### CHEMICALLY CROSSLINKED CELLULOSE-BASED HYDROGEL PREPARED FROM RICE STRAW FOR THE REMOVAL OF AQUEOUS HEXAVALENT CHROMIUM ION FROM WASTEWATER

### TRANG THI CAM TRUONG,<sup>\*</sup> VO VAN BAM,<sup>\*</sup> ANH PHUONG LE THI,<sup>\*\*</sup> NGAN THI THU PHAN,<sup>\*\*</sup> TAKAOMI KOBAYASHI,<sup>\*\*</sup> DUONG THI THUY NGA<sup>\*\*\*</sup> and KHOA DANG NGUYEN<sup>\*\*\*\*</sup>

\*Faculty of Environment, University of Science, Vietnam National University Ho Chi Minh City, Campus 1, 227 Nguyen Van Cu Std., Ward 4, District 5, Ho Chi Minh City, Vietnam

\*\*Department of Science of Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan

\*\*\* Ho Chi Minh City University of Natural Resources and Environment, 236B Le Van Sy Street, Tan Binh District, Ho Chi Minh City 70000, Vietnam

\*\*\*\* Faculty of Environment, Van Lang University, Ho Chi Minh City 70000, Vietnam © Corresponding author: Khoa Dang Nguyen, khoa.nd@vlu.edu.vn

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In this study, cellulose was chemically extracted from rice straw, which is one of the richest sources of agro-waste. Then, this purified cellulose was co-polymerized by the addition of acrylic acid and ammonium persulfate in the presence of N,N-methylenebisacrylamide as crosslinker to form a cellulose-based hydrogel for the removal of hexavalent chromium (Cr(VI)) from wastewater. Here, the impact of various parameters, such as pH, contact time, material dosage, and initial solution concentration, on the adsorption capacity of the hydrogel for Cr(VI) ions is systematically investigated. The experimental findings revealed that the highest adsorption capacity for the treatment of Cr(VI)-containing water reached 1.1 mg Cr(VI)/g at pH 1, contact time of 120 min, and the initial concentration in the aqueous solution of 10 mg/L for an applied adsorbent dosage of 0.2 g. In addition, the equilibrium adsorption data agreed well with the Langmuir isotherm and the maximum adsorption amount was 4.14 mg Cr(VI)/g. Additionally, this material demonstrated good reusability, supporting the notion that it can be efficiently regenerated for multiple uses, a crucial factor for its practical application towards reducing the environmental impact and increasing its economic value.

Keywords: rice straw, cellulose, hydrogel, adsorption, chromium

### INTRODUCTION

Numerous industrial activities, including metal smelting, combustion of fossil fuels, and agricultural pesticide production, pose a significant risk to environmental integrity. The discharge of chemicals and waste from these processes has the potential to contaminate groundwater, emphasizing the critical need for environmental stewardship and sustainable practices within these sectors.<sup>1</sup> In tandem with industrial development, environmental issues have risen to prominence globally. Notably, water pollution, attributed to the presence of heavy metals, has become a pressing concern. Hexavalent chromium (Cr(VI)), recognized as a toxic and carcinogenic heavy metal, is discharged into the environment by various industries, including chrome plating, textile dyeing, and

leather tanning. Addressing the challenges posed by such contaminants is imperative for ensuring environmental sustainability and public health.<sup>2,3</sup> Cr(VI) ion existing in water sources can cause a lot of diseases based on serious toxic effects, including cancer, brain damage or death, when the contamination damages our bodies,<sup>3,4</sup> which is much more toxic than Cr(III).<sup>5</sup> Therefore, it is imperative to treat Cr(VI)-containing wasterwater before release into external sources.

In response to this challenge, the adsorption process has emerged as a compelling and straightforward technique, garnering significant attention. This method offers promise for effectively removing heavy metal ions from wastewater, contributing to the ongoing efforts for water quality preservation and environmental protection.<sup>6</sup> Hence, the development of efficient adsorbents from waste materials is viewed as an economic approach with the potential to significantly reduce environmental pollution.

