Copen Access Full Text Article



Research Article

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



Use your smartphone to scan this QR code and download this article

Faculty of Materials Technology - Ho Chi Minh City University of Technology -Vietnam National University Ho Chi Minh City, Vietnam

Correspondence

Bui Thi Thao Nguyen, Faculty of University of Technology - Vietnam National University Ho Chi Minh City, Vietnam

Email: btnguyen@hcmut.edu.vn

History

- Received: 29-9-2023
- Accepted: 22-12-2023
- Published Online:

Check for updates

Copyright

© VNUHCM Press. This is an openaccess article distributed under the terms of the Creative Commons Attribution 4.0 International license.



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 mm 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

INTRODUCTION

Materials Technology - Ho Chi Minh City 2 Nowadays, water pollution has become an increas-3 ingly serious problem. Due to urbanization and in-4 dustrialization, the contamination of the water is get-5 ting worse. Especially, the existence of heavy metal 6 ions in wastewater endangers humans, animals, and ⁷ ecosystems¹. Heavy metal ions are metallic elements 8 and non-degradable materials. These take up the ma-9 jority of inorganic pollutants and could cause toxi-10 city at even low amounts in water. There are vari-¹¹ ous ions such as Cu^{2+} , Cr^{6+} , Cd^{2+} , Pb^{+2} , Hg^{2+} , and $_{12}$ As⁵⁺². Chromium ion is a serious pollutant released 13 from dye manufacturing, electroplating, textile indus-14 try, metal alloys manufacturing, leather tanning, dye, ¹⁵ and mining³. There are two stable forms of chrome, 16 including trivalent chrome (Cr(III)) and hexavalent 17 chrome (Cr(VI)). The hexavalent chrome form is eval-18 uated as more toxic for living organisms because of ¹⁹ its mutagenic and carcinogenic characteristics⁴. En-20 vironmental contamination by Cr(VI) has become

a worldwide issue, requiring effective approaches to 21 Cr(VI) elimination. There are various techniques to 22 treat and eliminate Cr(VI) from wastewater, such as 23 ion exchange, chemical precipitation, membrane sep-24 aration, and physicochemical methods⁵. However, ²⁵ most of the methods have high costs and low treat-26 ment efficiency. In recent years, considerable stud-27 ies have revealed that adsorption is a potential sim-28 ple method by outstanding benefits, including low en-29 ergy consumption, safety, cost saving, and nontoxicity $^{6-8}$. Therefore, the study investigated the removing 31 of Cr(VI) from aqueous solution by the adsorption. 32 Recently, there have been several researches using 33 materials from eco-friendly materials such as chi-34 tosan, cellulose, zeolite, and biocarbon for adsorb-35 ing Cr(VI)⁹. Bio-adsorbent based on chitosan/MoO3 biocomposite removed hexavalent chromium ions 37 effectively¹⁰. The activated biochar has a maxi-38 mum Cr(VI) adsorption capacity of 28.019 mg.g^{-1 11}. 39 Polyaniline/zeolite nanocomposite adsorbed Cr(VI)

Cite this article : Nguyen B T T, Giao N T Q, An N D, Tru N N. Crosslinked hydrogel based on Polyvinyl alcohol/chitosan/glyoxal for the removal of Crom(VI) ions from aqueous solution. Sci. Tech. Dev. J. -Engineering and Technology 2024; ():1-9.

⁴¹ on its surface, obeying the Freundlich isotherm¹².

⁴² Amongst adsorbents, hydrogels have become a po-⁴³ tential material for the adsorption of chromium ions.

⁴⁴ These hydrogels could be prepared from chitosan, cel-

45 lulose, and starch 13-15.

Chitosan is prepared from N-deacetylation of chitin, 46 which is the main component of the shells of shrimp, 47 crabs, and insects. Therefore, chitosan is a natural, renewable, abundant, and inexpensive adsorbent. 49 Due to polar groups, including hydroxyl group (-OH) and the amine group (-NH₂), chitosan easily inter-51 acts with contaminated metal ions in water sources 52 for ion adsorption and exchange^{16,17}. As another ad-53 sorbent, polyvinyl alcohol (PVA) is a biopolymer pos-54 sessing hydroxyl groups (-OH) which could interact with each other to create a hydrogel matrix¹⁸. More-56 over, these hydroxyl functional groups also form hy-57 drogen bonds with amine groups of chitosan, thus en-58 hancing the mechanical properties of hydrogels based 59 on PVA and chitosan. Many researchers are drawing from the advantages of the combination of PVA and 61 chitosan^{19,20}. 62 In this study, glyoxal was used as the crosslinker for 63

