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Adsorption of nitrate from aqueous solution by magnetic amine-crosslinked biopolymer based corn stalk and its chemical regeneration property

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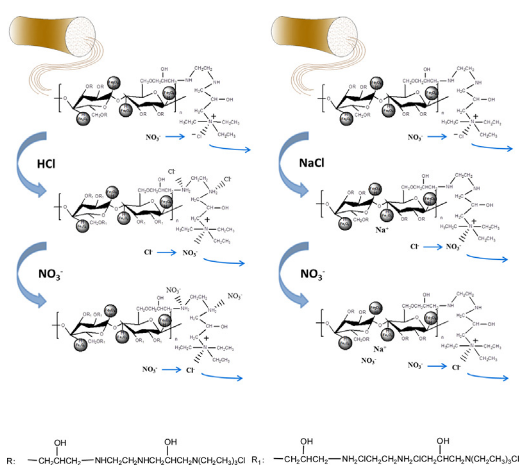
HIGHLIGHTS

- Magnetic amine-crosslinked bio-adsorbent was prepared for nitrate uptake.
- The characters of adsorbent were determined by VSM, TGA, XRD, SEM, TEM, FT-IR and XPS.
- This novel bio-adsorbent could achieve rapid separation from effluents.
- Chemical regeneration of the saturated magnetic bio-adsorbent was conducted.
- The adsorption followed the pseudo second order model and Langmuir model.

GRAPHICAL ABSTRACT

Scheme of mechanism for HCl and NaCl regeneration of MAB-CS.



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ABSTRACT

A novel adsorbent of magnetic amine-crosslinked biopolymer based corn stalk (MAB-CS) was synthesized and used for nitrate removal from aqueous solution. The characters and adsorption mechanisms of this bio-adsorbent were determined by using VSM, TGA, XRD, SEM, TEM, FT-IR and XPS, respectively. The results revealed that the saturated magnetization of MAB-CS reached 6.25 emu/g. Meanwhile, the studies of various factors indicated that this novel magnetic bio-adsorbent performed well over a considerable wide pH range of 6.0~9.0, and the presence of PO_4^{3-} and SO_4^{2-} would markedly decrease the nitrate removal efficiency. Furthermore, the nitrate adsorption by MAB-CS perfectly fitted the Langmuir isotherm model (R^2 = 0.997–0.999) and pseudo second order kinetic model (R^2 = 0.953–0.995). The calculated nitrate adsorption capacity of MAB-CS was 102.04 mg/g at 318 K by Langmuir model, and thermodynamic study showed that nitrate adsorption is an spontaneous endothermic process. The regeneration experiments indicated its merit of regeneration and stability with the recovery efficient of

Abbreviations: CS, corn stalk; MB-CS, magnetic biopolymer based corn stalk; MAB-CS, magnetic amine-crosslinked biopolymer based corn stalk.

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118∼147%. By integrating the experimental results, it was found that the removal of nitrate was mainly via electrostatic attraction and ion exchange. And this novel bio-adsorbent prepared in this work could achieve effective removal of nitrate and rapid separation from effluents simultaneously.

1. Introduction

Nitrate contamination of water resource has been frequently present in many countries. Concentrations of the harmful nitrogen-containing compounds, including ammonia, nitrate and nitrite are frequently found in drinking water and various types of wastewater [1]. Sources of these compounds can be attributed to the improper treatment of industrial wastewater and extensive use of nitrogen fertilizers. Furthermore, high concentrations of nitrate, which is a potential human health hazard, would cause the health problem known as blue baby syndrome (methemoglobinemia) [2]. Meanwhile, the harmful nitrite ions transformed from nitrate ions in the human body is a precursor to the carcinogenic nitrosoamine. So, the World Health Organization (WHO) has set an acceptable concentration level of 25 mg/L for NO_3^- in drinking water [3]. In China, the total concentration of NO_3-N is also limited to 20 mg/L, as defined by the notification of the Environment Ministry in 2007.

Different technologies have been developed to remove NO_3^- from wastewater, such as nitrification, denitrification, adsorption, reverse osmosis, ammonia stripping, chemical coagulation, filtration and electrodialysis [4]. However, the conventional technologies, including reverse osmosis, catalytic and biological processes are relatively costly [5]. Therefore, adsorption has been well studied due to its simplicity, sludge free operation, easiness in handling and availability of various adsorbents. In general, a number of materials, including biosorbents, natural sorbents, miscellaneous adsorbents and agricultural by-products, could be used for adsorption process. Among them, adsorbents based on agricultural by-products have been attracted attention because of the special features of biodegradability, biocompatibility and renewability [6,7]. However, the conventional adsorbents based on agricultural by-products are too light and small to be separated except by high speed centrifugation or filter. Fortunately, the adsorbents anchoring magnetic iron oxide in the polymer matrix exhibit the high settlement rates. So, the technology of magnetization for biosorbent could be considered as an efficient way to purify the polluted water.

