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Technical Note

REMOVAL OF COBALT IONS FROM AQUEOUS SOLUTION USING CHITOSAN GRAFTED WITH MALEIC ACID BY GAMMA RADIATION

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Chitosan was modified by gamma radiation–induced grafting with maleic acid and then used for the removal of cobalt ions from aqueous solutions. Chitosan-g-maleic acid was characterized by FT-IR. The effect of the dose (1–5 kGy) and monomer concentration (0.3–1.3%, m/v) on the grafting ratio was examined. The adsorption kinetics and isotherms were also investigated. The results showed that the optimal dose for grafting was 2 kGy. When monomer concentration was within the range of 0.3–1.3% (m/v), the grafting ratio increased almost linearly. For the adsorption of cobalt ions by chitosan-g-maleic acid beads, the pseudo second-order kinetic model ($R^2 = 0.99$) and Temkin isotherm model ($R^2 = 0.96$) were able to fit the experimental data reasonably well. The equilibrium adsorption capacity of cobalt ions increased from 2.00 mg/g to 2.78 mg/g after chitosan modification.

1. Introduction

^{60}Co is a typical radioisotope that is common in the wastewater of nuclear power plants. Because of its radioactivity and long half-life, it can do prolonged damage to the ecosystem. Various methods have been studied to remove cobalt ions from wastewater [1–5]. Adsorption is commonly used to remove it from aqueous solutions [6,7]. With their great biocompatibility, nontoxicity, and availability abundance, natural biopolymers have been received increasing attention in recent years [8–10].

Chitosan is the deacetylation product of chitin, which is the second most abundant natural biopolymer. With large amounts of amino and hydroxyl functional groups, chitosan is a good adsorbent for heavy metal ions [11]. In addition, modifying chitosan is an important way to improve its properties and increase its adsorption capacity [12–14].

Although there are many ways to modify chitosan, grafting is one of the most important methods. Various materials have been studied for the purpose of increasing chitosan's adsorption capacity of heavy metal ions [10,15]. When grafting was achieved, new functional groups were incorporated into the backbone of chitosan; this not only changed the pH range for the adsorption of metal ions but also added more adsorption sites. Different functional groups, including carboxylate, hydroxyl, sulfate, phosphate, amide, and amino, in the polymeric materials are responsible for metal adsorption via coordination or electrostatic attraction [6,16–18]. So far, our group has by various methods successfully modified chitosan to increase its adsorption capacity for removal of heavy metals and radioisotopes from aqueous solutions [15,18–22].

Compared with conventional chemical routines, the radiation method, in which neither chemical initiators nor cross-linkers are needed, has several advantages. For example, the products are free of toxic additives. The radiation-induced modification of chitosan through grafting with either vinyl or acrylate monomers has been investigated [23–26]. Considering that chitosan is already rich in amino groups, it is interesting to incorporate carboxyl groups into chitosan [27–29]. Chitosan modification via grafting with maleic acid has not been studied yet; maleic acid, which is rich in carboxyl groups, may be useful to improve the adsorption of heavy metal ions.

The objective of this study was to explore the feasibility of using gamma radiation to graft maleic acid onto chitosan and to evaluate the performance of the resulting material for cobalt ion adsorption.

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2. Materials and methods

2.1. Chemicals

Chitosan (molecular weight: 130 kDa, degree of deacetylation: 90%), acetic acid, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. Maleic acid and cobalt chloride were purchased from Aladdin. All chemicals were used as received without further purification.

2.2. Radiation grafting

Chitosan powder and maleic acid were dissolved in 1% acetic acid solution (v/v) and irradiated under a certain dose rate (31.98 Gy/min) for a given time at the Institute of Nuclear and New Energy Technology (INET), Tsinghua University, Beijing, China. After irradiation, the pH of the grafted solution was adjusted to 10–12 by adding 15% NaOH solution (m/v). The precipitate was separated by filtration and washed with distilled water several times to remove unreacted monomers and homopolymer. Then, it was dried in an air oven at 50°C to a constant weight. The percentage of grafting was calculated by the following equation:

$$\text{grafting ratio}(\%) = (W_2 - W_1)/W_1 \tag{1}$$

where W_1 and W_2 are the weights of chitosan and grafted chitosan, respectively.

