SYNTHESIS OF POLYVINYL ALCOHOL/CHITOSAN HYDROGELS AND INVESTIGATION OF THE ADSORPTION FOR CROM (VI) IONS

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ABSTRACT

In this work, the hydrogels based on polyvinyl alcohol and chitosan were prepared. The glyoxal was used as a crosslinker with the aim of forming the three-dimensional network for the structure of these hydrogels. The adsorption capacity of the hydrogels for Cr(VI) ions was investigated with the various concentrations of glyoxal. The adsorption isotherm studies were conducted at 30^{o}C and pH 7 with Langmuir and Freundlich models. The pseudo-first-order and the pseudo-second-order kinetic models were applied to study the adsorption kinetics. The results showed that the experimental data fitted the Langmuir and pseudo-second-order kinetic models. This indicated that Cr(VI) adsorbed on the hydrogel surface by monolayer coverage and chemical adsorption. The removal efficiency for Cr(VI) ion from aqueous solution attained the excellent achievement of 92%, contributed by the prepared hydrogel with a glyoxal content of 31 wt%. Additionally, the characterization of hydrogels was revealed by several analytical methods, including Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and UV–visible spectrophotometry (UV-Vis).

TỔNG HỢP HYDROGEL TRÊN CƠ SỞ POLYVINYL ALCOHOL/CHITOSAN VÀ NGHIÊN CỨU KHẢ NĂNG HẤP PHỤ CROM (VI) CỦA HYDROGEL

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TỪ KHÓA

Polyvinyl alcohol
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Hấp phụ
Hydrogel

TÓM TẮT

Trong nghiên cứu này, các hydrogel được tổng hợp từ polyvinyl alcohol và chitosan. Glyoxal được sử dụng làm chất liên kết ngang với mục đích hình thành mạng lưới ba chiều cho cấu trúc của các hydrogel. Khả năng hấp phụ đối với các ion Cr(VI) đã được nghiên cứu với các mẫu hydrogel được tổng hợp với nồng độ khác nhau của glyoxal. Nghiên cứu đẳng nhiệt hấp phụ được thực hiện ở 30^{o}C và pH 7 với mô hình Langmuir và Freundlich. Mô hình giả động học bậc nhất và giả động học bậc hai được áp dụng để nghiên cứu động học hấp phụ. Kết quả cho thấy dữ liệu thực nghiệm phù hợp với mô hình Langmuir và mô hình giả động học bậc hai. Điều này chỉ ra rằng Cr(VI) được hấp phụ trên bề mặt hydrogel bằng lớp phủ đơn lớp và theo cơ chế hấp phụ hóa học. Hiệu suất hấp phụ ion Cr(VI) đạt 92% đối với hydrogel có hàm lượng glyoxal là 31%. Ngoài ra, tính chất của hydrogel cũng được khảo sát bằng một số phương pháp phân tích, bao gồm quang phổ hồng ngoại biến đổi Fourier (FTIR), kính hiển vi điện tử quét (SEM) và phép đo quang phổ UV-Vis.

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1. Introduction

Water contamination is considered a global emergency issue due to the serious negative impact of the pollutants on the ecosystem and human beings. Industrialization and agricultural activities lead to the overload of waste discharged into water. Besides various toxic chemicals that might be released from industrial production, pesticides and nitrogen fertilizers from agriculture significantly cause water pollution. It was found that a 10% increase in pesticide use brought about a 1% increase in the medical disability index for rural residents 65 years and older in China [1]. Pesticide residues and various kinds of heavy metal discharged in wastewater threaten food safety and human health. Wastewater might penetrate the surface and underground sources, adversly affecting plants and animals, which risks other species due to polluted feed from poisoned organisms [2]. Amongst heavy metal ions, chromium ion has become a dangerous pollutant from metal alloy manufacturing, leather tanning, dye manufacturing, electroplating, and textile industry. Groundwater with high concentrations of hexavalent chromium is a serious factor for water pollution [3]. Urbanization and industrialization increase water contamination of the water by chromium ions, which is a risk factor causing several diseases [4] - [6]. According to data from Palestine, people who drink municipal water without household-filtering are more likely to suffer from diseases such as diarrhea [7]. Previous studies reveal a obvious relationship between cholera and contaminated water and diarrhoeal diseases account for 21% of annual deaths of children under 5 years of age in developing countries [8], [9]. Water with high hexavalent chromium concentration will bring about high carcinogenicity that causes human respiratory cancer [3]. According to data from Taiwan, high levels of chromium pollution have the relationship with gastric cancer incidence [10].

