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Novel synthesis of a versatile magnetic adsorbent derived from corncob for dye removal

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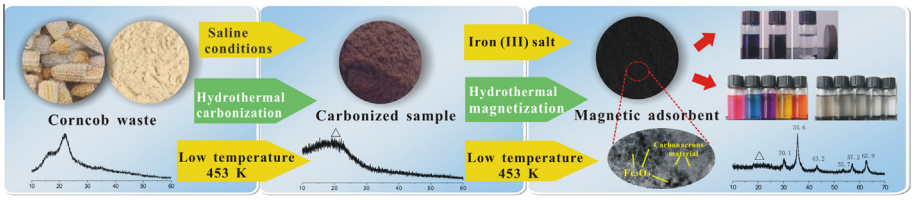
HIGHLIGHTS

- Corncob was converted into a novel magnetic adsorbent (MCA) for dye removal.
- Hydrothermal method was employed under saline and low temperature conditions.
- $FeCl_3$ acted as both Fe precursor and an *in suit* catalyst to yield porous structure.
- Adsorption process of MCA fitted Langmuir isotherm and pseudo-second-order model.
- MCA was an versatile adsorbent for removal of anionic and cationic dyes.

GRAPHICAL ABSTRACT



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ABSTRACT

Corncob, an agricultural waste, was successfully converted into a novel magnetic adsorbent by a low-temperature hydrothermal method (453 K), including carbonization under saline conditions and magnetization using iron (III) salt. The resultant magnetic carbonaceous adsorbent (MCA) exhibited a porous structure with a higher specific surface area and more oxygen-containing functional groups than its carbonaceous precursor (CP), which can be attributed to the catalytic effect of Fe (III). The adsorption behaviors of both MCA and CP could be described well by Langmuir isotherm and pseudo-second-order model. The adsorption capacity for Methylene blue (MB) revealed by adsorption isotherms were 163.93 mg/g on MCA and 103.09 mg/g on CP, respectively. Moreover, MCA was demonstrated as a versatile adsorbent for removal of both anionic and cationic dyes, and it showed good reusability in regeneration studies. This work provides an alternative approach for effective conversion of biomass waste and application of them in pollutant removal.

1. Introduction

Currently, synthetic dye becomes one of the major pollutants in the industrial effluents. Most of dyes in the effluents contain non-degradable aromatic structure, and are considered to be toxic and even carcinogenic, which results in negative influences on human health and ecological security. Therefore, the treatment and disposal of dye-containing wastewater is urgently needed and has aroused worldwide concern. Adsorption technology has been considered as one of the most effective methods to remove pollutants from aqueous solutions, due to its easy operation, high efficiency and wide adaptability (Huang and Keller, 2013; Mohan et al., 2014). Although a number of adsorbents have been developed to remove dyes from wastewater (Chang et al., 2013; Yang et al.,

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2014), most of them may suffer from inconvenient separation by centrifugation or filtration. Adsorbent magnetization is an emerging water remediation area to overcome separation problems of non-magnetic adsorbents in recent years. Magnetic adsorbents can easily be separated in the presence of external magnetic fields (Devi and Saroha, 2014; Lu et al., 2013). Nevertheless, the high cost is a major obstacle to the wide applications of these adsorbents. It is highly desirable to develop more economic, efficient and practical adsorbents for the dye removal.

Agricultural waste would be an attractive starting precursor for carbonaceous materials because of its abundance, low cost, excellent properties and special structures (Liu et al., 2014; Zhu et al., 2014). Accordingly, numerous carbonaceous materials derived from renewable biomass have been reported, and some of them were applied in water purification (Foo et al., 2013; Mittal and Mishra, 2014). However, to date, little attention has been paid to the fabrication of magnetic adsorbents using natural agriculture waste. Also, the known magnetic adsorbent often lacked the versatile adsorption capacity for both cationic and anionic pollutants due to its single surface charge (Lin et al., 2011). In addition, most of the reported magnetic adsorbents were synthesized in hash conditions with high temperature and toxic reagents, which was uneconomic, energy-intensive and non-environmentally friendly. Therefore, it is of great importance to develop a novel approach to synthesize biomass-derived magnetic adsorbent under mild conditions.