Vietnam has been known as the second largest exporter of rice globally.7 The economic significance of developing adsorbents from agricultural waste is undeniable. However, a substantial volume of agricultural waste, notably rice straw (RS), poses a significant environmental problem. Reports indicate that approximately onethird of RS is openly burned in fields, leading to a substantial emission of carbon dioxide into the atmosphere. This practice contributes to the greenhouse gas effect, heightened posing environmental challenges that need urgent attention.<sup>8,9</sup> Therefore, the recycling of RS for specific and impactful purposes is crucial to minimize environmental pollution. This is particularly significant within the domain of modern chemical technology, where repurposing agricultural waste can contribute substantially to sustainable practices and environmental conservation.10

Cellulose, a pivotal biopolymer in plants, plays a vital role in various applications and has been discovered to constitute approximately 35-40% of the chemical composition of RS.<sup>11</sup> This benign material is well-known in various fields owing to its biocompatibility, biodegradation, and friendliness.12 especially environmental Moreover, cellulose-based adsorbents are recognized as promising candidates for the adsorption process. This is attributed to the presence of hydroxyl groups in their chemical structure, which significantly enhances the removal efficiency of heavy metal ions in aqueous solutions<sup>13</sup> (Fig. 1). However, it was observed that recovering cellulose-based adsorbents after the removal process was challenging because of their fibrous shape, limiting their potential application.

To address this issue, cellulose-based hydrogels have been prepared. Leveraging the hydrophilic structure inherent in polymeric materials, hydrogels exhibit the capability to retain large amounts of water within their threedimensional network. This modification aims to enhance the recoverability and practical application of cellulose-based materials in the adsorption process. With the hydrophilic structure of polymeric materials, a hydrogel is capable of holding large amounts of water in its threedimensional network,<sup>14</sup> which easily lowers the concentration of heavy metal ions in the aqueous solution. Biopolymer-based hydrogels prove exceptionally effective in water treatment, primarily due to the high affinity between the biopolymer chains and water molecules. This affinity translates into enhanced capability for efficiently lowering the concentration of heavy metal ions in aqueous solutions, highlighting the significant advantages these hydrogels offer in the realm of water purification.<sup>15</sup>

In the preparation of hydrogels, the copolymer method has been reported to enhance the gelation. This method is preferred due to its simplicity and effectiveness, which enhances the elasticity and reduces the solubility of the polymer in the solvent.<sup>16</sup> A cellulose-based hydrogel using acrylic acid (AA), in the presence of N,Nmethylenebisacrylamide as crosslinker, was successfully prepared and applied for dye adsorption from wastewater.<sup>17</sup> In this method, the persulfate initiator undergoes decomposition under heating, generating sulfate anion radicals. These radicals extract hydrogen from the hydroxyl groups of cellulose, initiating radicals on the polysaccharide chains. This persulfatecellulose redox system creates active centers on the substrate, facilitating radical initiation within Consequently, the the system. resulting copolymer is characterized by a crosslinking structure.<sup>18-20</sup> Thus, this facile preparation has been selected for the synthesis of the cellulosebased hydrogel in the present work.

In this study, cellulose was chemically extracted from RS and then a hydrogel was synthesized via the copolymerization treatment for the removal of aqueous Cr(VI) ion from wastewater. The conducted adsorption experiment systematically explored the effects of various conditions, including pH dependence, contact time, adsorbent dosage, and initial concentration. Furthermore, the research was extended to assessing the regeneration of the adsorbent, evaluating its potential for reusability. This multifaceted approach not only contributes to mitigating environmental pollution, but also taps into the economic potential of the adsorbent. By effectively transforming abundant agricultural waste into a valuable hydrogel material, the study addressed a sustainable solution for adsorbing heavy metal ions from aqueous solutions for environmental concerns.



Figure 1: Chemical structure of cellulose (a), acrylic acid (b), *N*,*N*-methylenebisacrylamide (c) and ammonium persulfate (d)

### EXPERIMENTAL

### Material

Rice straw (RS) was collected in Dong Thap Province, Vietnam. Ethanol ( $C_2H_5OH$ ), nitric acid (HNO<sub>3</sub>), acrylic acid (AA), ammonium persulfate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (APS), *N*,*N*-methylenebisacrylamide (MBA) – Figure 1, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Xilong Chemical Reagent Company, China. Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) was received from Merck, Germany. All chemicals used for the extraction of cellulose, the preparation of the hydrogel, and the adsorption experiment of Cr(VI) ion were analytical grade.

### Methods

#### Extraction of cellulose from rice straw

The cellulose isolation process was performed according to the procedure described in a previous study.<sup>21</sup> Rice straw (RS) was washed in distilled water sevaral times to remove impurities and dried at 60 °C for 5 h. After that, about 10 g of the dried RS was soaked in 200 mL of 0.5 M NaOH aqueous solution for 24 h to remove lignin and hemicelluloses. Next, the alkalized-treated RS was immersed and refluxed with a mixture of ethanol:HNO<sub>3</sub> (4:1 (vol%)) for 3 h. Notably, the chemical reagents were changed every 1 h. The refluxed RS was then filtered and washed with distilled water until neutral pH was reached, followed by drying at 50 °C for 3 h. After this step, the extracted cellulose was obtained. The purification process of cellulose from RS is illustrated in Figure 2 (a).