2.3. Preparation of chitosan beads

Grafted chitosan (1 kGy and 1% m/v monomer concentration) was dissolved in 6% acetic acid (v/v) to form a mixed solution (5%, w/v) and stirred for 3 hours. After bubbles arising from the agitation had disappeared, the mixed solution was injected into 15% NaOH solution (m/v). The chitosan-g-maleic acid beads were washed with distilled water to eliminate any remaining sodium hydroxide. Then they were dried in an air oven at 50°C to a constant weight.

The preparation of chitosan beads was similar, except that the grafted chitosan was replaced with chitosan.

2.4. Co^{2+} adsorption experiments

Co^{2+} adsorption experiments were carried out by adding chitosan-g-maleic acid or chitosan beads to $CoCl_2$ solution at 26°C; solution was then shaken at a rate of 150 rpm for a given time. The adsorption capacity (q_t) and equilibrium adsorption capacity (q_e) can be calculated by the following equations:

$$q_t = (C_0 - C_t)V/m \tag{2}$$

$$q_e = (C_0 - C_e)V/m \tag{3}$$

where C0, Ce, and Ct are the initial concentration, equilibrium concentration, and concentration of cobalt ions at time t, respectively; V is the volume of the solution; m is the mass of the dry adsorbents.

2.5. Analytical methods

To study the structure of the grafted polymer, FT-IR spectra were obtained by a VERTEX 70 FT-IR (Bruker). The concentration of cobalt ions was measured using a ZA3000 Polarized Zeeman Atomic Absorption Spectrophotometer (HITACHI, Japan).

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectra are shown in Fig. 1. The main characteristic bands of chitosan were 3,413 cm^{-1}, 2,877 cm^{-1}, and 1,659 cm^{-1}, which were assigned to O-H stretching vibration, polymer backbone C-H stretching vibration, and N-H bending vibration, respectively [24,30,31]. In addition to the characteristic bands of chitosan, the spectrum of chitosan-g-maleic acid exhibited newly added bands at 1,572 cm^{-1} and 1,432 cm^{-1}, which may be due to the COO asymmetrical stretch vibration and COH in-plane bending vibration in carboxyl groups, respectively. Besides this, the disappeared band at 1,659 cm^{-1} in the chitosan-g-maleic acid spectrum indicated that maleic acid might be connected to the amino group [27].

3.2. Effect of dose

The effect of the dose on grafting is depicted in Fig. 2. The concentrations of maleic acid and chitosan were both 1% (m/v). With increasing of the dose from 1 kGy to 2 kGy, the grafting percentage increased at the same time. With further increases of the dose, an obvious decrease in the grafting ratio was observed. As is well-known, graft polymerization is initiated by radicals produced by irradiation and radical reactions [32]. Thus, the grafting yield depended on the number of radicals formed in the system. With the increase of the absorbed dose, the radicals formed in the system increased, which resulted in the increase of the grafting yield. At lower doses, the increase of the grafting percentage may be due to the increasing concentration of free radicals formed in the polymeric solution. It has been reported that the grafting process and the polymerization reaction take place at the same time during irradiation [33]. Beyond a certain dose value (2 kGy), the rate of homopolymerization may exceed that of the grafting reaction, resulting in a decrease in the grafting percentage. A similar trend was observed by Casimiro et al. [34].

3.3. Effect of monomer concentration

The effect of the monomer concentration on the grafting ratio was studied at 2 kGy and 1% chitosan (m/v); the results are presented in Fig. 3. It can be seen that the grafting percentage

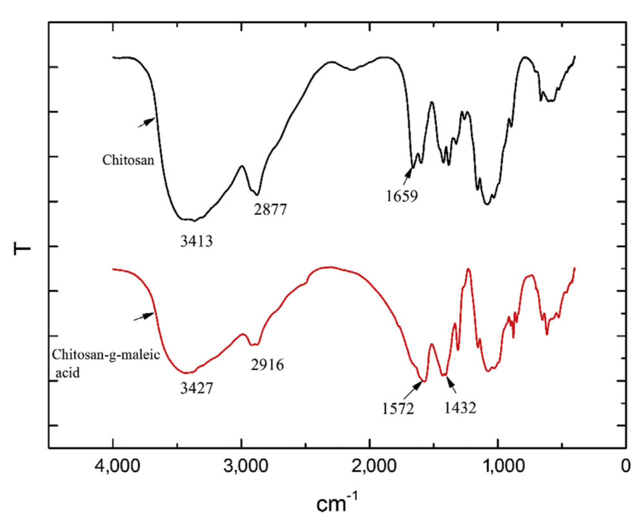

Fig. 1. FT-IR spectra of chitosan and chitosan-g-maleic acid.

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