Removal of hexavalent chromium using polyphenol-based functional materials

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Abstract: Chromium from industrial wastewater, waste, pesticides, fertilizers, etc., always causes serious environmental problems. High levels of chromium pollution can have adverse effects on environments and living organisms. In this study, titanium salt was used to react with green tea extract to form a composite material, and the material was further used to remove hexavalent chromium in solution. The removal effect of hexavalent chromium was investigated under different reaction conditions, namely temperature, time, pH, and initial chromium concentration. The results showed that the chromium removal effect was the best under the conditions of acid to neutral pH, 45℃, reaction time of 24 h, and initial chromium concentration of 80 mg/L. This study provides a feasible method to solve the problem of chromium pollution and has high application value in wastewater treatment.

1. Introduction

Chromium (Cr) is one of the common contaminants in the industry. The pollution sources of Cr include inferior cosmetic raw materials, leather preparations, metal surface treatment, industrial pigments, leather tanning, etc. [1]. The pollutants containing Cr released to the environment can pollute soils and waters. It has been reported that the content of Cr in much of global surface water has far exceeded the permissible limit (0.1 mg/L) recommended by the World Health Organization [2]. According to the list of the International Institute of Carcinogens, metal Cr is in the list of class 3 carcinogens [3]. The toxicity of Cr is related to its valence state. Hexavalent chromium (Cr(VI)) is 100 times more toxic than trivalent chromium (Cr(III)), which is more likely to infect the human body, such as skin lesions, respiratory and digestive system damages, liver and kidney failures, etc. In addition, Cr(III) and Cr(VI) can be converted into each other. Many functional materials, including metal-organic frameworks (MOFs), graphene oxides, multi-wall carbon nanotubes, etc., have been used and applied to reduce Cr contamination in environments. Nevertheless, their high cost and tedious manufacture hinder their wide application in real scenarios.

Plant polyphenols are mainly found in nature in the seed skin, pulp, and leaf and fruit shell, and their content in plants is second only to lignin, hemicellulose, and cellulose [4]. As a ubiquitous biomass, plant polyphenols have the characteristics of low cost, non-toxic, strong metal chelation ability, and good adhesion properties to various substrates. Recently, plant polyphenols and their coordination polymers have been recognized as powerful tools for engineering functional nanomaterials. Plant polyphenols and metal conjugates refer to the complex formed by plant polyphenolic compounds and metal ions. Metal-polyphenol nanoparticles (MPNs) have a broad application prospect in environmental science because of their characteristics of antioxidant and free radical elimination [5]. For example, tannic acid and ferric iron can be complexed to form a nanocoating while uniformly loaded on the surface of the microporous wall, and the functionalized microporous material was used to remove antibiotics [6]. However, most of the current MPNs were produced based on iron and copper; the ability of other metals to form the greater family of MPNs has yet to be fully discovered, and their ability to remediate Cr contamination remains unclear.

In this study, titanium sulfate solution and green tea extract were used to synthesize a titanium-polyphenol powder material, which was characterized by scanning electron microscopy (SEM), infrared spectroscopy (FTIR), and surface potential. The adsorption effect of the MPN material on Cr(VI) in water was also studied. This study of the method and mechanism of removing Cr(VI) is of great practical significance for improving the efficiency of water quality treatment technology and reducing cost.

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2. Methods and Materials

2.1 Synthesis of metal-polyphenol composites

Ground green tea powder (60 g) was boiled in a 60°C water bath for 30 min in 1 L pure water. After filtering the filter paper, the filtrate was collected to obtain 500 mL of the green tea extract. Meanwhile, 2.4 g of anhydrous titanium sulfate (Ti(SO$_4$)$_2$) was dissolved in 50 mL of pure water to make a Ti(SO$_4$)$_2$ solution (2 mol/L). Then, it was mixed with the green tea extract on an oscillator at 100 r/min for 30 min. The reaction immediately generated a reddish-brown flocculent precipitate. The solution was centrifuged at 5000 r/min for 5 min. After centrifugation, the products were vacuum-dried at 60°C for 24 h. The dried product (yield 8.9 g) was then put in the agate mortar, ground into powder, and named Ti-polyphenol composites (TPC). The TPN was kept at 4°C for subsequent experiments. The production procedure is illustrated in Fig. 1.