The yield of the extracted cellulose (RSC) was calculated by the equation below:

Yield (%) = 
$$(m_0 - m) \times 100/m_0$$
 (1)

where  $m_0$  (g) is the initial amount of RS and m (g) is the dry weight of RSC after the chemical treatment.

The preparation of the cellulose-based hydrogel was performed according to a similar method to that of Trang *et al.*<sup>17</sup> 1 g of cellulose was immersed in 100 mL of distilled water and stirred at 90 °C for 90 min. After that, 8 mL of the suspended solution was taken out, followed by adding 1.6 mL of AA, 1 g of APS and 0.2 g of MBA. This mixture was stirred at 60 °C for 2 h until a homogeneous solution was obtained. Then, this mixture was left to rest at 60 °C for the copolymerization process. After 5 h, the chemically crosslinked cellulose-based hydrogel (CH) was formed. The prepared CH was washed with distilled water and dried at 60 °C for 24 h prior to measurements. The preparation procedure of the cellulose-based hydrogel is presented in Figure 2 (b).

### Characterization of extracted cellulose and cellulosebased hydrogel

Fourier-transform infrared spectroscopy (FT-IR) spectra of dried RS, RSC and CH were recorded using a JASCO FT-IR/4100 spectrometer. The samples were prepared by grinding with potassium bromide (KBr) in the absorbance mode, covering a wavelength range from 4500 to 400 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup>. This analytical approach provides insights into the molecular structure and functional groups present in the samples.

Scanning electron microscopy (SEM) was employed to investigate the surface and cross-sectional morphology of the prepared CH. Sample preparation involved fracturing the samples in liquid nitrogen, followed by a 24-hour freeze-drying process. Subsequently, a conductive layer was formed through gold sputtering, and the analysis was conducted using the JSM-5300LV instrument from JEOL, Japan.

The values of water content (WC) of the CH were measured at room temperature by immersing  $20 \text{ mm} \times 20 \text{ mm}$  strips of the dry samples in distilled water.

After the given soaking period, the hydrogel was removed and quickly wiped with tissue paper and finally weighed. The value of WC was calculated for each sample using the equation:

WC (%) = 
$$\frac{(m - m_0)}{m_0} \times 100$$
 (2)

where  $m_0$  is the dry weight, and m is the weight of the samples after immersing in distilled water.

## Adsorption studies of Cr (VI) ion *Effect of pH condition*

The experiment focused on assessing the influence of pH on the adsorption process within a pH range spanning from 1 to 6. Utilizing 0.2 g of cellulose-based hydrogel (CH) as adsorbent, it was immersed into a container containing 25 mL of Cr(VI) solution with a concentration of 10 mg/L. The experimental conditions included agitation at 180 rpm and a temperature of 25 °C, sustained over a period of 120 min.

### Effect of contact time

In this study, the adsorption capacity of the material was scrutinized in relation to contact time. The investigation spanned over a range from 30 to 180 min, employing agitation at 180 rpm and maintaining a temperature of 25 °C. The initial concentration of Cr(VI) ions was set at 10 mg/L with a pH of 1, utilizing 0.2 g of adsorbent mass.

### Effect of adsorbent dose

In order to determine the optimal adsorption conditions, the study investigated the effect of material dosage. The experiment involved varying the amount of CH from 0.05 to 0.3 g and agitating it for 120 min at 25 °C, using a Cr(VI) solution of 10 mg/L, at pH 1 within 120 min.

