

Original Research

Removing Cr(VI) from Aqueous Solutions via Absorption by Green Synthesized PGA-PL-tannin Gel

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Abstract

Hexavalent chromium Cr(VI) has been proven to be harmful to human health and the environment. Polyglutamic acid (γ -PGA), polylysine (ϵ -PL), and tannin can be designed to make a gel (PGA-PL-tannin) that can efficiently remove Cr(VI). In this study, the mechanism of Cr(VI) adsorption by PGA-PL-tannin gel was investigated. The results showed that the rate of Cr(VI) removal by this gel exceeded 90% at pH 6-9. A thermodynamic study of the parameters of Cr(VI) adsorption by PGA-PL-tannin gel indicated that the process conformed to the Freundlich isothermal adsorption and pseudo second-order adsorption dynamics models, and was a spontaneous and endothermic process. Owing to the interaction between charged functional groups, Cr(VI) was reduced to trivalent chromium [Cr(III)] after adsorption to the PGA-PL-tannin gel surface. This study demonstrates that PGA-PL-tannin gel could be used as an adsorbent for Cr(VI) pollution control.

Keywords: PGA-PL-tannin, Cr(VI), adsorption, thermodynamics, equilibrium

Introduction

With rapid industrialization occurring globally, pollution by heavy metal ions has become an urgent environmental problem, causing harm to humans

and the environment [1]. Among the heavy metals, hexavalent chromium [Cr(VI)] is classified as a carcinogen by the International Agency for Research on Cancer due to its strong mutagenicity and teratogenicity [2, 3]. Chromium is released into waterbodies through wastewater from electroplating, batteries, phosphate fertilizers, mining, pigments, stabilizers, and alloys [4, 5]. Therefore, the removal of chromium-contaminated

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water is imperative. Many methods for removing heavy metal ions and other types of contaminated water, including ion exchange, precipitation, membrane filtration, electrodialysis, use of a photocatalyst, and adsorption, have been developed [6-8]. The adsorption method is simple, widely applicable, and effective, making it one of the most promising options for sewage purification. Biological macromolecule gels and metal ions in water can form complexes to remove Cr(IV) effectively [9]. Min et al. synthesized CS-MWNT-PAA-PADPA (FG) gel to remove Cr(VI) from water [10], and at pH 2 the removal rate of Cr(VI) exceeded 90%. Similarly, Karthik et al. synthesized polyaniline/silica gel for the removal of Cr(VI) from water [11]; the adsorption capacity of the gel reached 63.41 mg/g. In addition, Amalraj et al. reported that the combination of threonine and a polypyrrole nanocomposite [12] resulted in a high removal rate of Cr(VI) at pH 2. However, there were some problems associated with the above-mentioned synthetic biological macromolecule gels, such as non-biodegradable material being used in adsorption, complicated preparatory procedures for these gels, and the results being dependent on the pH of the waterbody.

In this study, we aimed to design a novel biological macromolecule gel (PGA-PL-tannin) that consists of polyglutamic acid (γ -PGA), polylysine (ϵ -PL), and tannin. To gain insights into the mechanism of Cr(VI) adsorption by PGA-PL-tannin, Fourier transform infrared (FT-IR) spectroscopy, solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy (^{13}C -NMR), inductively coupled plasma (ICP) emission spectrometry, X-ray photoelectron spectroscopy (XPS), and differential scanning calorimetry (DSC) were used to characterize the structure of PGA-PL-tannin. The research results should be helpful for removing Cr(IV) from the environment.

Materials and Methods

Materials

We created a gel containing polyglutamic acid (γ -PGA), polylysine (ϵ -PL), and tannic acid, which did not require a chemical cross-linking agent for synthesis. These materials are biodegradable and benign to the environment. γ -PGA ($M_w = 1000 - 1200$ kDa) was obtained from Tianjin Peiyang Biotrans Biotech Co., Ltd. ϵ -PL ($M_w = 3500 - 5000$ Da) was obtained from Zhejiang Silver-Elephant Bio-engineering Co., Ltd. Tannic acid was obtained from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) used for chromium analysis was of GR grade, and sodium hydroxide (NaOH), hydrochloric acid (HCl), and other reagents used were all of AR grade. Distilled water was used in the experiments described below.