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(vinylalcohol), chitosan were synthesized and their prop-

⁷⁰ erties were investigated by analytical methods such

⁷¹ as FTIR, SEM, and UV-Vis, EDX. Moreover, the hy-

⁷² drogel was evaluated for Cr(VI) ion adsorption ca-

73 pacity. Langmuir and Freundlich's isotherm adsorp-

74 tion models were included in the research process to

75 study the maximum adsorption capacity of hydro-

76 gels. The kinetics were researched with the pseudo-

77 first and pseudo-second-order kinetic models.

78 MATERIALS AND METHODS

79 Materials

⁸⁰ PVA (Mw = 125,000 g.mol⁻¹, 98-99 % hydrolyzed)
⁸¹ and chitosan (Mw = 500,000 g.mol⁻¹, 82 % deacety⁸² lated) were obtained from Sigma Aldrich (Germany).
⁸³ Glyoxal was received from Wako Chemical Indus⁸⁴ tries (Japan). All other chemicals, including acid hy⁸⁵ drochloric, acetic acid, and potassium dichromate,
⁸⁶ were supplied from Guangdong Guanghua Sci-Tech
⁸⁷ Company (China).

Preparation of PVA/chitosan/glyoxal hy-drogels

90 Firstly, chitosan powder was added to a 2 wt% aque-91 ous solution of acetic acid and stirred overnight at room temperature until a homogenized solution. In 92 addition, PVA was dispersed in hot deionized water 93 and stirred at 80°C about 90 minutes to achieve a solution. A mixture of chitosan and PVA solution was 95 stirred for one hour at 60° C to form a homogeneous 96 solution. Next, slowly add glyoxal into the solution. 97 Continue stirring for one hour to homogenize the glyoxal with the solution. After that, pour the solution 99 containing glyoxal into the Petri dish and place it in 100 the oven for curing at 80°C for 90 minutes^{21–23}. 101

102

Adsorption Isotherms

The experiments of equilibrium adsorption were con- 103 ducted with the initial concentration (C_o) of Cr(VI) 104 solutions which varied in the range 10 - 50 mg, L^{-124} . 105 The hydrogel samples were weighed and sank into 106 Cr(VI) solutions which had different equilibrium 107 concentrations at room temperature (about 32°C) 108 and pH 7. In adsorption tests, the hydrogel and 109 Cr(VI) solution were put in an erlen and stirred at 110 room temperature. When the process reached the 111 equilibrium, filtration was carried out to remove the 112 samples, and the Cr(VI) solution concentrations (C) 113 were determined through the relationship between 114 the absorbance and concentration of colored solutions (ISO 18412 : 2005). The adsorption capacity q 116 $(mg.g^{-1})$ and removal efficiency E (%) were achieved 117 by the following equations⁶: 118

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

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

Where C_o and C (mg.L⁻¹) were the beginning and119equilibrium concentrations of the Cr(VI) solution, re-120spectively; V (L) was considered as the volume of the121Cr(VI) solution, and m (g) was the weight of dried ad-122sorbent hydrogel.123

The adsorption was also studied with using Langmuir (3) and Freundlich isotherm (4) models⁹. ¹²⁵ These models investigated the interaction between ¹²⁶ absorbents and Cr(VI) ions and predicted the adsorption mechanism of the adsorbent. The Langmuir ¹²⁸ isotherm model supposed that adsorbate linked on ¹²⁹ the adsorbent surfaces like monolayers, while the Freundlich isotherm model assumed that adsorbate concentrated at the surfaces like multilayers⁹. ¹³²

$$\frac{c}{q} = \frac{C}{q_{\infty}} + \frac{1}{bq_{\infty}} \tag{3}$$

$$\ln q = \frac{1}{n} \cdot \ln C + \ln K \tag{4}$$

¹³³ Where q_{∞} (mg.g⁻¹) was the maximum adsorption ¹³⁴ capacity, b (L.m⁻¹.g⁻¹) and K (mg.g⁻¹) were Lang-¹³⁵ muir and Freundlich constants respectively, relating ¹³⁶ to the adsorption energy of adsorbent material, and ¹³⁷ 1/n was the Freundlich coefficient.