### Effect of initial concentration

The maximum absorption capacity of the material is highly dependent on the initial concentration of the contaminant solution. In this study, the input concentrations of Cr(VI) solutions were varied from 5 to 50 mg/L, while the solution pH remained at 1 and the adsorbent dose was kept at 0.2 g. After shaking within 120 min at 25 °C, the suspensions with CH were filtered using a 0.45- $\mu$ m membrane filter. The residual metal ion was analyzed using an atomic absorption spectrophotometer (AAS Shimadzu Co. Ltd., Japan). The removal efficiency H (%) of the CH was determined by Equation 3:

The removal percentage (H %) was:

$$H(\%) = \frac{C_0 - C_t}{C_0} \times 100$$
(3)

where H is the removal capacity of Cr(VI) ion adsorbed (%), C<sub>o</sub> and C<sub>t</sub> are the concentrations of Cr(VI) ion in the solution (mg/L) at the initial time and at time t, respectively. Adsorption capacity at any time  $q_t$  (mg/g) and the adsorption capacity at equilibrium  $q_e$  (mg/g) were determined using Equation 4:

$$q_{t,e} = \frac{(C_o - C_{t,e}) \times V}{M}$$
(4)

where  $C_o$  and  $C_t$  (mg/L) are the concentrations of the solution at the initial time and at time t (h), respectively;  $C_e$  (mg/L) is the equilibrium concentration of Cr(VI) aqueous solution; V (L) is the volume of the contaminated solution and m (g) is the weight of the dried adsorbent.



Figure 2: Procedure of cellulose extraction (a) and preparation of the cellulose-based hydrogel (b)

## Desorption and reusability of the cellulose-based hydrogel

For the desorption process, 0.2 g of Cr(VI)adsorbed CH was immersed in 20 mL of 0.1M HCl aqueous solution for 24 h at 25 °C. Following that, the CH was filtered through a 0.45- $\mu$ m membrane filter and dried at 60 °C before assessing its regeneration performance. The concentration of desorbed metal ions was determined in the filtrate using AAS and the percentage of metal ions desorbed was determined by the following equation:<sup>22</sup>

% Desorption = 
$$\frac{C_D \times V_D}{q_e \times m_D}$$
 (5)

where  $C_D$  (mg/L) is the concentration of metal ion in the desorbed solution,  $V_D$  (L) is the volume of desorbed solution,  $m_D$  (g) is the mass of adsorbent used for desorption studies and  $q_e$  (mg/g) is the adsorption capacity of the adsorbent for Cr(VI) ions.

In the reusability experiment, 0.2 g of the desorbed CH were placed in 25 mL of 10 mg/L of Cr(VI) aqueous solution, which was adjusted to pH 1 and stirred at 180 rpm at room temperature. After 120 min, the CH was removed and the remaining concentration of the Cr(VI) aqueous solution was measured by an atomic absorption spectrophotometer (AAS, Shimadzu Co. Ltd., Japan). After each adsorption test, the material was repeatedly desorbed within 24 h at 25 °C. The removal efficiency of the CH adsorbent was consecutively conducted to determine the reusability and enhance the practical app<u>lication</u>.

### **RESULTS AND DISCUSSION**

# Appearance of cellulose extracted from rice straw and cellulose-based hydrogel

Extraction of cellulose from rice straw

The appearance of purified cellulose from RS is depicted in Figure 3 (a). Initially, RS exhibits a yellowish color. After undergoing chemical treatment with alkaline and acidic aqueous solutions, the extracted RSC is purified, resulting in an ivory-white color. This change is attributed to the removal of lignin and hemicellulose content. The yield achieved, approximately 35%, aligns with findings reported in the literature.

### Preparation of cellulose-based hydrogel

As seen in Figure 3 (b), the prepared cellulosebased hydrogel (CH) was well-formed after chemical crosslinking with MBA. To enhance the contact area, the size of the obtained CH was reduced to about 1 mm  $\times$  3 mm pieces and the material turned slightly yellowish after the drying process.



Figure 3: Appearance of (a) rice straw (RS) and extracted cellulose (RSC), and (b) the prepared cellulose-based hydrogel (CH) from original form to a dried state



Figure 4: FT-IR spectra of (a) RS and RSC, and (b) the prepared cellulose-based hydrogel

# Characterization of cellulose-based hydrogel *FT-IR spectroscopy*

The FT-IR spectra of RS and RSC are presented in Figure 4 (a). Notably, the absorption bands at 1430 and 1370 cm<sup>-1</sup>, associated with C=O in the chemical structure of lignin, exhibited a significant decrease in intensity after the chemical treatment during cellulose isolation. Additionally, the band at 1160 cm<sup>-1</sup>, indicative of arabinoxylans and assigned to hemicelluloses, displayed a similar trend, suggesting a reduction post-treatment. The enhanced intensity of the absorption band at 1605 cm<sup>-1</sup>, related to O-H stretching of free water molecules, indicated the increased hydrophilicity of the prepared cellulose. Moreover, the hydroxyl group intensity at 3400 cm<sup>-1</sup> was higher than that in the raw RS, implying reduction in lignin and hemicellulose а components through the pre-treatment process. In the case of the crosslinked cellulose-based hydrogel (CH), the FT-IR spectrum is displayed in Figure 4 (b). The polymerization process combined the functional groups of C=C stretching and C=O stretching at absorption bands of 1402 cm<sup>-1</sup> and 1725 cm<sup>-1</sup>, respectively, corresponding to AA. The N-H stretching band of MBA appeared in the 3500 cm<sup>-1</sup> region for the (N-H-C=O) group stretching vibration. A strong absorption band at 3200 cm<sup>-1</sup> was attributed to -