Instrumentation

An FT-IR spectrophotometer (NEXUS 670; Nicolet, USA), solid-state ^{13}C -CP/MAS NMR (AVANCE AV 400; Bruker, Switzerland), ICP-OES (Optima 5300DV; PerkinElmer, USA), XPS (Kratos Axis Ultra; Kratos, UK), DSC (DSC204F1 Phoenix; Netasch, Germany), and a thermostat oscillator (SKY-2112B; SUKUN, China) were used in this work.

Experimental Methodology

Preparation of PGA-PL-tannin Gel

At room temperature, 50 mL of 60 g/L γ -PGA solution was mixed with 50 mL of 60 g/L tannic acid solution and 30 mL of 60 g/L ϵ -PL solution, followed by stirring slowly for 10 min. The process did not require pH adjustment.

Adsorption of Cr(VI) by PGA-PL-tannin Gel

A total of 0.6 g of the PGA-PL-tannin gel was added to 100 mL of 3 mg/L $\text{K}_2\text{Cr}_2\text{O}_7$ in a 500 mL Erlenmeyer flask. Next, the mixed solution was placed in a rotary shaker and stirred at 20°C and 150 r/min, and the solution was adjusted to pH 7 using 0.2 mol/L HCl or 0.2 mol/L NaOH. Samples were collected at specific intervals to measure the residual concentration of chromium ions using ICP-OES instruments. Three parallel samples were analyzed.

The percentage removal of Cr(VI) ions was calculated using the following equation:

$$R(\%) = \frac{c_0 - c_t}{c_0} \times 100 \quad (1)$$

...where C_0 (mg/L) is the initial concentration of Cr(VI) ions and C_t (mg/L) is the concentration at time t .

Removal capacity (mg/g) was obtained from the following equation:

$$q_e = \frac{(c_0 - c_t) V}{m} \quad (2)$$

...where (L) is the volume of the Cr(VI) ion solution and m is the amount of gel in g.

Influence of pH on Gel Adsorption of Cr(VI)

To determine the influence of pH on the gel adsorption of Cr(VI), 0.2 mol/L HCl or 0.2 mol/L NaOH was added into a 500 mL conical flask containing 100 mL of 3 mg/L $\text{K}_2\text{Cr}_2\text{O}_7$ solution (initial concentration) to adjust the pH to 2, 3, 4, 5, 6, 7, 8, 9, and 10. A total of 0.6 g of gel was added into the 500 mL conical flask and the solution was shaken at 150 r/min in a thermostatic oscillator. The concentration of chromium ions remaining in the solution after 3 h was

analyzed. Three parallel samples were run for each pH value.

Influence of Time and Initial Concentration on Gel Adsorption of Cr(VI)

To determine the influence of time and initial concentration on gel adsorption of Cr(VI), a total of 100 mL of Cr(VI) with initial concentrations of 3, 4, 5, 6, 7, and 8 mg/L was placed into 500 mL conical flasks. Then, 0.6 g of gel was added into each flask and the solution was shaken at 150 r/min in a thermostatic oscillator. Contact times were 2, 3, 4, and 5 h. The liquid adsorption of residual chromium ions was analyzed. Three parallel samples were run for each contact time.

Adsorption Isotherms

The Cr(VI) adsorption was tested using two classic isotherms (i.e., Langmuir and Freundlich) under varying experimental conditions. The correlation coefficient (R^2) was derived from the degree of fit between the experimental data and isotherms.

The Langmuir adsorption model is widely used in the study of adsorption. It measures the accumulation of a single monolayer on an energetically uniform surface, across which the adsorbed molecules do not interact [13, 14]. The general Langmuir isotherm relationship can be transformed into a linear form for easy computation of primary parameters [15]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L c_e q_m} \quad (3)$$

...where (mg/g) is the binding capacity at equilibrium concentration of c_e , q_m (mg/g) is the maximum adsorption capacity, and K_L (L/mg) is a parameter related to the energy of adsorption.

