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# Synthesis and environmental application of zirconium–chitosan/graphene oxide membrane

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## ABSTRACT

A zirconium–chitosan (CTS)/graphene oxide (GO) membrane (Zr–CTS/GO) was synthesized by the immobilization of Zr(IV) on CTS and GO. Scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS), Attenuated total reflection Fourier-transform infrared spectroscopy (ATR–FTIR), and X-ray diffraction (XRD) patterns were applied to investigate the possible synthesis mechanism. ATR–FTIR results showed that the active epoxy and carboxyl groups in graphene reacted with the amino groups in CTS. XRD results demonstrated that stacked GO sheets were retained in the Zr–CTS/GO composite. The thermal stability and dynamic mechanical properties of the membrane were examined by thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA). The results showed that the thermal stability and mechanical strength of Zr–CTS/GO were enhanced compared with that of CTS and GO. The Zr–CTS/GO membrane was applied for the removal of anions from groundwater collected in Inner Mongolia. The membrane could effectively remove fluoride within a wide temperature scope, from 15 °C to 40 °C, and reached adsorption equilibrium within 60 min. Zr–CTS/GO presented high affinities toward fluoride, bicarbonate, and sulfate.

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## 1. Introduction

In recent years, graphene oxide (GO) has drawn increasing attention and has been widely used in many fields, such as medicine, environmental applications, and electrode modification, due to its special structure and properties [1–3]. GO, a graphene derivative, has a layered structure with a very large surface area of 2630 m<sup>2</sup>/g [4]. GO possesses numerous epoxy and hydroxyl groups on its graphitic backbone and carbonyl or carboxyl groups at the edges of the oxidized graphene sheet, which confer unique characteristics suitable for environmental applications [5]. Moreover, GO can enhance the strength as well as the electrical conductivity of polymer composites [6]. On the other hand, chitosan (CTS) has a large number of hydroxyl and amino groups and has the advantages of environmental friendliness, resource abundance, and outstanding membrane-forming abilities [7]. However, the application of CTS is limited by its degradation and release in acidic environments [8].

Many studies focusing on GO/CTS complex materials have been reported. The modification of GO with CTS can not only effectively

improve the dispersion state of GO but also simultaneously reduce and noncovalently modify it while expanding the pH scope of the application of CTS [7]. It is reported that GO/CTS complex materials show high adsorption capacity toward metal ions such as copper, lead, chromium, and mercury, as well as organic dyes such as methyl blue, acid orange 7 and hydroquinone [8–13]. As yet, GO/CTS complex has not been applied to remove anions in water. To widen the application of GO/CTS complex for water purification, modifications should be made to improve the adsorption capacity of the complex toward anions, such as fluoride and sulfate ions, as well as to enhance its mechanical strength.

To solve these problems, Zr(IV) was employed to modify GO/CTS complex in this study because Zr(IV) is highly electropositive and has a strong affinity for highly electronegative fluoride ions. Zr(IV) ions are oxophilic; thus, they can strongly coordinate to the oxygen-containing functional groups on the surfaces and edges of GO [14]. It is reported that Zr(IV) ions in metal complexes can attract fluoride ions and that the displacement of –OH in Zr complexes by fluoride can occur [15].

This study aims (1) to develop a zirconium–CTS/GO membrane (Zr–CTS/GO) by loading zirconium oxychloride onto CTS/GO complex, thus improving the adsorption capacity of CTS/GO for anions in groundwater, (2) to examine the thermal and mechanical

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properties of the membrane, and (3) to investigate the potential use of the membrane for environmental applications.

## 2. Materials and methods

### 2.1. Reagents

CTS (deacetylation degree 80.0% to 95.0%) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (China). GO was purchased from Hengqiu Tech. Inc. (China). 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), N-hydroxyl succinimide (NHS), Sodium fluoride (NaF), zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ), glycerin, and acetic acid were also purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (China). The groundwater was collected from a city in Inner Mongolia. The experimental water sample was synthesized by adding sodium fluoride to the groundwater.

### 2.2. Preparation of Zr-CTS/GO

To activate the carboxyl groups of GO, 0.05 M NHS and 0.05 M EDC were added to 0.75% GO dispersion and the mixture was sonicated at room temperature for 2 h. Then, 2.5% CTS and 2% acetic acid were added, and the mixture was continuously stirred for 0.5 h. After 2%  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was added (corresponding to 0.56% Zr(IV)), the mixture was stirred for another 20 min. Next, 5% glycerin was added to increase the flexibility of the membrane and enhance its mechanical strength. The mixture was then poured onto a glass plate and oven-dried at 65 °C for 4 h. The Zr-CTS/GO membrane was obtained by this process.

### 2.3. Adsorption experiments

Adsorption experiments were conducted to study the performance of Zr-CTS/GO for the removal of fluoride from fluoride-contaminated groundwater by reacting 50 ml groundwater in conical flasks with 0.15 g Zr-CTS/GO membrane. The conical flasks were allowed to stand for 1 h at room temperature. The water quality parameters of the fluoride contaminated groundwater were measured before and after fluoride adsorption.