OH in –COOH, and an absorption band at 1174 cm<sup>-1</sup> representing C–O–C.<sup>23</sup> The presence of these functional groups in the IR spectra indicated the successful preparation of the hydrogel after the copolymerization process. The analysis of the spectra provides insights into the chemical changes occurring during the RS-to-RSC transformation and the subsequent development of the cellulose-based hydrogel.

### Morphological observation

Figure 5 (left) illustrates the surface of the CH, presenting a relatively tight and dense structure. The inclusion of MBA as a cross-linker played a crucial role in promoting additional junctions and pores during co-polymerization, contributing to the compact surface of the prepared CH. In Figure 5 (right), the cross-sectional view of the CH reveals a rougher internal structure prepared from RSC. The resulting CH exhibits a more porous configuration, offering increased active binding sites relative to the surface area. This porous structure enhanced the effective adsorption capacity for heavy metal ions in aqueous solutions. The combination of tight surface morphology and porous internal structure recommends the CH as a promising adsorbent for efficient metal ion removal.



Figure 5: SEM images of the surface (left) and cross-section (right) of the cellulose-based hydrogel at the magnification of 1000×



Figure 6: Water content of the cellulose-based hydrogel

### Water absorption experiment

### *Hydrophilic property*

The water content (WC) is a vital physical property of hydrogel materials, indicative of their liquid absorption capacity. A higher WC value signifies enhanced durability in aqueous solutions and increased adsorption capacity. The results depicted in Figure 6 showcase the favorable water content of the formed hydrogel, registering at an impressive 115% within 8 h. It is noteworthy that cellulose-based hydrogels are recognized for their ability to retain substantial water amounts within their three-dimensional structure, owing to the strong affinity between water molecules and previously.<sup>24</sup> cellulose chains, as reported Although the CH in this study underwent chemical crosslinking, potentially leading to a lower WC value, it remained robust, maintaining a value exceeding 100%. This resilience further underscores the effectiveness of the hydrogel in retaining water within its structure.

## Adsorption of Cr(VI) ion onto CH adsorbent *Effect of pH condition*

The pH is one of the important conditions that influence the adsorption capacity of a material. As shown in Figure 7, the adsorption performance of

Cr(VI) ion decreased when the pH increased from 1 to 6. For different pH conditions, the material would have different adsorption capacity. Here, the maximum uptake amount of Cr(VI) was obtained at pH 1 with 87% removal efficiency. The pH of the system plays a pivotal role in governing adsorption by influencing both the surface properties of the adsorbent and the ionic forms of chromium solutions. The presence of various chromium ion species, including HCrO<sub>4</sub>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, and H<sub>2</sub>CrO<sub>4</sub>, is highly dependent on the surrounding solution pH. Existing reports indicate that  $HCrO_4^-$  and  $Cr_2O_7^{2-}$  are the primary forms at pH 1–6, while H<sub>2</sub>CrO<sub>4</sub> is formed at pH < 1. Understanding these pH-dependent variations is crucial for comprehending and optimizing the adsorption process.<sup>25</sup> At low solution pH, the cellulose chain was highly protonated and positively charged at the hydroxyl group. Therefore, the strong interaction between CH and Cr(VI) ion was formed through electrostatic attraction and the removal of Cr(VI) was performed at a relatively high level.