The Freundlich adsorption model assumes that different adsorption sites exist on an irregular solid-phase surface with different adsorption energy to interact with adsorbed species [16]. The general Freundlich isotherm relationship can be transformed into a linear form for easy computation of primary parameters [17]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (4)$$

...where K_F and n are constants representing adsorption capacity (mg/g) and intensity, respectively.

Thermodynamics of PGA-PL-tannin Gel Adsorption of Cr(VI)

The van't Hoff equation is the basic method for calculating adsorption thermodynamic parameters [18-20]. Thermodynamic parameters associated with the adsorption – that is, standard free energy change

(ΔG), standard enthalpy change (ΔH), and standard entropy change (ΔS) – were calculated using equations 5 and 6:

$$\Delta G = -RT \ln K_L \quad (5)$$

...where R (8.314 J/mol/K) is the ideal gas constant, T (K) is the absolute temperature, K_L (L/g) is the standard thermodynamic equilibrium constant, and ΔG is the standard free energy change of sorption (kJ/mol). The standard thermodynamic equilibrium constant can be expressed in terms of ΔH and ΔS as a function of temperature:

$$\ln K_L = -\frac{\Delta H}{R \times T} + \frac{\Delta S}{R} \quad (6)$$

...where ΔH is the standard enthalpy change (kJ/mol) and ΔS is the standard entropy change (kJ/mol/K). The values of ΔH and ΔS can be determined from the slope and intercept of linear regression of K_L vs. $1/T$.

Kinetics of PGA-PL-tannin Gel Adsorption of Cr(VI)

The dynamic curve of the rate of gel adsorption of Cr(VI) was obtained by pseudo first-order and pseudo second-order dynamic adsorption models [1, 21]. The pseudo first-order kinetic equation describes the total rate of adsorption using a kinetics equation, as shown in Eq. 7:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

...where q_e and q_t (mg/g) are the quantity of adsorption by quality at equilibrium or time (t), and k_1 (h^{-1}) is the pseudo first-order rate constant.

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 \cdot q_e^2} \quad (8)$$

The pseudo second-order adsorption kinetics rate equation (pseudo second-order rate equation) has been proposed by Ho [22, 23], as shown in Eq. 8. It also describes the adsorption of heavy metal ions and also belongs to the total rate equation describing adsorption kinetics [24].

Results and Discussion

Characterization of PGA-PL-tannin Gel Structure

PGA-PL-tannin gel is a polymer comprising γ -PGA, ϵ -PL, and tannin. It is efficient for Cr(VI) adsorption, and has good selectivity and stability. To identify the surface functional groups of PGA-PL-tannin gel, the FT-IR spectra of tannic acid, ϵ -PL, γ -PGA,

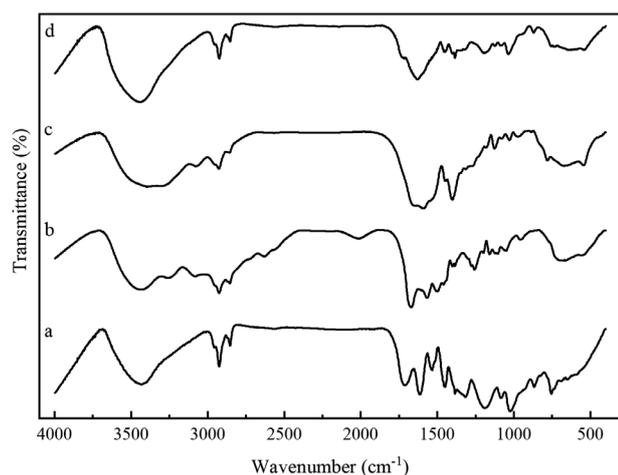


Fig. 1. FT-IR spectra: a) tannic acid; b) ϵ -PL; c) γ -PGA; d) PGA-PL-tannin gel.

and PGA-PL-tannin gel were measured. As shown in Fig. 1, a predominant peak at 3410 cm^{-1} associated with OH stretching vibration was identified, along with a peak at 1710 cm^{-1} assigned to C=O and -NHCO- stretch at around 1565 cm^{-1} . The other peaks of the PGA-PL-tannin gel did not differ with respect to those of γ -PGA,