### 2.4. Analytical methods

The fluoride concentration was measured using a fluoride ion selective electrode (F2021, DKK-TOA, Japan). The concentrations of chloride and sulfate were measured using ion chromatography (ICS900, Dionex, USA). Concentrations of major cations and trace elements were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectroscopy (ICP-MS) (7500C, Agilent, USA), respectively. Total organic carbon (TOC) was determined using a TOC analyzer (multi N/C 2100, Analytik Jena, Germany). Surface morphological analysis was conducted using scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS) (SSX-550, Shimadzu, Japan). Attenuated total reflection Fourier-transform infrared spectroscopy were recorded (ATR-FTIR) (Vertex 70 V, Bruker, Germany) from 4000 to 400  $\text{cm}^{-1}$  at a resolution of 0.4  $\text{cm}^{-1}$ . The crystalline structure of Zr-CTS/GO was determined by X-ray diffraction (XRD) patterns obtained with a step time of 10 s and  $2\theta$  of 0.02° (D8 Advance, Bruker, Germany). The thermal properties were investigated using thermogravimetric analysis (TGA) (Q500, TA Instruments, USA) from 18 °C to 900 °C with a heating rate of 10 °C per minute under a nitrogen (60 ml/min) environment. The dynamic mechanical properties of the Zr-CTS/GO membrane materials were measured

on a dynamic mechanical thermal analyzer (DMTA) (Q800, TA Instruments, USA) at room temperature (25 °C). The stress-strain curve tests were conducted in the stretch mode; the dimensions of the membrane samples were ca. 10.50 × 2.00 × 0.08  $\text{mm}^3$ . The creep curve tests were conducted using the DMA creep module in the stretch mode; the dimensions of the membrane samples were ca. 10.63 × 2.00 × 0.09  $\text{mm}^3$ , and the creep data was obtained at the same loading and unloading rate, with a hold time of 60 min, an unloading time of 60 min, and a force of 1.7 MPa.

## 3. Results and discussion

### 3.1. Characterization

The Zr-CTS/GO membrane is black with a thickness of 80  $\mu\text{m}$ . Fig. 1 showed a photograph (Fig. 1(A)), SEM images (Fig. 1(B) and (C)) depicting the surface and cross-section morphology of Zr-CTS/GO. The photograph showed that the surface of Zr-CTS/GO appeared crumpled and coarse. A similar result was observed in the SEM image ( $\times 155$ ), and the surface morphology was found to be uniform. The surface morphology was similar to that of the graphene oxide-chitosan nanocomposite films reported by Zhang et al. [10]. Stacked sheets structure was observed in cross-section of Zr-CTS/GO, indicating that the GO structure remained in Zr-CTS/GO so that Zr-CTS/GO had huge specific surface area. In addition, the presence of Zr element was confirmed by EDS with an atom percentage (AT%) of 2.97%, indicating that the Zr(IV) was wrapped within the CTS and GO complex.

Fig. 2(A) showed the ATR-FTIR spectra of CTS, GO, CTS/GO, and Zr-CTS/GO. The broad band at 3426  $\text{cm}^{-1}$  was assigned to the stretching vibrations of O–H superimposed on the N–H stretching band,  $\text{H}_2\text{O}$ , and intermolecular hydrogen, while the band in the region of 2857–3006  $\text{cm}^{-1}$  was assigned to C–H stretching vibrations [7]. The spectrum of CTS showed characteristic peaks at 1635, 1397, and 1086  $\text{cm}^{-1}$ , which were attributed to the vibrations of N–H in  $-\text{NH}_2$ , C–N, and C–O–C, respectively [8,9]. For GO, the peaks in the region between 1500 and 1800  $\text{cm}^{-1}$  were related to the overlap vibrations of C=C and C=O in the carboxyl and carbonyl groups; the peaks centered at 1405 and 1083  $\text{cm}^{-1}$  were due to the presence of C–O–C vibrations of epoxy or alkoxy groups and the C–H symmetric bending vibration in  $-\text{CHOH}$ , respectively [10,11]. Compared with CTS and GO, the newly emerged peaks at 921 and 857  $\text{cm}^{-1}$  for CTS/GO corresponded to O–H out-of-plane deformation and C–H out-of-plane deformation, respectively [12]. The appearance of a band at 1644  $\text{cm}^{-1}$  was assigned to the vibration of C=O in  $-\text{NHCO}-$ , and the primary amine groups ( $-\text{NH}_2$  in CTS) transformed into secondary amine groups ( $-\text{NH}-$  at 1578  $\text{cm}^{-1}$  in CTS/GO), indicating the occurrence of an epoxy-amino reaction [13]. Furthermore, the decrease in the intensity of the C–N band may be attributed to the formation of C–N–C in the epoxy-amino reaction; C–N–C is more stable than  $-\text{CNH}_2$  in CTS. In addition, the decreased intensity of the epoxy C–O–C band in CTS/GO also indicated that the epoxy groups in GO were involved in this process. A weak vibration band at 1088  $\text{cm}^{-1}$  was related to Zr=O from zirconyl groups, demonstrating that  $\text{ZrOCl}_2$  was complexed by CTS/GO [14], with the result of EDS that the Atomic Percentage (AT%) of Zr was 2.97%. The weak vibration of Zr=O was due to the low content of Zr(IV) added.

The XRD patterns of CTS, GO, CTS/GO, and Zr-CTS/GO are presented in Fig. 2(B). The peaks at  $2\theta$  of 14.34° and 19.9°, which were assigned to hydrated and anhydrous crystals, respectively, correspond to the crystalline structure of CTS [16]. The high crystallinity of CTS is generally due to intermolecular and intramolecular hydrogen bonds [17]. The XRD pattern of pure GO showed a peak at  $2\theta$  of 10.2°, which corresponds to the crystalline structure of GO, indicating that the interplanar distance between GO sheets was

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