### Effect of contact time

As depicted in Figure 8, the adsorption capacity exhibited a rapid increase from 30 to 120

min, with efficiency escalating from 70.9% to 87.4%. This resulted in a notable rise in adsorption capacity, progressing from 0.93 to 1.14 mg/g. Subsequently, from 120 to 180 min, both the removal efficiency and the adsorption capacity demonstrated a slower increase, ultimately reaching a plateau, attributed to the saturation of



Figure 7: Effect of solution pH on the adsorption of Cr(VI) ion onto CH

The kinetic adsorptions of Cr(VI) ion onto CH were investigated by the pseudo-first-order (PFO), pseudo-second-order (PSO) and and Weber-Morris (W-M) models, shown in these equations:<sup>26,27</sup>

$$Ln(q_e - q_t) = Lnq_e - k_1 t \tag{6}$$

$$\frac{1}{a_1} = \frac{1}{k_2 a_1^2} + \frac{t}{a_1}$$

$$\begin{array}{l} q_t \quad \kappa_2 q_e \quad q_e \\ q_e \quad (7) \end{array}$$

$$q_t \quad kt \rightarrow C$$
 (8)

where  $q_e$  and  $q_t$  are the adsorption capacity at equilibrium and at the time t (h), respectively. The  $k_1$  (1/h) and  $k_2$  (g/mg.h) are the rate constants for PFO and PSO, respectively, while k (mg/g.h<sup>1/2</sup>) is the intraparticle diffusion constant, and C (mg/g) is a constant related boundary layer thickness for the W-M model.

These kinetic models were employed to elucidate the adsorption process over time and evaluate the efficiency of Cr(VI) ion removal by CH. The PFO and PSO models provide insights into the adsorption rate constants ( $k_1$  and  $k_2$ ), while the W-M model characterizes the mechanism through the parameters k and t. The analysis of these models aids in understanding the dynamic aspects of the adsorption process and its underlying mechanisms.

The linear form of PFO, PSO and W-M models of the adsorption process as a function of contact time was presented in Figure 9. As seen from the results, the adsorbed amount of Cr(VI) ion on the CH gradually increased, with higher

binding sites. During this period, there was a marginal improvement in performance, with efficiency increasing by approximately 1%, and capacity edging up by only 0.02 mg/g. Consequently, the study determined the equilibrium time to be 120 min in this study.



Figure 8: Effect of contact time on the adsorption of Cr(VI) ion onto CH

contacting time up to 120 min. The fitting results of the experimental data for Cr(VI) ion were better fitted with the PSO model (Fig. 9 (a)), for which the R<sup>2</sup> reached 0.994, while its value was 0.8663 for PFO (Fig. 9 b). Therefore, the adsorption mechanism might also involve chemisorption between Cr(VI) ion and the prepared CH.<sup>28</sup> In addition, the diffusion rate of  $k_2$  was higher than that of  $k_1$ .

The application of PFO and PSO models, while commonly used in adsorption studies, has proved insufficient for identifying the diffusion mechanism of adsorbents, specifically porous ones. The adsorption process involving porous adsorbents can be conceptualized in three distinct stages: (i) contaminant transfer from solution to adsorbent surface – in the initial stage, the transfer of contaminants from the solution to the adsorbent surface occurs through a liquid boundary film, (ii) contaminant transfer from adsorbent surface to intraparticle active sites - following the initial stage, contaminants move from the adsorbent surface to the intraparticle active sites within the porous material, (iii) interactions with external and internal surfaces - the final stage involves interactions between contaminant molecules and the available sites on both the external and adsorbent.29 internal surfaces of the Understanding these stages is crucial for comprehending the intricacies of adsorption processes involving porous materials, where conventional models may fall short in capturing the complexities of diffusion mechanisms. Thus,

the W-M equation was used to further investigate the rate-controlling mechanism in the adsorption process. According to this model, in cases where intraparticle diffusion dominates, the relationship between the adsorbed amount  $q_t$  and the square root of time  $t^{0.5}$  manifests as a linear correlation. This analysis provides insights into the specific diffusion mechanisms at play during the adsorption process. Figure 9 (c) shows the plots of Cr(VI) uptake *vs.*  $t^{1/2}$  for the prepared CH. The data seem to fit best to this model, as the  $R^2$  was calculated as 0.9163, confirming the intrapartilcle diffusion process took place in the Cr(VI) ion adsorption experiment using the prepared CH adsorbent. Table 1 summarizes the kinetic parameters for the adsorption of Cr(VI) onto the prepared CH.