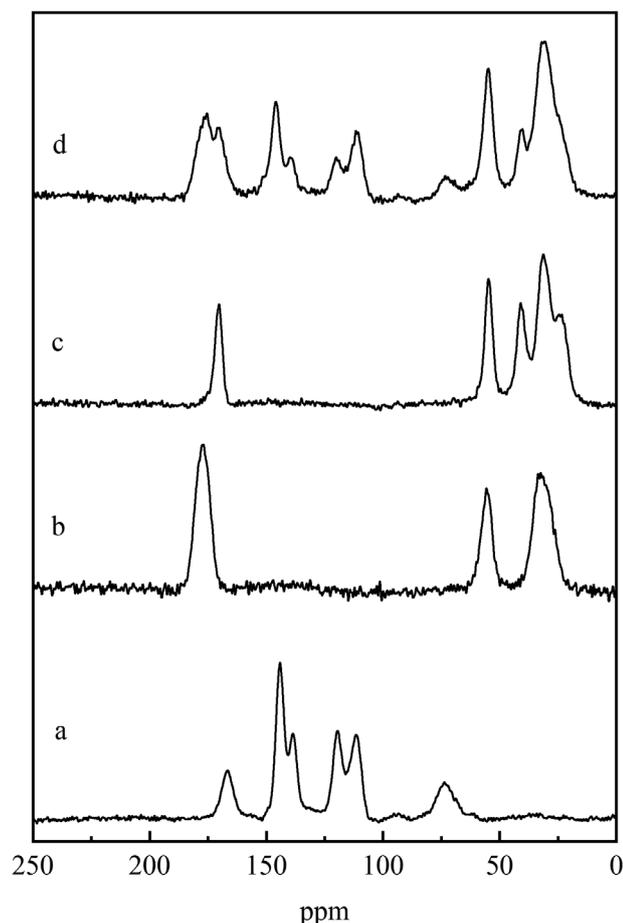


Fig. 2. Solid-state ^{13}C -NMR spectrum of the gel: a) tannic acid; b) ϵ -PL; c) γ -PGA; d) PGA-PL-tannin gel.

ϵ -PL, and tannic acid, which indicated that γ -PGA, ϵ -PL, and tannic acid were probably fixed through a mode of non-chemical interaction, such as electrostatic attraction or hydrogen bonding.

Fig. 2 shows the solid-state ^{13}C -NMR spectrum of the gel. The chemical shifts at 24.746 and 32.311 ppm are assigned to $-\text{CH}_2-$ groups. The chemical shifts at 169.449 and 175.196 ppm are assigned to $-\text{COOH}$ and $\text{C}=\text{O}$, respectively. The chemical shifts at 41.262 and 55.578 ppm are assigned to $-\text{CH}_2\text{-NH-}$ and $-\text{C-NH}_2$, respectively. Therefore, the structures γ -PGA and ϵ -PL can be considered to be present in the gel. Chemical shifts between 110.261 and 145.140 ppm are consistent with the production of tannins. Combined with the FT-IR spectra, the results show that the gel consisted of γ -PGA, ϵ -PL, and tannic acid, created through polymerization that occurs via hydrogen bonds and generates new biological macromolecules.

Effect of Solution pH on Gel Adsorption of Cr(VI)

Solution pH plays an important role in the process of metal ion sorption. Generally, the surface charge of the sorbents and the existing form of the heavy metal ions were affected by the solution pH [25]. PGA-PL-tannin gel has strong adsorption capacity, achieving removal of Cr(VI) at a rate of more than 90%. However, the gel adsorption of Cr(VI) was affected by the pH of the solution. To determine the effect of pH on Cr(VI) sorption by the PGA-PL-tannin gel, pH of the solution was adjusted to between pH 2 and 10. The results showed that the removal rate of Cr(VI) was increased between pH 2 and pH 6, and reached a maximum at pH 6, and then sharply dropped to below 40% at pH values greater than 9 (Fig. 3). Free amino and carboxyl molecules were protonated at lower pH; thus, the electrostatic adsorption of positively charged molecules with the solution of CrO_4^{2-} achieved the best removal rate. When the pH was

