Journal of Molecular Liquids 170 (2012) 25–29

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# Cr(VI) adsorption on an improved synthesised cross-linked chitosan resin

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ARTICLE INFO

*Article history:*
Received 26 December 2011
Received in revised form 17 March 2012
Accepted 20 March 2012
Available online 4 April 2012

*Keywords:*
Chitosan
Crosslink
Cr(VI)
Adsorption isotherm
Modelling

ABSTRACT

An improved drop-sphere-forming method to synthesise chitosan resin was investigated as a possible means to remove Cr(VI) from wastewater. Epichlorohydrin was used to cross-link the resin to enhance its rigidity. The Cr(VI) adsorption capacity of the cross-linked chitosan was investigated under the influence of time, pH, temperature and the initial concentration of Cr(VI). The pH was found to be the main factor determining adsorption capacity. After 2 h of adsorption at pH = 3.0 and 25 °C with an adsorbent dosage of 2 g $L^{-1}$, the maximum adsorption capacity was reached for an initial Cr(VI) concentration of 30 mg $L^{-1}$. The equilibrium adsorption experiments corresponded well with the Langmuir isotherm ($r^2 > 0.99$). The pseudo-first-order and pseudo-second-orders were applied to describe the kinetics of the process. Compared with a pseudo-first-order kinetic model, the pseudo-second-order kinetic model exhibited a better correlation with the experimental data ($r^2 > 0.99$).



## 1. Introduction

Chromium (Cr), a potential carcinogen, often causes both short-term and long-term adverse effects to humans, animals and plants [1]. Chromium is widely used in the chemical industry and acts as an important raw material in electroplating, leather tanning, cement preservation, paints, pigments, textiles, steel fabrication and canning industries [2]. In the production process, more and more pollution incidents have emerged that are associated with hexavalent chromium contamination. Therefore, the removal of chromium from waste products is an important concern around the world. Chromium exists in two main forms in aqueous systems: trivalent and hexavalent forms, but the latter is of greater concern because of its toxicity [3]. Cr(VI) is a highly toxic material that has been linked to cancer in humans following long-term inhalation and is also toxic to aquatic life, even at relatively low concentrations [4]. The maximum permissible limit of Cr(VI) in wastewater as recommended by the World Health Organization is 0.005 mg $L^{-1}$ [5]. The most commonly used techniques for Cr(VI) removal focus on physical–chemical methods including filtration, chemical precipitation, adsorption, electrodepositing and membrane systems [6]. However, conventional methods are often not economical and suffer from low efficiency. Consequently, there is an urgent need to find an effective method to remove Cr(VI) from wastewater. Recently, biosorption has emerged as an effective process to remove heavy metals [7], and biosorbents made from various agricultural wastes (e.g. maize bran, sugar beet pulp, microbial biomass, tea and chitosan) have been demonstrated [8].

Chitin, as one of the most abundant biopolymers in nature, is a main component of crustacean shells [9]. Chitosan, a product of chitin deacylation, is an economical and attractive biosorbent [10–12]. Moreover, chitosan can remove metal cations efficiently in acidic or near-neutral solutions because it contains numerous amino groups [13]. The conventional method of synthesising chitosan resin is the reversed suspension cross-linking reaction. In this experiment, an improved drop-sphere-forming method was developed to synthesise chitosan resin. Furthermore, wastewater containing Cr(VI) was prepared and treated by the synthesised resin. The main factors affecting adsorption capacity (including pH, temperature, and initial concentration of Cr) were also investigated.

## 2. Materials and methods

### 2.1. Materials and reagents

Chitosan with a deacetylation degree of approximately 92% was obtained from Sinopharm, epichlorohydrin was from Reagent Chemicals, acetic acid for dissolving the chitosan was from Shuanghuan, and acetone for preparing the diphenylcarbazide solution was from Haohua. All other regents were from Kermel. Potassium dichromate was dissolved in water simulate chromium wastewater. Sodium hydroxide was used to synthesise chitosan resin. Finally, diphenylcarbazide was used as the chromogenic reagent.

### 2.2. Instruments and apparatus

The chitosan resin was synthesised in an 85-2 digital constant temperature magnetic stirrer. The concentration of Cr(VI) in solution was assessed by a 722S spectrophotometer operating at 540 nm.

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doi:10.1016/j.molliq.2012.03.016

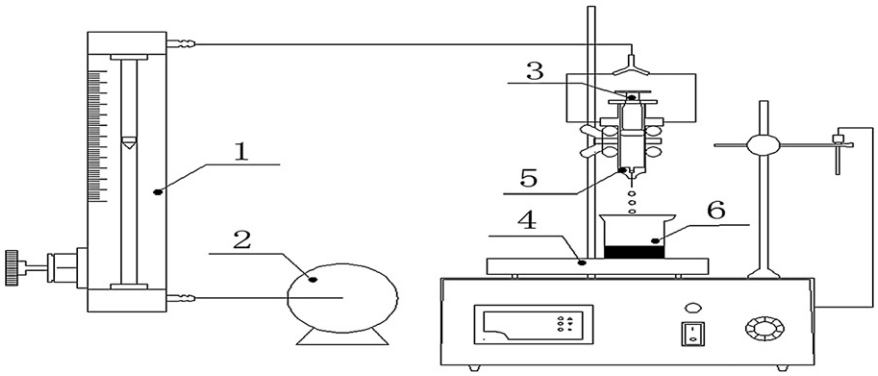


**Fig. 1.** Schematic synthesis processes of chitosan resin, (1) rotameter, (2) air pump, (3) syringe, (4) magnetic stirrer, (5) glass sleeve and (6) beaker.