2.2 Batch experiment

The adsorption effect of Cr(VI) in different concentrations of Ti(SO$_4$)$_2$ solution was studied. Various Ti(SO$_4$)$_2$ concentrations at 0.5 mol/L, 1 mol/L, and 2 mol/L were mixed with the green tea extract on an oscillator at 100 r/min for 30 min, and the precipitates were collected as above procedures. Cr(VI) solution was prepared using dichromate (K$_2$CrO$_7$) to make 50 mg/L, and the pH was unadjusted and measured to be 6.2. Afterward, 0.05 g TPC was weighed, put in the 50 mL of Cr solution, and shaken in a water bath at 60°C for 30 min. After the reaction, the solution was filtered using 0.22 μm membrane filters, and the residual Cr(VI) concentration after the reaction was measured by diphenylcarbacyl dihydrazide method on a visible spectrometer (721, Shanghai Jinghua, China) at 540 nm. The K$_2$CrO$_7$ solution with concentrations of 10, 30, 50, 80, 100, 150, and 200 mg/L was used in the isothermal adsorption experiment. The TPC of 20 mg was put into each conical flask containing 20 mL of Cr(VI) solution. After mixing, the solution was kept in a water bath and shaken at 200 r/min for 24 h. Likewise, a kinetics experiment was conducted using the same amount of TPC and 50 mg/L Cr solution, and the mixed solution was shaken for 0.5 h, 1 h, 1.5 h, 2 h, 3 h, 6 h, 12 h, and 24 h. All the above experiment was conducted at a room temperature of 25°C. The effect of temperature on adsorption was investigated following the above procedure but at water bath temperatures of 25°C, 35°C, and 45°C. The above Cr solutions were not adjusted with pH and measured to be 6.2 in the beginning. To study the effect of solution pH on Cr(VI) removal, the Cr(VI) solution was then initially adjusted to 3, 5, 7, and 9 using 1 mol/L hydrochloric acid or sodium hydroxide solution. The Cr(VI) concentration was tested as above. All experiments were conducted with at least three replicates.

2.3 Characterization

The structure and morphology of TPC were characterized by scanning electron microscopy (SEM, ZEISS Sigma 300, Germany), Fourier infrared spectroscopy (FTIR, Thermo Scientific iN10, USA), nanoparticles and surface potential analysis (DLS, Malvern Zetasizer Nano ZS90, UK).

2.4 Data processing

Origin2018 was used to process all the data and produce graphs. All the data were reported with means ± STD.

3. Results and Discussion

3.1 The effect of Ti(SO4)2 dosage on Cr(VI) removal

The effect of Ti(SO$_4$)$_2$ dosage on Cr(VI) removal is shown in Table 1. The Cr(VI) removal percentages increased with increasing Ti(SO$_4$)$_2$ dosages. When the concentration of Ti(SO$_4$)$_2$ solution was 2 mol/L, the TPC material had the best adsorption capacity for Cr(VI). However, the ongoing increase in Ti(SO$_4$)$_2$ dosage was not investigated further, considering the production cost. Therefore, the Ti(SO$_4$)$_2$ concentration of 2 mol/L was chosen in subsequent TPC synthesis.

<table>
<thead>
<tr>
<th>Ti(SO$_4$)$_2$ dosage (mol/L)</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI) adsorption capacity (mg/g)</td>
<td>2.3±0.05</td>
<td>33.7±0.4</td>
<td>47.8±0.04</td>
</tr>
</tbody>
</table>
3.2 TPC characterization

The TPC made using 2 mol/L Ti(SO$_4$)$_2$ solution was further characterized using SEM, FTIR, and DLS. By observing the SEM images of TPC materials, the surface morphology and microstructure of the materials can be clearly seen. The whole shape of the material was irregularly granular, and the particle size was mostly 150~200 nm (Fig. 2a).

The oxygen-bearing functional groups on the polyphenol-metal materials were determined by FTIR (Fig. 2b). The transmittance peaks at 3382 cm$^{-1}$, 1628 cm$^{-1}$, 1124 cm$^{-1}$, and 752 cm$^{-1}$ were assigned to -OH, C=C, C-O, and C-H group, respectively, indicating that the material contained polyphenol compounds [2].

The DLS results showed that the surface charge of the material was 22.2, 11.6, 4.4, -9.6, and -28.2 mV at pH=3, 5, 7, 9, and 11, respectively (Fig. 2c). Thus, the zero-point potential PZC was calculated to be 7.02. The material surface charge was positive at pH < 7.02 or negative at pH > 7.02.