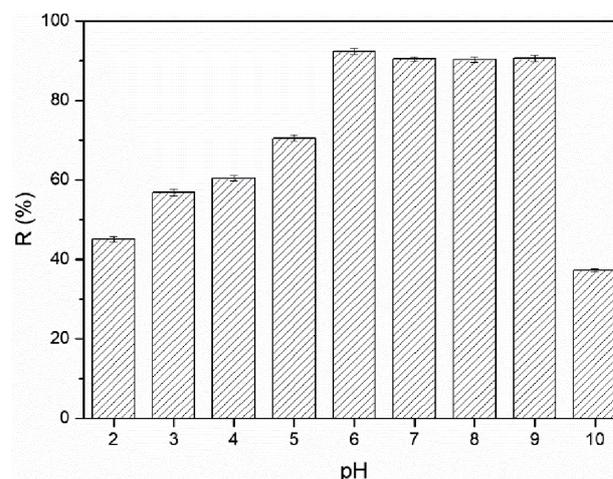


Fig. 3. Effect of initial pH on Cr(VI) adsorption by PGA-PL-tannin gel.

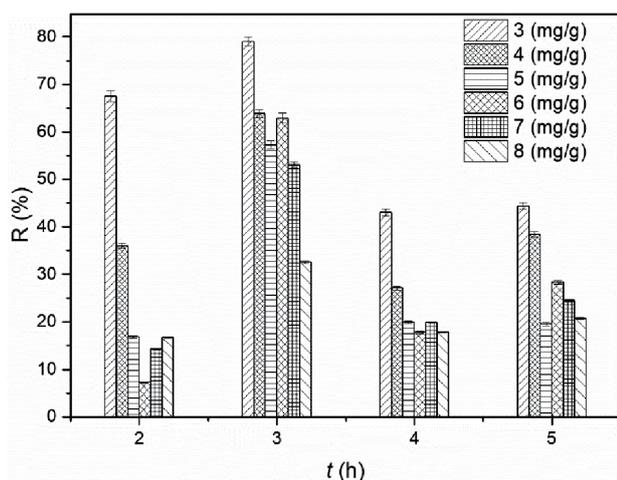


Fig. 4. Effect of reaction time and initial concentration on Cr(VI) adsorption by PGA-PL-tannin gel.

greater than 9, the removal rate of Cr(VI) was found to be low, which could be attributed to the competition between CrO_4^{2-} ions and OH^- ions for the sorption sites of the sorbent surface [26].

Effects of Reaction Time and Initial Concentration on Gel Adsorption of Cr(VI)

The gel adsorption of Cr(VI) was affected by both reaction time and initial concentration (Fig. 4). The results showed that the removal rate of Cr(VI) followed a downward trend with the increase of Cr(VI) concentration; when the initial concentration reached 3 mg/L, the removal rate of Cr(VI) was the highest (78.53%). When the reaction time was 3 h, which was favorable for the removal of Cr(VI) – especially for a higher initial concentration of Cr(VI), the removal rate of Cr(VI) was the highest. It was speculated that this may be related to the negative surface charge and number of gel adsorption sites (i.e., by amino groups on the gel/amino protons generated). For instance, a large number of active adsorption sites would allow high electrostatic attraction for Cr(VI) adsorption. Over time, there would be less residual adsorption until the point of saturation [26]. After gel adsorption saturation of Cr(VI), electrostatic repulsion dissociation would occur. Thus, the number of active sites of the gel would become the factor limiting the adsorption process [25].

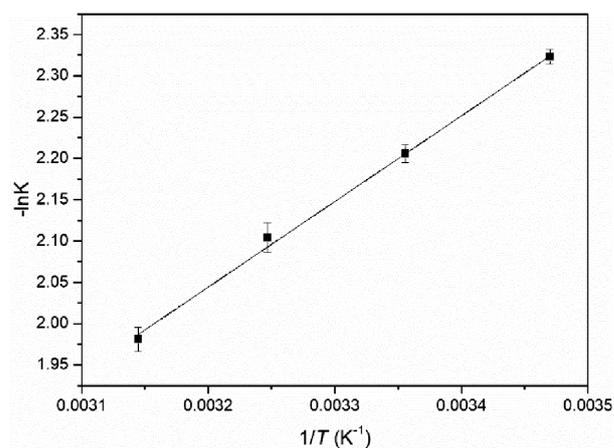


Fig. 5. Plots of $-\ln K$ vs. $1/T$ for the adsorption of Cr(VI) by PGA-PL-tannin gel.