Hydrothermal carbonization (HTC) is a novel thermal conversion process, which provides an eco-friendly approach to obtain various carbonaceous materials under mild conditions (up to 523 K). It shows distinct advantages over pyrolysis in that it can process wet biomass, thus avoiding a substantial drying cost for typically wet biomass feedstock. Moreover, HTC reactions can proceed with the same level of conversion efficiency as higher temperature processes (Mao et al., 2010). However, as carbon precursors, raw lignocellulosic biomass (e.g., agricultural wastes) has not received much attention in HTC conversion as other feedstocks, such as glucose, starch, and cellulose. This is mainly due to the extreme complexity of lignocellulosic structure and the diversity of components in different natural biomass. In addition, most of lignocellulosic biomass cannot be carbonized under a relatively low temperature (e.g., 453 K) as will be shown in the present work. Consistently, results from previous studies also indicated that hydrothermal carbonization of lignocellulosic biomass was usually performed by applying temperatures over 523 K when using water as the carbonization medium (Falco et al., 2011). In fact, the saline environment (i.e. using commonly available salts) is a potential reaction medium other than water in HTC process, because it contains very hydrophilic ions which is beneficial to lower the partial pressure of water and change its structure (Fechler et al., 2013). Therefore, the reaction, which may be difficult to occur under common conditions, can potentially be performed under saline but otherwise less extreme conditions (i.e. low temperature) as will be shown in the present work. Although it has been applied in hydrothermal carbonization of glucose (Fechler et al., 2013), the potential of saline conditions in HTC of lignocellulosic biomass is unknown. More surprisingly, to the best of our knowledge, no one has thus far employed HTC to synthesize magnetic adsorbents using waste biomass as the starting material.

In our efforts towards biomass waste disposal and resource recovery (Ma et al., 2009, 2013, 2014), we have developed a facile and low-cost approach for synthesizing a magnetic carbonaceous adsorbent from corncob under low temperature hydrothermal condition. This method involves hydrothermal carbonization of corncob under saline conditions to produce carbonaceous material, and subsequent hydrothermal magnetization using iron (III) salt to prepare a magnetic adsorbent. Both the magnetic adsorbent and its carbonaceous precursor were synthesized to study the adsorption kinetics and equilibrium isotherms for methylene blue (MB). In addition, other anionic dyes and cationic dyes were also selected to investigate the adsorption performance of the resulting adsorbent. The physical and chemical properties of the corncob-derived magnetic adsorbent were also characterized in detail with transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and the nitrogen sorption measurement.

2. Methods

2.1. Materials

Corncob was provided by the maize base of Anhui Agricultural University, Hefei, China. Before dried at 378 K for 24 h, it was milled into powder, and sieved through a 100-mesh sieve. The particle size of the corncob powder was 150 μm. Methylene blue (MB) and other dyes were provided by Sinopharm Chemical Regent Co., and all other regents were commercially available and of analytical grade.

2.2. Preparation of the carbonaceous precursor (CP)

The carbonaceous precursor of magnetic adsorbent was prepared *via* hydrothermal carbonization of corncob under saline conditions. In a typical synthesis, corncob powder (6 g), $ZnCl_2$ (9 g) and deionized water (30 mL) were maintained in a sealed, Teflon-lined autoclave (50 mL) at 453 K for 6 h. After cooling to room temperature, the solid product was collected by vacuum filtration, washed with deionized water and stirred in 1 L of deionized water overnight to remove the residual $ZnCl_2$. Then, the carbonized corncob was collected by vacuum filtration, and washed with deionized water and dried in a vacuum. For comparison, the hydrothermal carbonization of corncob without adding $ZnCl_2$ was also conducted under the same conditions mentioned above. In hydrothermal carbonization, the yields of the final solid residues obtained with and without adding $ZnCl_2$ were 51% and 60%, respectively, which was calculated based on the initial amount of corncob powder.

2.3. Preparation of the magnetic carbonaceous adsorbent (MCA)

The magnetic corncob-derived adsorbent was synthesized by hydrothermal magnetization of the carbonized corncob. Briefly, 4 g carbonized sample and 2 g $FeCl_3{\cdot}6H_2O$ was dispersed in 50 mL deionized water with stirring for 0.5 h to obtain a homogeneous dispersion. Then NaOH solution (2.5 M, 20 mL) was added into the above solution dropwise with vigorously stirring. The resulting mixture was then placed into a sealed, Teflon-lined autoclave (100 mL) and maintained at 453 K for 6 h. After cooling to room temperature, the magnetic corncob-derived adsorbent was collected by a magnet, washed with deionized water until neutral and dried in a vacuum. In hydrothermal magnetization, the yield of the final MCA obtained was 75%, which was calculated based on the initial amount of CP.

2.4. Characterization techniques

The microstructure of the magnetic adsorbent was analyzed using TEM (JEOL-2100F, Japan). The FTIR spectra were recorded on a Fourier transform infrared spectroscopy (Bruker EQUINOX55, Germany) to analyze the functional groups. The XRD analysis was performed using an 18-KW rotating anode X-ray diffractometer (MXPAHF, Japanese Make Co., Japan). The structural features of CP and MCA were analyzed by nitrogen