI) khác nhau, từ 10 - 50 (mg.L⁻¹). Dung lượng hấp phụ tối đa khoảng 344 (mg.g⁻¹) và hiệu suất hấp phụ đạt từ 82,35 % đến 89,99 %. Quá trình khảo sát đẳng nhiệt hấp phụ và động học cho thấy số liệu thực nghiệm phù hợp với mô hình đẳng nhiệt Langmuir và giả động học bậc hai. Những kết quả này dẫn đến khẳng định sự có mặt của đơn lớp ion Cr(VI) trên hydrogel và sự tồn tại tương tác hóa học giữa các ion kim loại và hydrogel trong quá trình hấp phụ. Do đó, hydrogel PVA/chitosan/glyoxal có thể được ứng dụng hiệu quả để loại bỏ Cr(VI) khỏi môi trường nước thải.

Từ khoá: Polyvinyl alcohol, chitosan, glyoxal, hydrogel, hấp phụ

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