Adsorption is one of the most efficient ways of water treatment by removing heavy metals from wastewater due to low-cost materials and easy manufacturing. There are different types of absorbents for treating wastewater due to outstanding properties such as large specific surface area, nontoxicity, safety and cost-saving materials. These absorbents include biochar, chitosan, cellulose, zeolite, and activated carbon [11]. Hydrogel is an efficient absorbent that has predominant qualities as biodegradability, biocompatibility, and super adsorption capacity. Based on the bonding inside the structure of hydrogels, there are two types of hydrogels, physical and chemical hydrogels which correspond to physical and chemical bonds respectively. According to the three-dimensional network structure, hydrogels have the excellent heavy metal adsorption and water absorption. On the other hand, the appearance of functional groups such as -OH, $-NH_2$, and-COOH in hydrogels enhances the interaction between adsorption sites and metal ions and promotes the removal of heavy metals from water [12]. Therefore hydrogels are applied for various fields, including industry, medical materials, biotechnology, and agriculture [13], [14]. There are many research in which scientists apply hydrogels based on chitosan, alginate, gelatin, lignin, cellulose, polyacrylic acid, and polyvinyl acetate, etc [15] - [17]. Lin synthesized hydrogels from corn starch and acrylic acid and these hydrogels could adsorb Cu^{2+} and Pb^{2+} with the capacity being 699 $mg.g^{-1}$ and 869 $mg.g^{-1}$, respectively [14]. Yang conducted research on the adsorption capacity of 3D composite hydrogels composed of graphene sheets and Fe_3O_4 nanoparticles, showing that the maximum removal ratio of Rhodamine B was 99.6% [18]. Li prepared ZnO-polyacrylic acid/cellulose fiber/polyethylene glycol hydrogel and the hydrogel had a removal efficiency for Cr(VI) being 97.22% [19].

In this study, the adsorbents based on the hydrogels composed of polyvinyl alcohol and chitosan were prepared. The glyoxal was used as a crosslinker for the hydrogels, which created chemical linkages in the three-dimensional structure of these adsorbents. The glyoxal content in the hydrogel varied by 17, 24, and 31 wt%. Langmuir and Freundlich adsorption isotherms investigated the adsorption capacity of these prepared hydrogels for Cr(VI) ion. FTIR, SEM, and UV-Vis characterized the properties of the hydrogel.

2. Materials and methods

2.1. Materials

Polyvinyl alcohol (PVA) and chitosan were purchased from Sigma Aldrich (Germany). PVA had average M_W and hydrolyzation being 125 000 $g.mol^{-1}$ and 98-99%, respectively. Chitosan had average M_W and deacetylation of 5000 $g.mol^{-1}$ and 82%, respectively. Glyoxal was supplied by Wako Chemical Industries (Japan). All other chemicals from Guangdong Guanghua Sci-Tech Company (China) were used without purification.

2.2. Preparation of PVA/chitosan hydrgels

At first, chitosan solution was prepared from distilled water, acetic acid, and chitosan. The solution was stirred overnight at room temperature to achieve good homogenization. Then, PVA was poured into hot distilled water and at 90^oC until the homogenous solution was obtained. The chitosan and PVA solution were mixed for about 1 hour. In the next step, glyoxal was added to the solution. After stirring for about 30 minutes, the solution mainly composed of glyoxal, chitosan, and PVA was put into the mold. Finally, the samples were cured at 80^oC for 1 hour to form a network structure for hydrogels. The prepared hydrogel samples with the glyoxal concentrations of 17, 24, and 31 wt% were named M-17, M-24, and M-31 respectively.

2.3. Study of adsorption isotherms

The adsorption equilibrium experiments were studied with the original concentration (C_o) of Cr(VI) solutions ranging from 10 to 38 mg/L. The hydrogel samples were put into Cr(VI) solutions; after adsorption process, the solution would reach equilibrium concentrations at 30^oC, pH 7. The agreement between the absorbance and the colored solutions calculated the equilibrium concentrations (C). Whereas the absorbance of the Cr(VI) solution was measured by UV-Vis spectrophotometer (UV/UV-NIR Horiba Dual-FL). The adsorption capacity q ($mg.g^{-1}$) and removal efficiency E (%) were determined by the following equations [17]:

$$q = \frac{(C_0 - C).V}{m} \quad (1)$$

$$E = \frac{C_0 - C}{C_0} \text{ x } 100\% \quad (2)$$

C_o and C (mg/L) were the original and equilibrium concentrations of the Cr(VI) solution, respectively. V (L) and m (g) were the volume of the Cr(VI) solution and the weight of the dried hydrogel, respectively.