Isotherms of PGA-PL-tannin Gel Adsorption of Cr(VI)

The relationship between the adsorbent and the adsorption capacities was elucidated via adsorption isotherms, where both the Langmuir and Freundlich adsorption models were used to describe the Cr(VI) adsorption on PGA-PL-tannin gel. Considering the Langmuir and Freundlich models for gel adsorption of Cr(VI), the R^2 values were greater than 0.89 and the curve fit better (Table 1) when adopting the Freundlich model; the results thus indicated that it was more suitable to describe gel adsorption of Cr(VI) than the Langmuir isotherm. Experimental results showed that the adsorption phenomena may be inhomogeneous on the surface in the multilayer adsorption process. Under the Freundlich model, the fit of the results could be further increased at temperatures between 288 K and 318 K; however, the value of n changed slightly with the increase of temperature.

Thermodynamics of PGA-PL-tannin Gel Adsorption of Cr(VI)

Gel adsorption of Cr(VI) was determined using the van't Hoff equation of linear regression analysis (Fig. 5), which was a plot of $-\ln K$ vs. $1/T$. The correlation was strong ($R^2 = 0.9993$), which indicated that the calculation method was suitable for the process of gel adsorption

Table 1. Parameters of Langmuir and Freundlich models for Cr(VI) adsorption onto gel.

| Temperature | Langmuir model | | | Freundlich model | | |
|-------------|----------------|--------------|--------|------------------|-------|--------|
| | K_L (L/mg) | q_m (mg/g) | R^2 | K_F | n | R^2 |
| 288K | 0.0233 | 0.5186 | 0.9027 | 0.2675 | 1.025 | 0.9018 |
| 298K | 0.5685 | 0.6768 | 0.9219 | 0.3243 | 2.332 | 0.8993 |
| 308K | 0.6525 | 0.5875 | 0.7079 | 0.2312 | 2.186 | 0.9803 |
| 318K | 0.7804 | 0.6533 | 0.7730 | 0.2806 | 2.285 | 0.9901 |

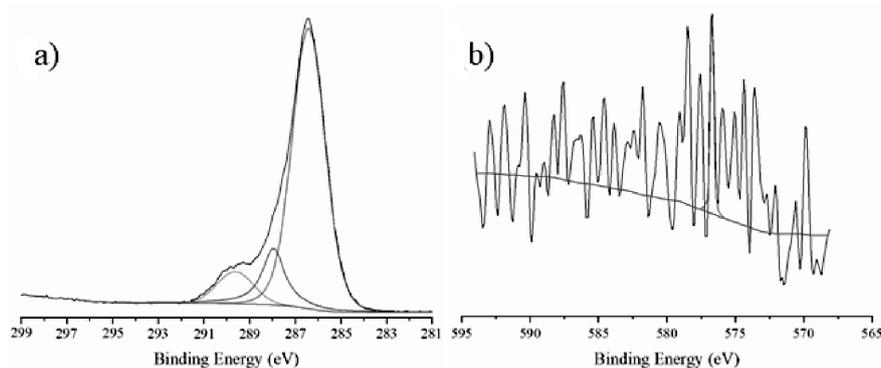


Fig. 6. XPS spectra of Cr(VI) adsorbed gel: a) gel C1s; b) gel after adsorption of Cr(VI).

of Cr(VI). In the process of Cr(VI) adsorption, the free energy change showed a downward trend with the increase of experimental temperature (288 k, $\Delta G = 5.537$ KJ/mol; 318 k, $\Delta G = 5.236$ KJ/mol). Experimental results showed that the spontaneous gel adsorption of Cr(VI) may be improved at higher temperatures. Furthermore, its endothermic nature was confirmed by the change of enthalpy ($\Delta H = 8.58$ KJ/mol) in the process of gel adsorption of Cr(VI), and the adsorption of Cr(VI) could be improved by increasing the temperature. For the Cr(VI) adsorption process ($\Delta S = 0.01045$ KJ/mol/K), that gel adsorption of Cr(VI) was a process of entropy increase; namely, the disorder of the adsorption system increased after the adsorption of Cr(VI) [21].