¹³⁸ The dimensionless equilibrium parameter, R_{L_2} indi-

139 cating the chemical affinity between the absorbent
 140 and the absorbate, was determined as follows³:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

¹⁴¹ The values of R_L could be good when R_L was less than ¹⁴² 1.

143 Kinetic study

144 The pseudo-first-order (6) and pseudo-second-order
145 (7) models were utilized for examining the experi146 mental data and evaluating the kinetic mechanism
147 of adsorption ^{5,11}, which were described by following
148 equations

$$\ln\left(q_e - q_t\right) = \ln\left(q_e\right) - k_1 t \tag{6}$$

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

¹⁴⁹ Where q_e (mg.g⁻¹) and q_t (mg.g⁻¹) were the ad-¹⁵⁰ sorption capacity at equilibrium state and after the ¹⁵¹ period of time, respectively; k_1 (min⁻¹) and k_2 ¹⁵² (g.mg⁻¹.min⁻¹) were the rate constants of first-order ¹⁵³ and second-order adsorption, respectively.

¹⁵⁴ For kinetics, 0.05 g PVA/chitosan/glyoxal was pre ¹⁵⁵ pared to adsorb Cr(VI) ions from 50 mL solution at

¹⁵⁶ the beginning concentration of 17 mg. L^{-1} and pH 7.

157 Characterization methods

The functional groups of hydrogels were examined by 158 FT-IR/NIR instrument (PerkinElmer Frontier, Amer-159 ica). The scan rate and speed were 4000 - 4500 161 cm^{-1} and 0.2 mm/s, respectively. The morphology of hydrogels was observed by SEM system (Hitachi S-162 4800, Japan). The absorbance of Cr(VI) solution was determined by UV-Vis spectrophotometer (UV/UV-164 NIR Horiba Dual-FL, Japan) based on reading the ab-165 166 sorbance value at the wavelength of 540 nm. The ex-167 istence of chemical elements of the hydrogel was con-168 firmed by EDX (JSM-IT 200 JeOL, Japan).

169 RESULTS AND DISCUSSION

170 Characterization

171 PVA/chitosan/glyoxal hydrogel

¹⁷² To study the interaction between chitosan and PVA ¹⁷³ in the hydrogel, the FTIR spectra of PVA, chitosan, ¹⁷⁴ and PVA/chitosan/glyoxal were described in Figure 1.

of

the

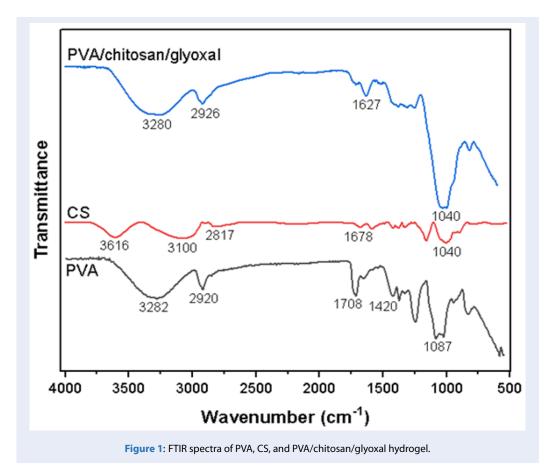
From the FTIR spectrum of PVA, the broad band at 175 3282 cm⁻¹ referred the stretch of OH groups. The 176 strong peaks appeared at 2920 cm⁻¹ and 1420 cm⁻¹ 177 reflected CH stretching and CH₂ bending respectively. The peak observed at 1708 cm⁻¹ described the 179 C=O stretching, presenting the existence of acetate 180 groups of PVA because of the hydrolyzation level of 181 the PVA. The peak showed at 1087 cm⁻¹ reflected the 182 C-O stretching in PVA ¹⁸. 183

For the FTIR spectrum of chitosan, the absorption 184 peak around 3616 cm⁻¹ could be assigned for -OH 185 stretching vibration. The absorption band around 186 3100 cm^{-1} indicated the stretching vibration of - 187 NH₂. The peak at 2817 cm⁻¹ referred to the CH₂ 188 stretching. The peak appeared at 1678 cm⁻¹ reflected 189 the stretch of C=O due to deacetylation. The absorption band around 1040 cm⁻¹ was characterized for C-O stretching²⁵. 192