Langmuir isotherm (3) and Freundlich isotherm (4) models were applied to study the adsorption process [17].

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

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

Where q_∞ ($mg.g^{-1}$) was the maximum adsorption capacity, b ($L.m^{-1}.g^{-1}$) was a Langmuir constant presented for the adsorption energy, K ($mg.g^{-1}$) was a Freundlich constant associated with the adsorption capacity of the adsorbent, and 1/n was the Freundlich coefficient relative heterogeneity.

2.4. Study of adsorption kinetics

The adsorption kinetics was studied with the pseudo-first-order and pseudo-second-order models. The pseudo-first-order (5) and pseudo-second-order (6) equations were shown by these equations [20]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1.t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{1}{q_e}.t \quad (6)$$

Where q_e (mg.g^{-1}) and q_t (mg.g^{-1}) were the adsorption capacity of the adsorbent at equilibrium and after the period, respectively; k_1 (min^{-1}) and k_2 (g.mg^{-1}.min^{-1}) were the rate constant of first-order and second-order adsorption kinetics, respectively. Both k_1 and k_2 described the adsorption rate constant and were calculated from the graph presenting adsorption kinetics [20].

For kinetic studies, 0.05 g PVA/chitosan hydrogel was prepared to adsorb Cr(VI) ions from 50 mL solution with the original concentration being 31 mg.L^{-1} at pH 7.0 and 30^{o}C.

2.5. Analytical methods

The properties of prepared hydrogels were characterized by FT-IR spectrometer (Brucker Tensor 7, German) at the Institute of Applied Materials Science, Ho Chi Minh City, Vietnam with the scan rate and speed being 4000 – 4500 cm^{-1} and 0.2 mm.s^{-1}, respectively and SEM system (Hitachi S-4800, Japan) at Research Laboratories of Saigon Hi-tech Park , Ho Chi Minh City, Vietnam. The surface area and the pore size of the hydrogel were measured by nitrogen adsorption isotherm at 77 K using an automatic adsorption equipment (Quantachrome Instruments Nova 4000E BET).

3. Results and discussion

3.1. Properties of the PVA/chitosan hydrogel

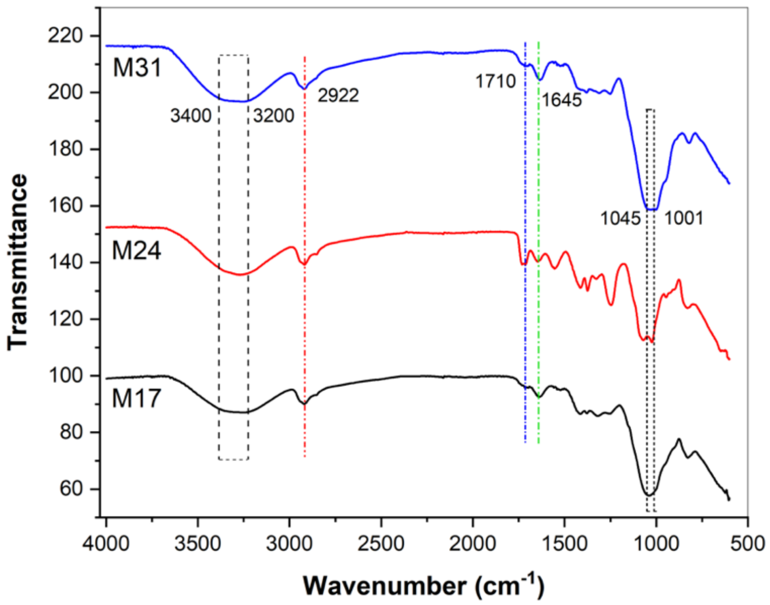

Figure 1. *The FTIR spectra of prepared hydrogel samples (M17, M24, and M31) with the glyoxal concentrations of 17, 24, and 31 wt% respectively*

To investigate the distinct properties of chitosan, PVA, and crosslinkage in the hydrogel, the FTIR spectra of PVA/chitosan hydrogels were measured and presented in Figure 1.