Figure 9: The linear form of (a) pseudo-first-order, (b) pseudo-second-order and (c) Weber-Morris models for the adsorption of Cr(VI) ion onto the prepared CH

 Table 1

 Kinetic parameters for Cr(VI) ion adsorption on the prepared CH

| Pseudo-first-order       |                     |                | Pseudo-second-order      |                            |                | Weber-Morris               |             |                |
|--------------------------|---------------------|----------------|--------------------------|----------------------------|----------------|----------------------------|-------------|----------------|
| q <sub>e</sub><br>(mg/g) | $\frac{k_1}{(1/h)}$ | R <sup>2</sup> | q <sub>e</sub><br>(mg∕g) | k <sub>2</sub><br>(g/mg.h) | R <sup>2</sup> | k (mg/g.h <sup>1/2</sup> ) | C<br>(mg/g) | $\mathbb{R}^2$ |
| 0.2                      | 1.7                 | 0.8663         | 1.2                      | 4.3                        | 0.9994         | 0.26                       | 0.73        | 0.9163         |

### Effect of adsorbent dosage

The adsorption efficiency exhibited a notable increase with a rising adsorbent mass, indicating a greater number of adsorption active sites. As illustrated in Figure 10, a continuous rise in CH adsorbent mass, ranging from 0.05 g to 0.2 g, correlated with an enhancement in removal capacity. The initial mass of 0.05 g of CH for Cr(VI) ion elimination resulted in an efficiency of 50.1%, progressively ascending to 87.8% at a 0.2 g dosage. However, a higher CH amount, specifically at 0.3 g, did not significantly elevate the removal percentage, reaching only 90.0%. This observation could be explained by intensified competition among Cr(VI) ions for active binding sites within the CH structure, while the saturation effect also occurred, where the solute concentration on the adsorbent surface surpassed that in the solution. Consequently, as the mass of the adsorbent increased over 0.2 g, the adsorption capacity diminished, leading to a decrease in the adsorbed Cr(VI) ions. Therefore, the optimal adsorbent dosage was identified as 0.2 g of CH.

### Effect of initial concentration

The initial concentration is a critical parameter influencing the capacity of hydrogel materials to eliminate Cr(VI) ions. Notably, as the initial concentrations of Cr(VI) ions varied from 5 to 50 mg/L, a gradual decrease in removal capacities was observed, declining from 88.7% to 56.7%, as illustrated in Figure 11. Higher concentrations of Cr(VI) ions tended to restrict the number of available adsorption sites within the CH. Consequently, this limitation resulted in a proportional decrease in removal percentage. In contrast, at lower initial concentrations of Cr(VI) ion in the solution, sufficient adsorption sites



The Langmuir and Freundlich models were selected to elucidate the relationship between the residual concentration of Cr(VI) ions in aqueous solution and the adsorption capacity of CH at a constant temperature. The linear equation of the Langmuir isotherm model was used as in the equation below:

$$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m} \tag{9}$$

where  $q_m$  (mg/g) is the maximum adsorption capacity, and  $K_L$  (L/mg) is the Langmuir constant.

The linear equation of the Freundlich isotherm model is presented as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{10}$$

where  $K_F$  (mg/g) and n are the Freundlich constants, associated with adsorption capacity and adsorption strength, respectively.

remained available for the effective sorption of Cr(VI) ions. This observation underscored the concentration-dependent nature of the adsorption process and emphasized the need to consider initial concentrations when evaluating the performance of hydrogel materials for Cr(VI) ion removal.



adsorption of Cr(VI) ion by CH

The results presented in Table 2 reveal high values of the relative correlation coefficient  $(R^2)$ for both the Langmuir and Freundlich isotherm models. Specifically, a notably higher R<sup>2</sup> value was observed for the Langmuir model, reaching 0.994, compared to 0.9704 for the Freundlich model. This finding implied that the adsorption of Cr(VI) ions onto CH was best described by a monolaver adsorption mechanism, occurring at specific homogeneous sites within the adsorbent. Furthermore, the Langmuir model indicated a maximum adsorption capacity of 4.14 mg/g for Cr(VI) ions by the CH adsorbent. It is known that, at lower pH, hydroxyl groups on the surface of CH are protonated, leading to the electrostatic attraction between protonated hydroxyl and negatively charged Cr(VI) ion.



Figure 12: Linear isotherms of (a) Langmuir and (b) Freundlich models at different initial concentrations of Cr(VI) ion



 Table 2

 Langmuir and Freundlich adsorption isotherm parameters for the removal of Cr(VI) by CH

Figure 13: Proposed adsorption mechanism of CH to Cr(VI) ion in aqueous solution

Moreover, the obtained data suggested an interaction between the hydrated Cr(VI) ions in aqueous solution and the hydroxyl groups on the surface of CH materials through hydrogen bonding, aligning with the Freundlich isothermal model, which also confirmed the chemisorption character indicated by PSO linear equation. Figure 13 presents the proposed adsorption mechanism of Cr(VI) ion in aqueous solution to CH.