In the term of PVA/chitosan/glyoxal FTIR, due to 193 the interaction of PVA and chitosan, the peak corresponding to OH stretching of chitosan and PVA 195 shifted to 3280 cm⁻¹. In addition, the peak around 196 1040 cm⁻¹ being attributed to C-O stretching increased its intensity due to appearing the crosslinkage between glyoxal and PVA. The peak obtained 199 at 1627 cm⁻¹ showed the presence of C=N group 200 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 203 chitosan, which could be considered in previous research²¹⁻²³. 205

The SEM images are presented in Figure 3, illustrating the microstructural surface of the hydrogel. The 207 SEM micrographs showed the pores of 10 – 50 mm 208 distributed across the surface. The unevenly sized 209 pores appeared with highly dense density, being created from the linkage between glyoxal and polymer 211 chains of PVA and chitosan. The micropores formed 212 a porous structure like 3D dimension space from the 213 inside to the outside of the hydrogel. The result 214 promised to provide the good water swelling ability 215 of the hydrogel. 216

EDX analysis was carried out to confirm the formation of Cr(VI) ions on the hydrogel after adsorption. 218 Figure 4a showed that Cr(VI) ions were not found on 219 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 222 could be observed by the peaks at 0.57, 5.41, and 5.95 keV in EDX spectrum. 224



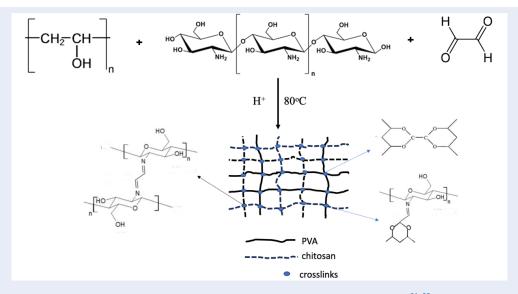


Figure 2: The schematic cross-linking mechanism of hydrogels by glyoxal^{21–23}.

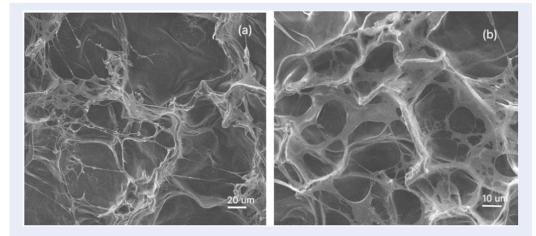


Figure 3: SEM images (a, b) of PVA/chitosan/glyoxal hydrogel with different magnification

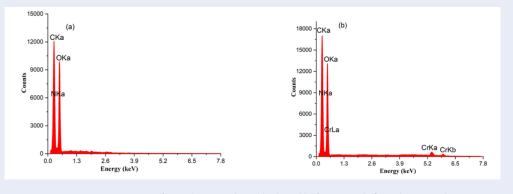


Figure 4: EDX patterns of PVA/chitosan/glyoxal hydrogel before (a) and after adsorption (b)

225 Adsorption isotherms

The equilibrium adsorption had been investigated by isotherm models, including Langmuir and Fre-227 undlich models. The equilibrium concentrations of 228 the Cr(VI) solution (C) were obtained at the equilib-229 rium state. The data was showed in Table 1 and Fig-230 ure 5. The Figure 5a presented the relationship be-231 232 tween q and C according to Langmuir model. The Figure 5b showed the relationship between lnq and 233 234 InC according to Freundlich model. According to 235 Langmuir model, the maximum adsorption capacity ²³⁶ of Cr(VI) ions $(q_{\rm Y})$ penetrated into the hydrogel were $_{237}$ derived by Langmuir model was about 344 (mg.g⁻¹). ²³⁸ The $q_{\rm F}$ for Cr(VI) on PVA/chitosan/glyoxal hydro-239 gel was compared with those of various adsorbents ²⁴⁰ from previous research (Table 2). From the Figure 5a ²⁴¹ and Figure 5b, it was found that the Langmuir curve 242 fitted the experimental parameters and the correla-²⁴³ tion coefficients (R²) of the linear graph for Lang-244 muir isotherm model were closer to 1.0 than that of Freundlich isotherm, demonstrating that Langmuir 245 model presented properly the Cr(VI) adsorption by 246 hydrogel adsorbents, illustrating the monolayer ad- 247 sorption of Cr(VI) ions on the hydrogel ^{26,27}. 248