Kinetics of PGA-PL-tannin Gel Adsorption of Cr(VI)

The pseudo first-order and pseudo second-order adsorption kinetics models were used for fitting analysis. The results showed that the pseudo second-order dynamics equation successfully described the gel adsorption kinetics of the Cr(VI) model ($R^2 = 0.9979$). The pseudo second-order adsorption rate constant k_2 increased with an increase in initial concentration, especially from a low concentration of Cr(VI). Thus, as the initial concentration increased from 3 to 6 mg/L, k_2 increased from -5.128 to 8.264 g/mg/h, and then decreased as the initial concentration of Cr(VI) continued to increase. At a low initial concentration, the influence of the solution concentration on the adsorption rate increased.

Mechanism of PGA-PL-tannin Gel Adsorption of Cr(VI)

To explore the mechanisms of PGA-PL-tannin gel adsorption of Cr(VI), three peaks were detected in XPS spectra and C1s spectra (Fig. 6a): the carbon in the C-N at 286.572 eV; the carbon in the amide bond O=C-NH at 287.973 eV; and the carbon in the acid ester O=C=O at 290.026 eV. Thus, the carbon in the gel is mainly from the C-N key carbon. From images showing that the binding energy is $Cr_{2p3/2}$, after adsorption, Cr(VI) in the gel appeared to be reduced to Cr(III) (Fig. 6b). In the process of adsorption, Cr(VI) and the first amino/amino combination allow the Cr(VI) to be reduced to Cr(III). With the gel on the surface, the $-NH_2$ hydrogen atoms, and the electronegativity of larger nitrogen atoms, shared electrons favor nitrogen atoms, making positively charged hydrogen atoms into almost naked protons. When negatively charged chromic acid is exposed to nearby radical anions, the protonation of amino acids on the gel and chromic acid radical anions in oxygen atoms produces electrostatic attraction (i.e., hydrogen bonding), which achieves the adsorption [27].

Conclusions

This paper introduces a method of Cr(VI) adsorption using PGA-PL-tannin gel. The adsorption of Cr(VI) onto PGA-PL-tannin gel were affected by contact time, initial concentration of gel, and pH. And the value of maximum removal rate of Cr(VI) was obtained when the initial concentration reached

Table 2. Calculated kinetic parameters for the adsorption of Cr(VI) onto gel.

| Concentration (mg/L) | Pseudo-first-order | | | Pseudo-second-order | | |
|----------------------|--------------------|--------------|--------|---------------------|--------------|--------|
| | k_1 (h^{-1}) | q_e (mg/g) | R^2 | k_2 (g/mg/h) | q_e (mg/g) | R^2 |
| 3 | 0.2221 | 0.2187 | 0.8027 | -5.128 | 0.2812 | 0.9979 |
| 6 | 0.1260 | 0.2037 | 0.8604 | 8.264 | 0.3181 | 0.9954 |
| 9 | 0.1336 | 0.3244 | 0.8723 | 3.571 | 0.3049 | 0.9909 |

3 mg/L and the reaction time was 3 h. PGA-PL-tannin gel adsorption of Cr(VI) aligns with the Freundlich isotherm adsorption model. Furthermore, the kinetics of PGA-PL-tannin gel adsorption of Cr(VI) aligns with the pseudo second-order equation $k_2 = 0.7927$ mg/g/h. In the process of adsorption, Cr(VI) and the first amino/ amino combination allow the Cr(VI) to be reduced to Cr(III) by PGA-PL-tannin gel. Desorption of chromium ions into chromium salts after recycling renders the adsorption gel biodegradable as harmless amino acids, such as glutamic acid and lysine. Adsorption thermodynamics, adsorption kinetics, and gel structure characterization results were combined to analyze the adsorption mechanism. Overall, PGA-PL-tannin gel proved to be a highly efficient adsorption material to remove Cr(VI) ions from water. Furthermore, PGA-PL-tannin gel is advantageous because its synthesis is simple, it is reusable and biodegradable, the metal ions can be recycled after desorption, and secondary pollution is not released into the environment.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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