



# High-capacity adsorption of dissolved hexavalent chromium using amine-functionalized magnetic corn stalk composites

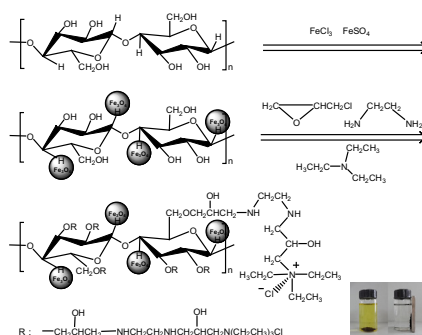
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## HIGHLIGHTS

- The amine-functionalized magnetic bio-sorbent was prepared for Cr(VI) uptake.
- The physicochemical characteristics were measured by XRD, SEM, FTIR, VSM and XPS.
- The optimum pH for high removal efficiency of Cr(VI) was found at 3.0(±0.1).
- The adsorption followed the pseudo second order model and Langmuir model.
- The adsorption process was spontaneous and endothermic.

## GRAPHICAL ABSTRACT



Preparation mechanism of AF-MCS

## ARTICLE INFO

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## ABSTRACT

Easily separable amine-functionalized magnetic corn stalk composites (AF-MCS) were employed for effective adsorption and reduction of toxic hexavalent chromium [Cr(VI)] to nontoxic Cr(III). The saturated magnetization of AF-MCS reached 6.2 emu/g, and as a result, it could be separated from aqueous solution by a magnetic process for its superparamagnetism. The studies of various factors influencing the sorption behavior indicated that the optimum AF-MCS dosage for Cr(VI) adsorption was 1 g/L, and the maximum adsorption capacity was observed at pH 3.0. The chromium adsorption perfectly fitted the Langmuir isotherm model and pseudo second order kinetic model. Furthermore, characterization of AF-MCS was investigated by means of XRD, SEM, TEM, FT-IR, BET, VSM and XPS analysis to discuss the uptake mechanism. Basically, these results demonstrated that AF-MCS prepared in this work has shown its merit in effective removal of Cr(VI) and rapid separation from effluents simultaneously.

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## 1. Introduction

Hexavalent chromium [Cr(VI)] has been extensively applied used in a variety of industries, such as pharmacy, electroplating, tanning, metallurgy, battery, textile and catalyst synthesis. Mean-time, it has drawn much attention because of its toxic and carcin-

ogenic influences on human health. As determined by the National Toxicology Program (NTP), the International Agency for Research on Cancer (IARC), Cr(VI) is a human carcinogen and may cause many problems such as bronchitis, bronchogenic carcinoma, liver damage and ulcer formation (Duranoğlu et al., 2012; Hu et al., 2005). Though American Environmental Protection Agency (EPA) limits the value of Cr(VI) to 0.05 mg/L in aqueous state. Cr(VI) still has been found in industrial effluents of United States with high concentrations of 1–2 mg/L. Therefore, to prevent its deleterious

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impact on the ecosystem and public health, it is necessary to remove Cr(VI) from industrial wastewater before discharging it into inland surface water.

Many treatment technologies such as reduction–precipitation, electrolytic recovery, membrane separation, ion exchange/chelation, adsorption and solvent extraction have been developed for eliminating the Cr(VI) from aqueous solution. Among them, adsorption has been well studied due to its simplicity, sludge free operation, easiness in handling and availability of various adsorbents. However, the application of commercial adsorbents is limited by their high costs (Owlad et al., 2010). Consequently, many investigators have studied the feasibility of low-cost substances for adsorptive removal of Cr(VI), such as clay materials, industrial by-products and all kinds of agricultural by-products (Anirudhan et al., 2013; Wartelle and Marshall, 2005). Especially, adsorbents based on agricultural by-products have been attracted attention because of the special features such as biodegradability, biocompatibility and renewability (Šćiban et al., 2008). However, the conventional adsorbents based on agricultural by-products are difficult to be separated and recovered except by high speed centrifugation or filter. Thus, in several studies, iron magnetic nanoparticles were used as the remediation applications because they possess high surface areas and can be easily separated and recovered by simply applying an external magnetic field. However, pure magnetite is susceptible to agglomeration, and real-life application is controversial due to its toxicity. Therefore, the hybrid systems with magnetic nanoparticles and agricultural by-products based adsorbents have shown its tremendous potential for adsorption process, which can achieve rapid adsorbent separation from medium through a simple magnetic process.

