



## Novel crosslinked chitosan for enhanced adsorption of hexavalent chromium in acidic solution



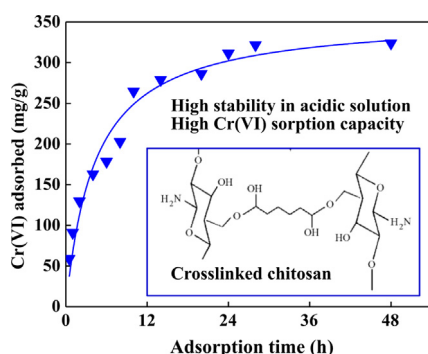
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### HIGHLIGHTS

- Diepoxyoctane (DEO) is effective for crosslinking chitosan (CS) beads.
- CS-DEO beads are stable in highly acidic solution.
- CS-DEO beads have the adsorption capacity of 325.2 mg/g for Cr(VI).
- CS-DEO beads can be easily regenerated and reused for five cycles.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Crosslinker  
Crosslinking reaction  
Chromium  
Adsorption capacity  
Chitosan beads

### ABSTRACT

To increase acid resistance, a water soluble diepoxy compound [1,2:7,8-diepoxyoctane (DEO)] as a new crosslinker was successfully used to crosslink chitosan beads (CS). The effects of crosslinking conditions (temperature, time, pH, and DEO concentrations) on weight loss and hexavalent chromium [Cr(VI)] adsorption performance of cross-linked chitosan beads (CS-DEO) in acidic solution were investigated. The prepared crosslinked chitosan beads were characterized by BET, SEM, TGA, XRD, and FT-IR analysis. Based on SEM images, morphological surface changes were observed after DEO treatment. TGA analysis results showed that thermal decomposition temperature of chitosan improved upon the crosslinking treatment. The XRD patterns demonstrated that crosslinking reaction resulted in a slight reduction in the adsorbent crystallinity. Furthermore, the prepared CS-DEO beads were stable in acidic solution and could efficiently adsorb Cr(VI). The CS-DEO beads cross-linked in 6 g/L of DEO solution at pH 10 and 50 °C for 5 h showed no weight loss but had high Cr(VI) adsorption capacity of 325.2 mg/g at pH 2.0, much higher than other reported chitosan-based adsorbents. The kinetic study of CS-DEO followed the pseudo-second-order kinetics. The adsorption isotherm of Cr(VI) on the CS-DEO beads could be fitted well by the Freundlich equation. Moreover, the prepared CS-DEO beads could be easily regenerated at least five times using 1 mol/L NaOH solutions without significant reduction in the Cr(VI) removal performance. DEO is a proper and favorable crosslinker for chitosan-based adsorbents. The prepared CS-DEO beads can be considered as a suitable and efficient adsorbent for Cr(VI) ions in aqueous solutions.

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## 1. Introduction

In recent years, with the aggravation of human activities, a lot of heavy metals are discharged into atmosphere, water and soil causing serious environmental pollution [1]. Hexavalent chromium Cr(VI) is ranked among the top 16 toxic heavy metals that have harmful effects on human health [2]. Its toxicity includes cancer as well as damage to the kidney and liver, vomiting, diarrhea, hemorrhage, skin irritation, and ulceration [3,4]. Due to the harmful effects associated with chromium, efficient methods for the removal of such pollutants and toxins need to be developed. Among the chromium removal methods, the adsorption process using effective adsorbents was one of the most effective method; it offers important advantages such as efficiency, ease of operation, profitability, availability, and low cost [5,6]. Different materials such as coal, sulfonated lignite, metal oxides, clay minerals, zeolites, organic resins, industrial by-products (e.g., coal, fly ash), and chitosan have been tried as adsorbents for Cr(VI) removal [7,8]. However, an efficient and environmental friendly adsorbent with high adsorption capacity and low cost for adsorption of Cr(VI) needs to be prepared. Chitosan has been extensively studied in the field of wastewater treatment due to its attractive properties such as low cost, abundance, non-toxicity, biocompatibility, biodegradability and macromolecular structure, and existence of high number of adsorption groups, versatility, selectivity, and high adsorption capability [9]. Chitosan is a cationic adsorbent in adsorption processes. In an acidic environment, chitosan molecules will be positively charged due to the protonation of the amino groups along the chitosan backbone [10]. During Cr(VI) adsorption process, the amino groups on chitosan adsorbents can be easily protonated to  $\text{NH}_3^+$ , and Cr(VI) appears mainly as  $\text{HCrO}_4^-$ ; therefore, positively charged amino groups can adsorb negatively charged Cr(VI) compounds via electrostatic attraction [11].

One weakness of chitosan is its low stability in acidic solutions; it dissolves and loses its capability of sorbate binding. Process waste streams from different industries, such as chromium plating and tanning, are characterized by high concentrations of chromium and very low pH value of 2.0–3.0 [12]. Hence, due to the dissolution tendency of chitosan at pH below 5.5, chitosan-based adsorbents cannot be used in acidic solutions [13]. Low stability of chitosan in effluents with low pH limits the use of chitosan for adsorption of heavy metals. Thus, to overcome of this problem, chitosan chains can be cross-linked by using different chemicals [9]. The stability of chitosan in acidic solution can be reinforced and improved. Furthermore, cross-linking can enhance chitosan mechanical resistance, pore size, hydrophilicity, and prevention of swelling [14].