From the FTIR spectra, the band from 3200 to 3400 cm^{-1} indicated O-H stretching of chitosan and PVA in the hydrogels. The peaks at 2922 cm^{-1} reflected C-H stretching. The peak at 1710 cm^{-1} referred to the C=O stretching in the acetate groups of PVA associated with the hydrolyzation percentage of the PVA molecular. The peak at 1645 cm^{-1} described C=O stretching in the chitosan due to deacetylation. Additionaly, the peak around 1015-1045 cm^{-1} could be assigned for C-O stretching appearing in the cross-linkage between glyoxal and hydroxyl groups from PVA and chitosan moleculars. The FTIR spectra revealed that the three-dimensional network in the hydrogel structure was formed from the reaction between glyoxal with hydroxyl groups which origined from the PVA and chitosan moleculars.

The surface morphology of the hydrogels before and after being soaked into Cr(VI) ion solution was observed by SEM images. Besides the adsorption for Cr(VI) ions, the absorption of water also occurred providing the smoothing surface for the hydrogel. Before the adsorption process, the surface area and the pore size of the hydrogel (Figure 2a) were about 69.33 $m^2.g^{-1}$ and 3.49 nm, respectively. SEM images in Figure 2a and 2b observed these surfacing state changes.

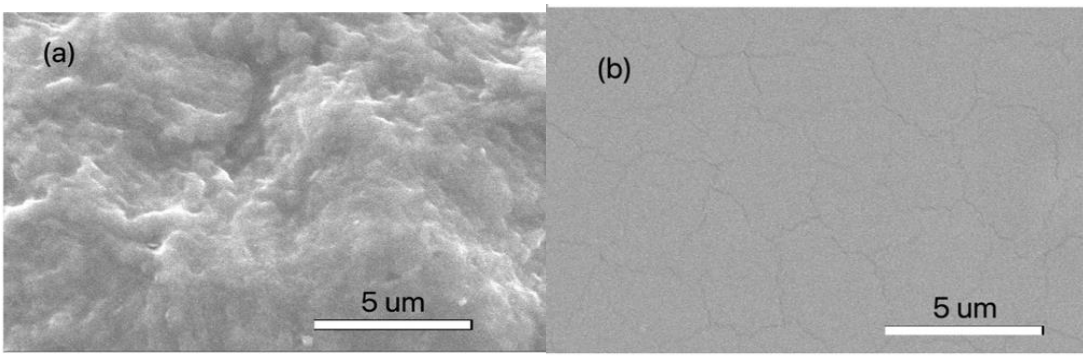

Figure 2. *SEM images of M31 sample before (a) and after (b) the adsorption process*

3.2. Study of adsorption isotherms

Langmuir and Freundlich models analyzed the equilibrium adsorption isotherms. The study was conducted to discover the adsorption mechanism on monolayer or multilayer depending on which isotherm model the data fitted. The process was applied for three samples M17, M24, and M31 at pH 7 and 30°C, showed by Figure 3 and Figure 4. The parameters of two models were showed in Table 1. The ageement between experimental data and isotherm models was evaluated by the correlation coefficients, R^2. According to Figure 3, the correlation coefficients of Langmuir models for three samples, M17, M24, and M31 were 0.993, 0.997, and 0.998, respectively, which were closer to 1 than the correlation coefficients of Freundlich models in Figure 4. Therefore, the Langmuir model described the best fit with experimental data compared to the Freundlich model. This result revealed that Cr(VI) ions adsorbed on the surface of the hydrogels by monolayer coverage, without interaction between the molecules on different sites. On the other hand, the multilayer adsorption on heterogeneous sites would occur if the experimental data obeyed the Freundlich model.