Influence of initial concentrations and ad- 249 sorption time on the adsorption process. 250

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 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) 263

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



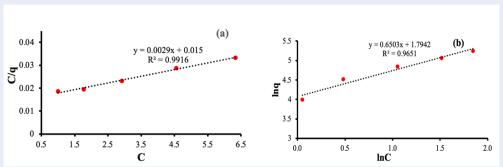


Figure 5: Adsorption isotherms of Cr(VI) on the hydrogel, Langmuir model (a), and Freundlich model (b).

and the removal efficiency was from 89.99 % to 82.35 264 %. These results revealed that the Cr(VI) ion adsorp-265 tion depended on the removing of Cr(VI) ions from 266 the solution to the surfaces of the hydrogels. With 267 increasing initial and equilibrium concentrations of 268 Cr(VI) solution, the amount of Cr(VI) ions which 269 penetrated on the surfaces of the hydrogel increased 270 to equilibrium 26 . 271

The experiment was conducted by soaking 0.05 g 272 VA/chitosan/glyoxal into 50 mL Cr(VI) ions solution with the beginning concentration of 17 mg. L^{-1} . 274 The effect of adsorption time on the adsorption pro-275 cess was observed (Figure 6b). The result showed that 276 the removal efficiency of Cr(VI) increased when the 277 experimental time increased and reached the equilib-278 rium after adsorption time attained 600 minutes. The removal efficiency was about 89 % for the initial con-280 centration of 17 mg.L⁻¹ as the adsorption reached the 281 equilibrium. 282

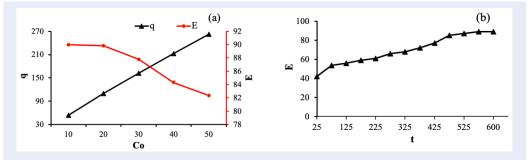
283 Kinetic models

Pseudo-first-order and pseudo-second-order kinet-284 ics were used for determining the experimental data. 285 The two models are depicted in Figure 7. The results of kinetic parameters of Cr(VI) ions adsorp-287 tion are presented in Table 3. According to the first-288 order kinetic model, the k1 constant was calculated 289 290 from the graph of $\ln(q_e-q_t)$ versus t. According to the second-order model, the k2 constant was also de-291 rived from the graph of t/q_t versus t. The R² cor-292 293 relation coefficient pseudo-second-order model was 0.9993, showing a good compatibility between experiment data and the pseudo-second-order model. ²⁹⁵ The pseudo-first-order model did not fit well with the data. The first-order kinetic was used in the case of ²⁹⁷ reversible reaction with the equilibrium state while ²⁹⁸ the second-order kinetic referred to chemical adsorption with limited rate. Cr(VI) ions adsorption on ³⁰⁰ the PVA/chitosan/hydrogel could obey the pseudosecond-order kinetic model. Therefore, it could predict that the chemical adsorption occurred between ³⁰³ Cr(VI) ions and the hydrogel ³⁰. ³⁰⁴

305

CONCLUSIONS

In the current study, the hydrogels based on PVA, 306 and chitosan were synthesized by using glyoxal 307 crosslinker. The adsorption process was investi- 308 gated by conducting a batch experimental proce- 309 dure. The parameters of adsorption isotherms were 310 achieved from the experiment of adsorbing Cr(VI) 311 from the aqueous solution, which was conducted at 312 32°C and pH 7. The maximum adsorption capac- 313 ity was obtained at about 344 mg.g⁻¹. The experimental data had good consistency with the Langmuir 315 isotherm, revealing the existence of Cr(VI) monolayer 316 on the hydrogel surfaces. Moreover, the kinetic data 317 agreed very well with the pseudo-second-order kinet- 318 ics, demonstrating that the mechanism of adsorption 319 is mainly related to chemical interactions between 320 metal cations and PVA/chitosan/glyoxal hydrogels. In 321 conclusion, the hydrogels can be used for the application relating to removing Cr(VI) ions from aqueous 323 solution. 324



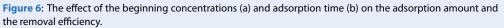


Table 2: Maximum adsorption capacity of cr(vi) on PVA/chitosan/glyoxal and other adsorbents

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	294	1-50	13
dots/nanocellulose/chitosan			
Activated carbon	28	10-50	11
Chitosan@MoO3	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, k_1 and k_2 were first-order and second-order rate constants, R^2 was correlation coefficient.