Scanning electron microscopy (SEM) images were obtained at 15.0 kV on a cold field scanning electron microscope after gold plating. Infrared spectra (4000–400 $cm^{-1}$) were recorded on a WQF-510 FT-IR spectrometer. The specific surface area and pore volume of the chitosan resin were measured with a NOVA4200e surface area analyser.

### 2.3. Synthesising chitosan resin

Synthesising the chitosan resin required two steps:

(i) Preparation of the chitosan resin. Three grammes of chitosan was added into 100 mL of 2% (v/v) acetic acid and mixed until the chitosan dissolved completely. After standing at room temperature for 12 h, the viscous solution was added into the improved chitosan resin synthesis device (Fig. 1). The solution was added dropwise to a sodium hydroxide solution (2.5 M) through the device's syringe needle under the pressure of a piston. The diameter of the resin was controlled by the air velocity around the syringe needle, and the air velocity was controlled by a rotameter. The chitosan resin was collected from the alkaline solution and washed with distilled water several times until the wash water became neutral. Then the chitosan resin was stored in distilled water.

(ii) Reaction with epichlorohydrin. Five millilitres of wet chitosan resin obtained in step (i) was put in 20 mL of distilled water and then added to 1 mL of epichlorohydrin. This mixture was stirred for 6 h at 80 °C. The cross-linked chitosan resin was filtered off and washed several times with distilled water and then dried for 4 h at 105 °C.

### 2.4. Solutions

A stock solution (30 mg $L^{-1}$) of potassium dichromate ($K_2Cr_2O_7$) was prepared in distilled water for use in the adsorption experiment. HCl (1%) and NaOH (1%) were used to adjust the pH of the solution. $H_2SO_4$ (50%) and $H_3PO_4$ (50%) were used to measure the concentration of Cr(VI).

### 2.5. Adsorption experiment

#### 2.5.1. Effect of time

After 0.05 g of dry resin was put into a flask with 50 mL of Cr(VI) solution (30 mg $L^{-1}$), the flask was shaken for 3 h on a THZ-82 constant temperature shaker at room temperature [14]. One millilitre of the sample (the solution of potassium dichromate) was extracted at different time intervals, and the residual concentration of the Cr(VI) was measured spectrophotometrically at 540 nm using the diphenylcarbazide method. The adsorbed capacity of the cross-linked chitosan resin for Cr(VI) was calculated as follows [15]:

$$q_t = V \times (C_0 - C)/m$$

where $C_0$ (mg $L^{-1}$) is the initial concentration of the Cr(VI) solution, C (mg $L^{-1}$) is the concentration of the solution, which was taken at each time interval, V (L) is the volume of the solution in the flask, and m (g) is the weight of the resin added into the flask.

#### 2.5.2. Effect of pH

Under a controlled pH environment, the adsorption of chromate anions by the cross-linked chitosan resin was tested. In this study, 0.05 g of dry resin was added to a series of flasks with 50 mL of potassium dichromate solution (30 mg $L^{-1}$) supplying the Cr(VI) ion. The specified pH was obtained using HCl or NaOH. The contents of the flasks were shaken for 2 h on a THZ-82 constant temperature shaker at 25 °C [16]. The residual concentration of the Cr(VI) ion was measured according to the method described above.

#### 2.5.3. Effect of temperature

Complete adsorption isotherms were obtained by soaking 0.05 g of dry resin in a series of flasks. Fifty millilitres of potassium dichromate

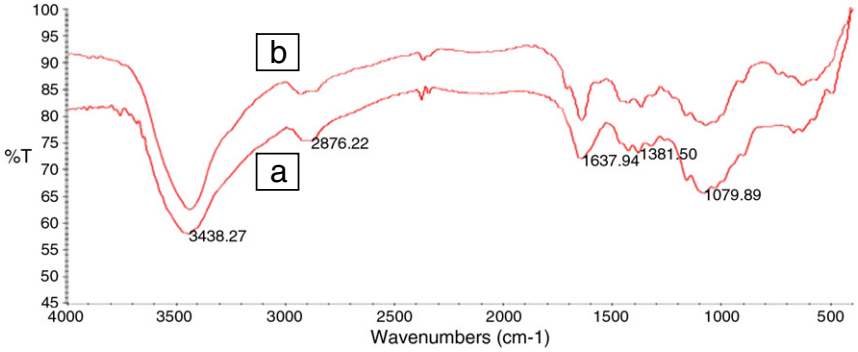


**Fig. 2.** FTIR spectra for the chitosan resin before (a) and after (b) crosslinked chitosan resins.