The nature of a cross-linker plays a key role in the adsorption performance of chitosan-based adsorbents. A cross-linking reaction involves the functional groups of the adsorbent responsible for the adsorption of adsorbate molecules; these functional groups reduce the adsorption capacity. Moreover, cross-linking decreases the accessibility of the adsorbate molecules to the adsorption sites, leading to decreased adsorbate uptake by the adsorbents [15]. Therefore, the use of a proper cross-linking agent can help produce a desirable adsorbent. Among the cross-linking agents, epoxy compounds have received increasing attention due to their unique properties that contrast those of other cross-linkers in several ways. Compared with other cross-linkers, such as glutaraldehyde, epoxy compounds possess higher water solubility, hydrophilicity, and interaction ability with both amine and hydroxyl groups. In addition, the epoxy group has an oxygen arm that can work as a flexible joint in the cross-linking bridge, in contrast to the carbon arm of the aldehyde groups in glutaraldehyde that are mechanically stiff joints [16]. The typical cross-linkers having epoxy groups reported earlier include epichlorohydrin and ethylene glycol diglycidyl ether; however, both cross-linkers have poor solubility in water, which is an obstacle to their use [17].

This study aims to use 1,2:7,8-diepoxyoctane (DEO) as a new and highly water soluble diepoxy cross-linker for decreasing weight loss,

improving acid stability, and enhancing Cr(VI) uptake of chitosan beads under acidic conditions. DEO has two epoxy groups located at both ends of each molecule and is thus expected to exhibit high reactivity. For this type of cross-linking agent, the opening of the epoxy groups and the interaction with the functional groups of chitosan can lead to a cross-linking reaction. To the best of our knowledge the use of DEO as a cross-linker agent for crosslinking of chitosan based adsorbents has not been applied. This gap in knowledge motivated us to prepare a novel crosslinked chitosan beads for adsorption of Cr(VI). To achieve this objective, the chitosan beads were crosslinked using DEO. The main conditions of crosslinking treatment, such as temperature, pH, time and DEO concentration, on stability of chitosan on acidic condition were investigated. The adsorption behavior including adsorption kinetics, isotherms, and pH effect of Cr(VI) on the cross-linked chitosan beads were studied. Moreover, the prepared beads were characterized to elucidate the adsorption behavior. Finally, the regeneration and reuse of this adsorbent was evaluated.

## 2. Materials and methods

### 2.1. Materials

Medium molecular weight CS (75–85% deacetylated), 1,2,7,8-diepoxyoctane (97%) and diphenylcarbazine were obtained from Sigma–Aldrich, Co. Sodium hydroxide (NaOH), acetic acid, and chromate potassium were all purchased from Beijing Chemical Works. All the chemicals were of analytical grade. The chemicals were used directly without further purification.

### 2.2. Adsorbent preparation

The chitosan solution was prepared by dissolving 1.5 g of chitosan flakes in 100 mL of 1% (v/v) acetic acid solution in a magnetic stirrer for 5 h. Chitosan hydrogel beads were prepared by adding chitosan solution dropwise into 2 mol/L NaOH solution. The mixture of chitosan beads and NaOH solution was then continuously stirred slowly overnight to neutralize the acetic acid. The beads were then separated from the NaOH solution and washed using deionized water to remove NaOH until a natural pH was obtained. They were then stored in deionized water for future use. The DEO solution was prepared by mixing the DEO in NaOH solution.

Cross-linking treatment was performed by immersing the prepared chitosan beads into the DEO solution under stirring at the desired time and temperature. After the cross-linking reaction, the cross-linked beads were washed using deionized water and dried at 50 °C for 24 h. To study the effect of NaOH concentration, cross-linking treatment was conducted in NaOH solutions at different pH values ranging from 8 to 14. The effect of DEO concentration was assessed by carrying out the cross-linking treatment at 50 °C using the desired amounts of DEO (0, 2, 4, 6, 8, and 10 g/L). To evaluate the effect of temperature and time, cross-linking treatment was performed at different temperatures (30 °C, 40 °C, 50 °C, 60 °C, 70 °C and 80 °C) and different time (from 1 to 10 h).

### 2.3. Characterization

The Fourier transfer infrared spectroscopy (FT-IR) spectra data of the cross-linked chitosan beads were recorded using FTIR (FT-IR NEXUS) in the range of 500–4000  $\text{cm}^{-1}$ . A scanning electron microscope (SEM) (Phenom Prox-Phenomword) was used to study the surface morphology of the prepared beads. An automated gas adsorption analyzer (Quantachrome, autosorb-iQ, USA) was employed to measure the textural property of the beads. Thermogravimetric analysis (TGA) was carried out by a METTLER-TOLEDO TGA/DSC 1 STAR System from 25 °C to 600 °C in  $\text{N}_2$  environment. The X-ray diffraction (XRD) measurements of CS and CS-DEO beads were determined using a D/MAX-RB (Rigaku) X-ray diffractometer (Rigaku corp., Japan) equipped with a

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