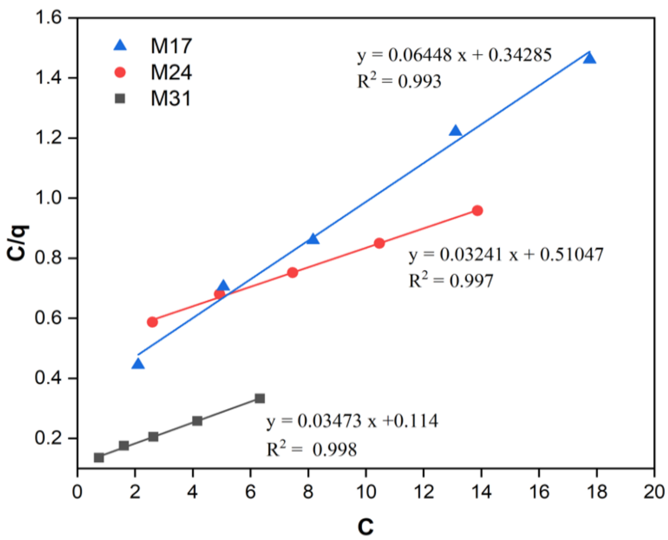

Figure 3. *Langmuir models for M17, M24, and M31 sample*

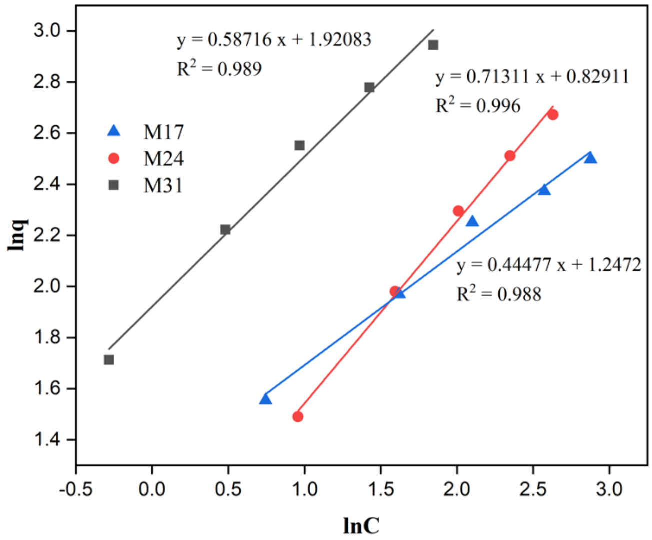

Figure 4. *Freundlich models for M17, M24, and M31 sample*

Table 1. *The parameters of Langmuir and Freundlich isotherm models*

Samples	Langmuir Isotherm			Freundlich Isotherm		
	q_∞(mg.g^{-1})	b (l.m^{-1}g^{-1})	R^2	1/n	K	R^2
M17	15.5087	0.1881	0.993	2.484	3.4806	0.988
M24	30.8547	0.0635	0.997	1.4023	2.2913	0.996
M31	28.7936	0.3047	0.998	1.7031	6.8266	0.989

3.3. Effect of glyoxal content on adsorption capacity

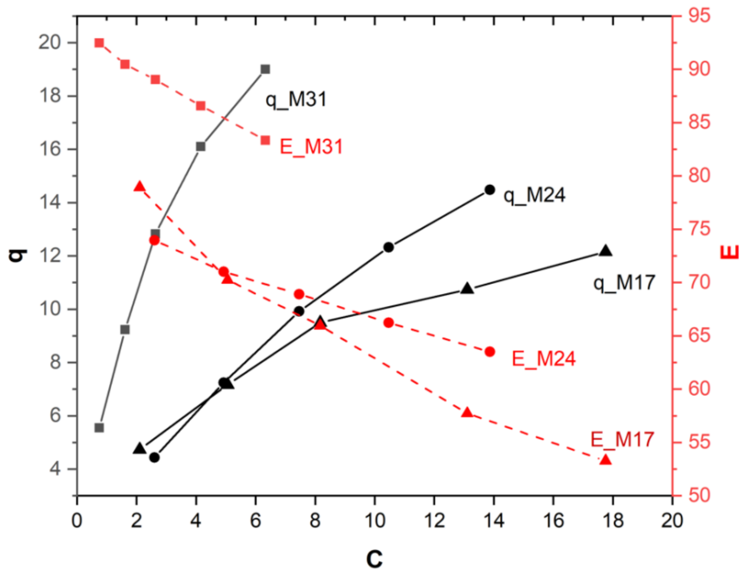

Figure 5. *The effect of glyoxal content on adsorption capacity q and removal efficiency E*

The adsorption capacity of three prepared hydrogels, M17, M24, and M31 was investigated at pH 7 and 30^{o}C. It could be seen from Figure 5, the M-31 with the 31 wt% glyoxal content had the highest value of the amount of Cr(VI) adsorption. At the equilibrium concentration about 2.1 mg.g-^{1}, the adsorption capacity of M17 and M24 samples mainly was the same. However, when the equilibrium concentration was in the range of 6 to 14 mg.g^{-1}, the adsorption capacity of the

M17 sample was consistently lower than that of the M24 sample. The adsorption capacity of three pieces increased when the equilibrium concentration increased and the highest adsorption obtained from the M31 sample.