### **Regeneration of CH adsorbent**

In the present study, the regeneration of the CH adsorbent for the removal of Cr(VI) ion was tested. The use of an acidic aqueous solution resulted in the replacement of Cr(VI) ion by H<sup>+</sup> ion, leading to the release of heavy metal ions into the elute solution. The desorption process lasted for 24 h to gain a 90% release percentage of Cr(VI) ion into the eluate solution. After this duration, the desorption seemed to remain constant, as no higher release percentage was observed. Therefore, the desorption time was set to 24 h. The formed hydrogel emerged as a promising candidate for addressing heavy metal ion pollution in wastewater, owing to its adsorption capacity and excellent recyclability.

With an initial processing efficiency of 86.6%, the first regenerated material still exhibited a respectable processing efficiency of 60.8%. However, with each subsequent regeneration, the processing efficiency decreased until it reached 18.1%. This trend was in line with the relative ease of use, recoverability, and processing efficiency. During regeneration cycles, the observed decline in processing efficiency was attributed to the diminished availability of active sites within the composite adsorbent or potential material loss.<sup>30</sup> The adsorption sites inside the materials gradually became saturated, resulting in an equilibrium of metal ions adsorption.<sup>31</sup> Despite this decrease, the material retained its efficacy. emphasizing its practical utility in the removal of heavy metal ions from wastewater and its potential for multiple regeneration cycles.

# Comparison of various adsorbents for Cr(VI) ion removal

The adsorption of chromium (VI) has been the subject of extensive investigation, with various materials explored as potential adsorbents. This included the exploration of low-cost alternative materials, including those prepared from agricultural residues. In Table 3, we presented a comparative analysis of the maximum adsorption capacities for Cr(VI) of different adsorbents reported in the literature. Notably, the cellulose hydrogel adsorbent prepared in this study exhibited higher efficiency compared to other adsorbents reported in the literature.

Furthermore, it is worth highlighting a crucial aspect that underscores the potential of the CH hydrogel for the development of cost-effective and environmentally friendly adsorbents – this

distinctive feature lies in the abundant availability of RS for the extraction of cellulose. The utilization of this readily obtainable resource not only enhances the sustainability of this adsorbent, but also addresses concerns related to waste disposal. Importantly, this hydrogel-based adsorbent can be easily retrieved from wastewater, and its recyclability is robust, making it wellsuited for industrial-scale applications.



Figure 14: Regeneration of CH adsorbent for the removal of Cr(VI) ion

| Table 3  |
|--|
| Comparison of adsorption efficiency of different adsorbents towards Cr(VI) ion |

| No | Adsorbent                                | Maximum adsorbed amount (mg/g) | Reference  |
|----|--|--------------------------------|------------|
| 1  | Truffle peels powder                     | 0.2776                         | 32         |
| 2  | Waste olive pomace                       | 0.96 - 3.35                    | 33         |
| 3  | Vegetable waste mixture                  | 1.089                          | 34         |
| 4  | Rice husk ash                            | 3.25                           | 35         |
| 5  | Humic acid coated magnetite              | 3.37                           | 36         |
| 6  | Dried brown marine algae (Sargassum sp.) | 3.69                           | 37         |
| 7  | Rice straw cellulose-based hydrogel      | 4.14                           | This study |

### CONCLUSION

The cellulose-based hydrogel was successfully prepared by the co-polymerization process with the addition of crosslinker, and applied as a potential adsorbent to remove Cr(VI) from wastewater. The chemical structure of the obtained hydrogel was observed to indicate the presence of functional groups of the additive components, leading to a denser morphology noted both on the surface of the material and in cross-section. In addition, a moderate water content value provided good durability during use in an aqueous environment. According to the data of the adsorption experiments, the removal of Cr(VI) ion was found to follow the Langmuir model, with a maximum uptake of 4.14 mg Cr(VI)/g at pH 1 after 120 min, using 0.2 g of adsorbent mass at 25 °C. The cellulose-based hydrogel adsorbent was also demonstrated to be

reusable, as the removal capacity was maintained at 40% after two recycling runs. In the present research, the concentration of the cellulose solution used to prepare the hydrogel was 1%. It is noteworthy that an increment in the polymer concentration might provide enhanced adsorption capacity due to the higher numbers of active hydroxyl groups. This hydrogel is considered to be a good bio-template material that could be used in future studies for incorporating other components, such as nanoparticles", to enhance the removal capacity of Cr(VI) ion from wastewater.

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