Pseudo-first-order model		Pseudo-second-order model		
$k_1 \text{ (min}^{-1}\text{)}$	R ²	$k_2 (g.mg^{-1}.min^{-1})$	R ²	
0.0129	0.7555	0.0016	0.9993	

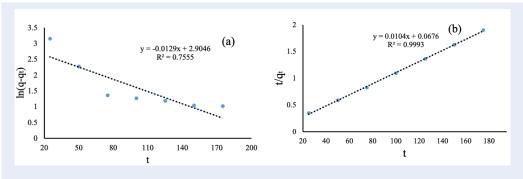


Figure 7: Kinetic studies for pseudo-first-order adsorption (a), and pseudo-second-order adsorption (b).

325 ACKNOWLEDGEMENTS

326 We acknowledge Ho Chi Minh City University of

327 Technology (HCMUT), VNU-HCM for supporting 328 this study.

329 CONFLICT OF INTEREST

³³⁰ The authors have no conflict of interest to declare.

AUTHORS' CONTRIBUTIONS

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

336 REFERENCES

- 1. Shivam , Megha R, Lakhani V, Vala S, Dharaskar S, Reddy Palu-
- vai N et al. Removal of heavy metals and dyes from its aqueous
 solution utilizing metal organic Frameworks (MOFs): review.
 Mater Today Proc. 2023;77:188-200;Available from: https://
 doi.org/10.1016/i.matpr.2022.11.193.
- Hosny NM, Gomaa I, Elmahgary MG. Adsorption of polluted dyes from water by transition metal oxides: a review. Appl Surf Sci Adv. 2023;15:100395;Available from: https://doi.org/ 10.1016/i.apsadv.2023.100395.
- Ya V, Martin N, Chou Y, Chen Y, Choo K, Chen S et al. Electrochemical treatment for simultaneous removal of heavy metals and organics from surface finishing wastewater using sacrificial iron anode. J Taiwan Inst Chem Eng. 2018;83:107-14:Available from: https://doi.org/10.1016/i.itice.2017.12.004.
- 4. Shih Y-J, Hsieh H-L, Hsu C-H. Electrochemical Fe(III) me-
- diation for reducing hexavalent chromium Cr(VI) on templated copper-nickel foam electrode. J Cleaner Prod. 2023;384:135596;Available from: https://doi.org/10.1016/j.
- 355 jclepro.2022.135596.
- Alyüz B, Veli S. Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins. J Hazard Mater. 2009;167(1-3):482-8;PMID: 19201087.
- Available from: https://doi.org/10.1016/j.jhazmat.2009.01.006.
- 6. Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal
- S, Tkachev AG et al. Adsorption of heavy metals on conven tional and nanostructured materials for wastewater treatment
 purposes: a review. Ecotoxicol Environ Saf. 2018;148:702 12;PMID: 29174989. Available from: https://doi.org/10.1016/
- 365 j.ecoenv.2017.11.034.
- Chai WS, Cheun JY, Kumar PS, Mubashir M, Majeed Z, Banat F et al. A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application.
 J Cleaner Prod. 2021;296:126589;Available from: https://doi.
- J Cleaner Prod. 2021;296:126589;Ava org/10.1016/j.jclepro.2021.126589.
- Jadoun S, Fuentes JP, Urbano BF, Yáñez J. A review on adsorption of heavy metals from wastewater using conducting polymer-based materials. J Environ Chem Eng. 2023;11(1):109226;Available from: https://doi.org/10.1016/j. jece.2022.109226.
- Morais da Silva PM, Camparotto NG, Grego Lira KT, Franco Picone CS, Prediger P. Adsorptive removal of basic dye onto sustainable chitosan beads: equilibrium, kinetics, stability, continuous-mode adsorption and mechanism. Sustain Chem Pharm. 2020;18:100318;Available from: https://doi.org/ 10.1016/j.scp.2020.100318.
- Taha AA, Kandil S, Mohamed LA, Sallam MG, Heiba HF. Surface investigations of selective biosorption and reduction of hexavalent chromium ions Cr(VI) over chitosan@MoO3 and chitosan-cellulose@MoO3 biocomposite. J Mol Struct.
 2023;1288:135716;Available from: https://doi.org/10.1016/j.
- 387 molstruc.2023.135716.