In this work, a novel magnetic amine-crosslinked biopolymer based corn stalk (MAB-CS) has been synthesized successfully and used to remove nitrate from water. Physicochemical properties of the MAB-CS have been confirmed by VSM, TGA, XRD, SEM, TEM, FT-IR and XPS. At meantime, to fully understand the adsorption behavior, the effects of pH, adsorbent dosage, contact time, temperature, co-anions and reusability on adsorption capacity were also evaluated. Furthermore, the experimental data were evaluated using the pseudo-first-order, pseudo-second-order and intraparticle models. The adsorption thermodynamics of nitrate ions were investigated by Langmuir, Freundlich and Temkin models, respectively. Our results demonstrate that MAB-CS exhibits tremendous potential for effective removal of nitrate and fast separation performance in aqueous media simultaneously.

2. Materials and methods

2.1. Biopolymer and reagents

The raw corn stalk used in this study was obtained from Zhouping, Shandong province, China. It was washed with deionized water, dried at 100 °C by the oven and smashed to pieces with practical size of 20∼500 μm. All chemicals including $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, NaOH, HCl, $KNO_3 \cdot H_2O$, $K_2SO_4 \cdot H_2O$, $K_3PO_4 \cdot H_2O$, KCl, NaCl, $NH_3 \cdot H_2O$, $H_6N_2O_3S$, triethylamine, *N*,*N*-dimethylformamide, epichlorohydrin, ethylenediamine and diphenylcarbazide were purchased from Tianjin Damao Chemical Reagents Co. (Tianjin, China). The stock NO_3^- solution with concentration of 1000 mg/L was prepared by dissolving 1.631 g KNO_3 in 1000 mL distilled water.

2.2. Preparation of magnetic amine-crosslinked biopolymer based corn stalk

The novel bio-sorbent was prepared by two step reactions. First, 12.17 g $FeCl_3 \cdot 6H_2O$ and 6.26 g $FeSO_4 \cdot 7H_2O$ were respectively dissolved in 300 mL deionized water. Then 3.0 g of raw corn stalk (CS) was suspended in the 300 mL mixed solution with Fe^{3+} and Fe^{2+} at 70 °C for 10 min. The reaction system was kept in an oxygen-free condition by purging with N_2. Then 10 mL of $NH_3 \cdot H_2O$ (25%) was added into the flask and the mixture was stirred (300 rpm) at 70 °C to keep it as sufficient suspension. After 4 h of stirring, the products were washed with deionized water, and dried in a vacuum oven at 80 °C for 4 h, which named magnetic biopolymer based corn stalk (MB-CS). Thereafter, *N*,*N*-dimethylformamide (20 mL) and epichlorohydrin (20 mL) were reacted with MB-CS, and the mixture was stirred (300 rpm) for 1 h at 90 °C. Then 6 mL of ethylenediamine was added and stirred (300 rpm) for 1 h, followed by adding 20 mL of triethylamine [7]. Finally, the precipitates were collected by magnetic separation and washed immediately with deionized water for several times. After dried overnight at 104 °C, the products were obtained and named magnetic amine-crosslinked biopolymer based corn stalk (MAB-CS).

2.3. Physicochemical characteristics of MAB-CS

VSM. The magnetic properties of magnetic particles were assessed with a vibrating sample magnetometer (VSM, LDJ9500) at room temperature. TGA. The thermogravimetric analysis of samples were evaluated by an SDT-simultaneous TGA-DTA model, which was carried out in air atmosphere (100 mL/min) at rate of 10 °C/min, and the temperature was between 30 and 800 °C. XRD. Structural characterization of the newly formed biopolymer based adsorbent was collected on a Rigaku D/MAX-YA diffractometer (Cu-Kα radiation at 40 kV and 40 mA). Scans were collected in the 2θ range of 10° to 70° with a step size of 0.01° and a scan speed of 0.5 s per step. SEM, TEM. The morphology of the particles was observed in scanning electron microscope (S4800, Japan) and transmission electron microscopy (FEI Tecnai G20, US). FTIR, XPS. The surface chemical characterizations of the samples were performed using Fourier transform infrared spectroscopy (PerkinElmer "Spectrum BX" spectrometer with pectrum scanned from 400 to 4000 cm^{-1}) and X-ray photoelectron spectroscopy (Thermo ESCALAB 250XI).

2.4. Batch adsorption experiments

In order to clarify the effects of adsorbent dose on NO_3^- adsorption, the batch experiments was carried out in 100 mL glass flask at