About the removal efficiency, the M31 sample was the hydrogel which had excellent value in the range from 82 % to 92 %. Therefore, this hydrogel with 31 wt% glyoxal content that had the highest adsorption capacity and removal efficiency was a good candidate for adsorption application. With the increase of the glyoxal content, more cross-linkages were formed in the hydrogel, and more three-dimensional networks occurred in the hydrogel structure. Therefore, more Cr(IV) ions would be inserted into three-dimensional structure and was kept in the hydrogel.

3.4. Study of adsorption kinetics

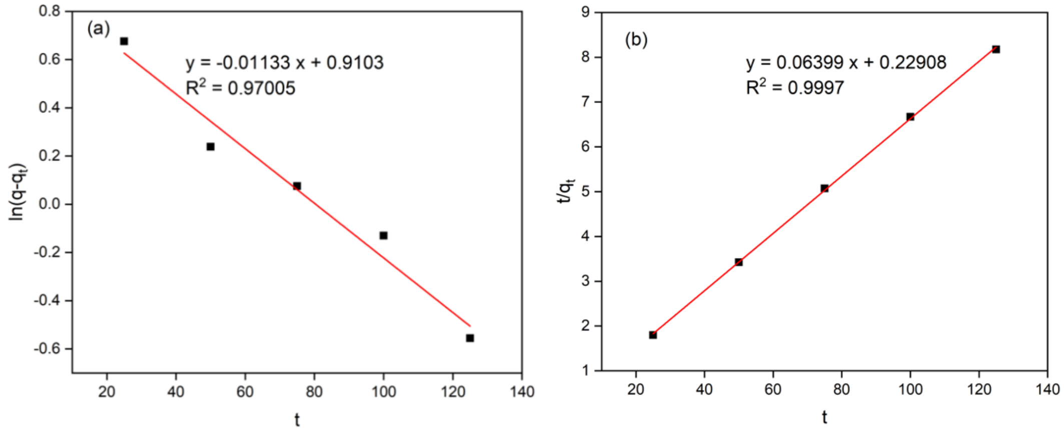

Figure 6. *The pseudo-first-order kinetic model (a) and pseudo-second-order kinetic model (b)*

For further study of the adsorption process, the adsorption of the M-31 hydrogel for Cr(VI) ions was investigated with adsorption kinetics, including the pseudo-first-order kinetic and the pseudo-second-order kinetic equations. The kinetic equations and parameters were presented in Figure 6 and Table 2, respectively. The correlation coefficients of every model reflected the fit level between experimental data and the model. The correlation coefficient of the pseudo-second-order kinetic model is greater than that of the pseudo-first-order kinetic model and closer to 1. This indicated that the pseudo-second-order kinetic model is the best fit, showing that the process was chemical adsorption. The Cr(VI) diffused from the solution to the surface of the hydrogel, then penetrated the interior and formed the chemical interaction between Cr(VI) ions and the active parts of the hydrogel. The finding was suitable with monolayer adsorption isotherms.

Table 2. *The parameters of kinetic studies*

Pseudo-first-order model			Pseudo-second-order model		
q_e	k_1 (min^{-1})	R^2	q_e	k_2 ($g.mg^{-1}.min^{-1}$)	R^2
2.4851	0.0113	0.970	15.6274	0.0178	0.999

4. Conclusion

In this study, the hydrogels were successfully synthesized from PVA, and chitosan with using a glyoxal crosslinker. The adsorption process was studied by adsorption isotherm models, pseudo-first-order kinetic model, and pseudo-second-order kinetic model. The results of the adsorption process were obtained from the experiment conducted at 30°C and pH 7. The maximum removal efficiency for adsorbing Cr(VI) ions was about 92%, contributed by the hydrogel containing 31 wt% glyoxal content. The experimental data were suitable for the Langmuir isotherm model, showing that the adsorption process formed monolayer coverage on the hydrogel surfaces. Additionally, the kinetic data fitted the pseudo-second-order kinetic model, indicating that the adsorption mechanism mainly was chemical adsorption. Consequently, the PVA/chitosan hydrogels could be applied to remove Cr(VI) ions from the aqueous solution.

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