3.3 The effect of initial Cr(VI) concentration

The change of Cr(VI) adsorption affected by the initial Cr(VI) concentration followed a ‘first up and then down’ trend (Fig. 3a). When the initial Cr(VI) concentration was low (10-50 mg/L), the adsorption of the material gradually increased with the Cr(VI) concentration and reached the maximum $Q_e$ (75.2 mg/g) at around the initial Cr(VI) concentration of 80 mg/L. However, the Cr(VI) adsorption began to decrease as the initial Cr(VI) concentration exceeded 80 mg/L. This unusual trend showed that the material had reached saturation and could not adsorb but release Cr(VI) at high concentrations. Because of the decreasing adsorption capacity at high Cr(VI) concentrations, the adsorption data cannot be well fitted with either Langmuir or Freundlich models. Therefore, the adsorbed material had the best adsorption effect on Cr(VI) in water under the initial chromium concentration of 80 mg/L.

3.4 The effect of reaction time

The adsorption capacity of the material increased over time (Fig. 3b). The adsorption capacity of the material increased rapidly in 0-10 h and then increased slowly in the next 10-24 h. The final equilibrium time was 24 h when the adsorption capacity of the material reached its maximum value. The influence of time on the adsorption of Cr(VI) may include two main aspects: First, the contact opportunity between the active site on the surface of the material and the Cr(VI) increased under the growth of time, so the adsorption capacity to Cr(VI) in water was constantly enhanced. Second, with the extension of time, the reaction of Cr(VI) with the material was almost complete, leading to the decreased Cr(VI) adsorption capacity. The application of pseudo-first and pseudo-second-order kinetic models also suggested that the adsorption also followed the pseudo-first-order kinetic better due to the higher $R^2$ value (0.9942), indicating the reaction was more of a physisorption.

3.5 The effect of temperature

Thermodynamic enthalpy change represents the energy change of endothermic or exothermic heat during the reaction process. The change of Gibbs free energy ($\Delta G$), change of enthalpy ($\Delta H$), and change of entropy ($\Delta S$) were calculated (Table 2) according to classic equations.

<table>
<thead>
<tr>
<th>Temperature (℃)</th>
<th>$\Delta G$ (J/mol)</th>
<th>$\Delta H$ (J/mol)</th>
<th>$\Delta S$ (J/(mol/K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-14.7 × 10$^3$</td>
<td>1.41 × 10$^3$</td>
<td>5.43</td>
</tr>
<tr>
<td>35</td>
<td>-17.2 × 10$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>-22.5 × 10$^3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The adsorption reaction was an endothermic reaction that can be carried out spontaneously. The thermodynamic enthalpy and entropy of the system increased as the temperature increased. The temperature increase shifted the reaction to the adsorption direction, significantly improving the adsorption capacity (Fig. 3c).

3.6 The effect of pH

Solution pH is one of the key factors affecting the effect of Cr(VI) adsorption. It can be seen from the effect diagram that the removal of Cr(VI) remained at high levels (99.5%) irrespective of the pH values of 3, 5, and 7 (Fig. 3d). This is because under acidic or neutral conditions, as known from the above pH and surface charge diagram (Fig. 2c), the surface of the material had
a positive charge. In this case, the negatively charged Cr(VI) was electrostatically attracted to the surface of the material and thus effectively removed. However, when the pH value rose to 9, the adsorption capacity of the material decreased, and the removal rate also decreased to 98.5%. This is because Cr(VI) was converted into a more stable hydroxy chromate ion (CrO$_4^{2-}$) under alkaline conditions, which had more negative charges and repelled against the negative surface of the material, resulting in a decrease in the adsorption effect. However, the TPC material can still be regarded as an effective adsorbent as it can be applied in a wide pH range (98.0%-99.5% from pH 3-7), out-competing many existing materials.

4. Conclusion

In this study, the effects of polyphenol-metal composite material TPC on Cr(VI) removal under different conditions were investigated. It was found that the TPC had the best Cr(VI) removal result (75 mg/g) at 24 h and at the initial Cr(VI) concentration of 80 mg/L, which is better than many existing adsorbents. The adsorption of Cr(VI) on TPC was less affected by pH value than other Cr(VI) adsorption materials; thus, it can have a good adsorption effect in the range of acid and neutral pH values. However, it should be noted that the TPC is mainly suitable for the removal of low concentrations of Cr(VI) in water, while the removal of high concentrations of Cr(VI) could be relatively poor. The adsorption and reduction capabilities of polyphenol-metal materials can also be enhanced by changing their surface chemical properties and microstructure or combine with other materials to improve pollution remediation efficiency in the future.

![Figure 3](image_url)

**Figure 3** The effect of (a) concentration, (b) sampling time, (c) temperature, and (d) pH on Cr(VI) adsorption capacity and removal efficiency

Acknowledgment

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