- Acharya J, Sahu JN, Sahoo BK, Mohanty CR, Meikap BC. Removal of chromium(VI) from wastewater by activated carbon developed from Tamarind wood activated with zinc chloride.
 Chem Eng J. 2009;150(1):25-39;Available from: https://doi.org/ 10.1016/j.cej.2008.11.035.
- Shyaa AA, Hasan OA, Abbas AM. Synthesis and characterization of polyaniline/zeolite nanocomposite for the removal of chromium(VI) from aqueous solution. J Saudi Chem Soc. 2015;19(1):101-7;Available from: https://doi.org/10.1016/j.jscs. 2012.01.001.
- Chen X, Song Z, Yuan B, Li X, Li S, Thang Nguyen T et al. Fluorescent carbon dots crosslinked cellulose Nanofibril/chitosan interpenetrating hydrogel system for sensitive detection and efficient adsorption of Cu (II) and Cr (VI). Chem Eng J. 2022;430:133154;Available from: https://doi.org/10.1016/j. 402 cej.2021.133154.
- Solis-Ceballos A, Roy R, Golsztajn A, Tavares JR, Dumont M-J. Selective adsorption of Cr(III) over Cr(VI) by 405 starch-graft-itaconic acid hydrogels. J Hazard Mater Adv. 406 2023;10:100255;Available from: https://doi.org/10.1016/j. 407 hazadv.2023.100255. 408
- Luo Q, Huang X, Luo Y, Yuan H, Ren T, Li X et al. Fluorescent chitosan-based hydrogel incorporating titanate and cellulose nanofibers modified with carbon dots for adsorption and de-tection of Cr(VI). Chem Eng J. 2021;407:127050;Available from: https://doi.org/10.1016/j.cej.2020.127050. 413
- Gkika DA, Mitropoulos AC, Kokkinos P, Lambropoulou 414
 DA, Kalavrouziotis IK, Bikiaris DN et al. Modified 415
 chitosan adsorbents in pharmaceutical simulated 416
 wastewaters: a review of the last updates. Carbohydr 417
 Polym Technol Appl. 2023;5:100313;Available from: 418
 https://doi.org/10.1016/j.carpta.2023.100313. 419
- Karimi-Maleh H, Ayati A, Davoodi R, Tanhaei B, Karimi F, Malekmohammadi S et al. Recent advances in using of chitosanbased adsorbents for removal of pharmaceutical contaminants: a review. J Cleaner Prod. 2021;291:125880;Available from: https://doi.org/10.1016/j.jclepro.2021.125880.
- Nambiar AP, Pillai R, Vadikkeettil Y, Sanyal M, Shrivastav 425 PS. Glutaraldehyde-crosslinked poly(vinyl alcohol)/halloysite 426 composite films as adsorbent for methylene blue in water. 427 Mater Chem Phys. 2022;291:126752;Available from: https:// 428 doi.org/10.1016/j.matchemphys.2022.126752. 429
- Perez-Calderon J, Marin-Silva DA, Zaritzky N, Pinotti A. Ecofriendly PVA-chitosan adsorbent films for the removal of azo dye Acid Orange 7: physical cross-linking, adsorption process, and reuse of the material. Adv Ind Eng Polym Res. 2023;6(3):239-54;Available from: https://doi.org/10.1016/ j.aiepr.2022.12.001.
- Zhang KY, Li D, Wang Y, Wang LJ. Carboxymethyl chitosan/polyvinyl alcohol double network hydrogels prepared by freeze-thawing and calcium chloride crosslinking for efficient dye adsorption. Int J Biol Macromol. 439 2023;253(3):126897;PMID: 37709214. Available from: 440 https://doi.org/10.1016/j.ijbiomac.2023.126897. 441
- Agha HM, Abdulhameed AS, Jawad AH, Sidik NJ, Aazmi S, 442 ALOthman ZA et al. Physicochemical fabrication of chitosan and algae with crosslinking glyoxal for cationic dye removal: 444 insight into optimization, kinetics, isotherms, and adsorption 445 mechanism. Int J Biol Macromol. 2023;253(5):127112;PMID: 446 377774818. Available from: https://doi.org/10.1016/j.ijbiomac. 447 2023.127112.
- Wang L, Stegemann JP. Glyoxal crosslinking of cell-seeded 449 chitosan/collagen hydrogels for bone regeneration. Acta Biomater. 2011;7(6):2410-7;PMID: 21345389. Available from: 451 https://doi.org/10.1016/j.actbio.2011.02.029. 452
- Cheng M, Kong R, Zhang R, Wang X, Wang J, Chen M. 453 Effect of glyoxal concentration on the properties of corn starch/poly(vinyl alcohol)/carvacrol nanoemulsion active 455 films. Ind Crops Prod. 2021;171:113864;Available from: 456 https://doi.org/10.1016/j.indcrop.2021.113864. 457
- 24. Arslan H, Eskikaya O, Bilici Z, Dizge N, Balakrishnan D. 458