Comparing with the traditional adsorbents, magnetic agricultural by-products based adsorbents are separated and recovered effectively by applying an external magnetic field (Reddy and Lee, 2013). More recently, the applications of magnetic agricultural by-products based adsorbents have been focused on the removal of dyes and anionic As(III) from aqueous solutions. For example, Ye prepared the magnetic wheat straw nanocomposite by using in-situ co-precipitation method and used these nanocomposite for arsenic removal (Tian et al., 2011). However, there is few studies on the removal of Cr(VI) using adsorbents based on magnetic agricultural by-products. In this work, corn stalk was used as the raw material for preparing the magnetic adsorbents. Firstly, virgin corn stalk was loaded with Fe<sub>3</sub>O<sub>4</sub> nanoparticles via co-precipitation technology, and then modified with amine groups through cross-linking of epichlorohydrin followed by reaction with ethylenediamine (EDA) and triethylamine. The physicochemical characteristics of the amine-functionalized magnetic corn stalk (AF-MCS) were determined by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Fourier transformation infrared spectrum (FT-IR), Brunauer–Emmett–Teller (BET) principle, vibrating sample magnetometer (VSM) and X-ray photoelectron spectroscopy (XPS). At meantime, to fully understand the sorption behavior, the effects of pH, adsorbent dosage, contact time, temperature, co-anions and reusability on adsorption capacity were also evaluated in bath experiments. Our results demonstrate that AF-MCS exhibits tremendous potential for effective removal of Cr(VI) and fast separation performance in aqueous media simultaneously.

## 2. Methods

### 2.1. Chemicals and materials

Corn stalk was purchased from Zhouping, Shandong province, China. The virgin corn stalk 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<sub>3</sub>, KCl, FeSO<sub>4</sub>, NaOH, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HCl, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub>, alcohol, N,N-dimethylformamide epichlorohydrin, ethylenediamine, diphenylcarbazine, triethylamine were purchased from Tianjin Damao Chemical Reagents Co. (Tianjin, China). A stock Cr(VI) solution with concentration of 1000 mg/L was prepared by dissolving 2.8286 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 1000 mL distilled water.

### 2.2. Preparation of AF-MCS

The preparation of AF-MCS was conducted in a two-step reaction. The Fe<sub>3</sub>O<sub>4</sub> loaded corn stalk was first produced by the in-situ co-precipitation method. In the co-precipitation process, virgin corn stalk (1.5 g) was suspended in a 150 mL mixed solution with FeSO<sub>4</sub> of 0.25 mol/L and FeCl<sub>3</sub> of 0.50 mol/L (Ahmed and Soliman, 2013). The reaction system was kept in an oxygen-free condition by purging with N<sub>2</sub>. After adding 10 mL of NH<sub>3</sub>·H<sub>2</sub>O (25%), the reaction temperature was raised to 70 °C and held for about 4 h. Then the Fe<sub>3</sub>O<sub>4</sub> loaded corn stalk was washed with deionized water and dried in a vacuum oven at 85 °C for 4 h (Tian et al., 2011). Thereafter, 10 mL of epichlorohydrin and 10 mL of N,N-dimethylformamide were reacted with 2 g of Fe<sub>3</sub>O<sub>4</sub> loaded corn stalk and the mixture was stirred for 1 h at 90 °C. Ethylenediamine (3 mL) was then added and stirred for 1 h, followed by adding 10 mL of triethylamine (Xu et al., 2010). After 2 h of stirring, the products were washed with deionized water, and dried overnight at 104 °C. The specific reaction mechanism was shown in graphical abstract.

### 2.3. Physicochemical characteristics of AF-MCS

VSM, XRD, FT-IR, BET, SEM and TEM were used to evaluate the physicochemical characteristics of AF-MCS.

The magnetic properties of all samples were measured as VSM by magnetometer (LDJ9500) at room temperature. Crystal structure of all samples was determined by a Rigaku D/MAX-YA diffractometer using Cu K $\alpha$  radiation at 40 kV and 40 mA over the 2 $\theta$  range of 20–70. Scanning electron microscopy (SEM) images and Transmission electron microscopy (TEM) of the sorbents before and after modified were obtained with NoVa™ Nano SEM 250 and FEI Tecnai G20, respectively. The functional groups in virgin corn stalk and AF-MCS were evaluated by using the FTIR technique (Perkin–Elmer “Spectrum BX” spectrometer) with spectrum scanned from 400 to 4000 cm<sup>-1</sup>. The textural structure including BET surface area, pore volume and pore size was determined by nitrogen adsorption/desorption isotherms at –196 °C according to the Brunauer–Emmett–Teller (BET) principle (JW-BK122W, Beijing JWGB Sci. & Tech. Co., Ltd., China).

### 2.4. Adsorption/desorption tests of AF-MCS for Cr(VI)

Batch adsorption experiments were performed on a thermostat water-wash shaker (SHZ-82A, China) with a shaking speed of 180 rpm.

In the pH experiments, 100 mL of Cr(VI) solution with concentration of 100 mg/L (pH range of 2.0–9.0) was mixed with 0.1 g of AF-MCS in a 250 mL glass flask. The pH was adjusted by 1 mol/L HCl and 1 mol/L NaOH. In the dosage tests, 0.025–0.2 g dosages of AF-MCS were added to batch 100 mL of Cr(VI) solution (100 mg/L, pH: 3.0). All the suspensions were shaken for 8 h at 30 ± 0.5 °C.

Adsorption isotherms were carried out by maintaining the water bath at 25, 35, 45 °C. Typically, 100 mL of Cr(VI) solutions with concentrations of 50–600 mg/L were mixed with 0.1 g of AF-MCS. The suspensions were shaken for 8 h to allow attainment of equilibrium at constant temperatures. Adsorption kinetic exper-

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