- 459 Comparison of Cr(VI) adsorption and photocatalytic re-
- duction efficiency using leonardite powder. Chemosphere. 460
- 2022;300:134492;PMID: 35398064. Available from: https://doi. 461 org/10.1016/j.chemosphere.2022.134492.
- 462 463 25
- Wang Q, Zuo W, Tian Y, Kong L, Cai G, Zhang H et al. An 464
- ultralight and flexible nanofibrillated cellulose/chitosan aerogel for efficient chromium removal: adsorption-465 reduction process and mechanism. Chemosphere. 466 467 2023;329:138622;PMID: 37037357. Available from: https://doi.org/10.1016/j.chemosphere.2023.138622. 468
- 469 26. Pourmortazavi SM, Sahebi H, Zandavar H, Mirsadeghi S. Fab-
- rication of Fe3O4 nanoparticles coated by extracted shrimp 470
- 471 peels chitosan as sustainable adsorbents for removal of 472 chromium contaminates from wastewater: the design of ex-
- periment. Compos B Eng. 2019;175:107130;Available from: 473
- https://doi.org/10.1016/j.compositesb.2019.107130. 474
- Sathiyaseelan A, Vishven Naveen K, Zhang X, Han K, Wang M-475 27.
- 476 H. Research progress on chitosan-zinc oxide nanocomposites 477 fabrication, characterization, biomedical and environmental applications. Coord Chem Rev. 2023;496:215398;Available 478
- from: https://doi.org/10.1016/j.ccr.2023.215398. 479
- Sun Y, Liu X, Lv X, Wang T, Xue B. Synthesis of novel 480 28 481 lignosulfonate-modified graphene hydrogel for ultrahigh adsorption capacity of Cr(VI) from wastewater. J Cleaner 482 483 Prod. 2021;295:126406;Available from: https://doi.org/10.
- 1016/j.jclepro.2021.126406. 484
- 485 29. Kwak HW, Lee H, Lee KH. Surface-modified spherical lignin particles with superior Cr(VI) removal efficiency. Chemo-486 sphere. 2020;239:124733;PMID: 31526991. Available from: 487 https://doi.org/10.1016/j.chemosphere.2019.124733. 488
- Liu K, Zhu B, Feng Q, Wang Q, Duan T, Ou L et al. Ad-489 30. sorption of Cu(II) ions from aqueous solutions on modified 490
- chrysotile: thermodynamic and kinetic studies. Appl Clay 491 Sci. 2013;80-81:38-45;Available from: https://doi.org/10.1016/
- 492 493 j.clay.2013.05.014.

Open Access Full Text Article

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

Bùi Thị Thảo Nguyên^{*}, Nguyễn Thị Quỳnh Giao, Nguyễn Đức An, Nguyễn Nhị Trự



Use your smartphone to scan this QR code and download this article

Khoa Công nghệ Vật liệu - Trường Đại học Bách khoa Tp. HCM - Đại học Quốc gia Thành phố Hồ Chí Minh, Việt Nam

Liên hệ

Bùi Thị Thảo Nguyên, Khoa Công nghệ Vật liệu - Trường Đại học Bách khoa Tp. HCM -Đại học Quốc gia Thành phố Hồ Chí Minh, Việt Nam

Email: btnguyen@hcmut.edu.vn

Lịch sử

• Ngày nhận: 29-9-2023

• Ngày chấp nhận: 22-12-2023

Ngày đăng:

DOI:



Bản quyền

© ĐHQG Tp.HCM. Đây là bài báo công bố mở được phát hành theo các điều khoản của the Creative Commons Attribution 4.0 International license.



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(VĪ) 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 – 50mm 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 đinh sư có mặt của đơn lớp ion Cr(VI) trên hydrogel và sư 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