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Adsorption of anionic dyes from aqueous solutions using chemically modified straw

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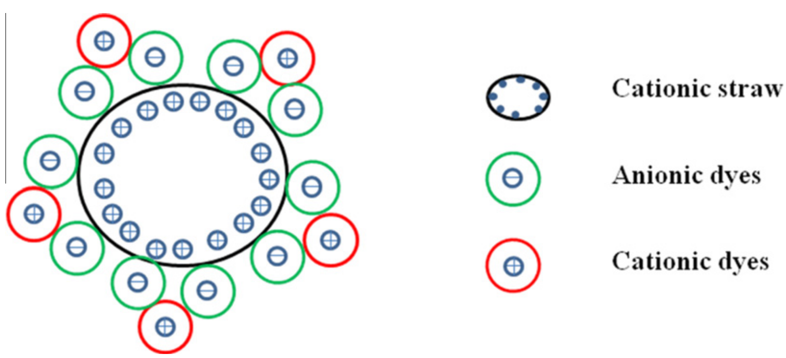
HIGHLIGHTS

- A quaternary ammonium cationic modified straw (MWS) was prepared.
- The fundamental adsorption behavior of MWS for two anionic dyes was studied.
- They followed a monolayer chemical adsorption mechanism with ion exchange process.
- The used adsorbent was effective in removal of cationic dye in secondary adsorption.

GRAPHICAL ABSTRACT

The cationic modified wheat straw adsorbent showed high removal efficiency for two anionic dyes. Then, the anionic dyes loaded adsorbents were successfully applied to eliminate a cationic dye in the secondary adsorption.



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ABSTRACT

The effective disposal of redundant straw is a significant work for environmental protection and full utilization of resource. In this work, the wheat straw has been modified by etherification to prepare a kind of quaternary ammonium straw adsorbents. The adsorption behaviors of the modified straw for methyl orange (MO) and acid green 25(AG25) were studied in both batch and column systems. The adsorption capacity of the straw for both dyes improved evidently after modification. The maximal MO and AG25 uptakes were more than 300 and 950 mg g^{-1}, respectively. Furthermore, the adsorption equilibrium, kinetics and column studies all indicated that the adsorption behavior was a monolayer chemical adsorption with an ion-exchange process. In addition, after adsorption of anionic dyes, the used adsorbents were successfully applied to adsorb a cationic dye directly at suitable conditions in the secondary adsorption. This was due to the altered surface structures of the used adsorbents.

1. Introduction

Nowadays, with the rapid development of modern industries, the environmental contamination associated with the dyes present in wastewater of various industrial sections, such as dyeing, printing, textile, leather, and coating industries, has drawn much attention. It is estimated that more than 70,000 tones of dyes are discharged in effluent from textile and associated industries in the world every year. The release of dyes has posed serious environmental problems. Colored dye effluents may interfere with light penetration in the receiving water bodies thereby disturbing the

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biological processes. In addition, some dyes degrade into compounds that have toxic influences on mammals and aquatic organisms.

Diverse techniques, including adsorption, flocculation, oxidation and electrolysis, have been employed for removal of dyes from wastewaters. Among these methods, adsorption is superior since it is more efficient and economical than others (Ngah et al., 2011). Activated carbon, the commonly used adsorbent, is effective in eliminating dyes but comparatively costly. Therefore, many biological materials, especially agricultural residues including peanut hull (Tanyildizi, 2011), sugarcane bagasse (Yu et al., 2011), coir pith (Khan et al., 2011), and maize cob (Sonawane and Shrivastava, 2009), have been investigated for removal of dyestuff in recent years.

As a type of reproducible crop wastes, straw materials are not only abundant in nature but rich in available reactive groups existing in cellulose, hemicellulose and lignin structures. However, about 300 million tons of straw is incinerated or deserted in China every year, which is not only destruction of soil and atmospheric environment, but waste of resources. One of promising ways to utilize this precious bioresource is to produce straw-based adsorbents (Oei et al., 2009; Xu et al., 2011). Although the adsorption capacity of raw straw is unsatisfactory, various chemical modifications by introducing some functional groups can be applied to improve the adsorption capacity.

In our previous work, wheat straw materials were modified by carboxymethylation to prepare a sort of anionic adsorbents, which were proved effective in eliminating cationic dyes through electrostatic interaction (Zhang et al., 2011). In this work, cationic modified straws were prepared by introducing quaternary ammonium groups through etherification. The cationic adsorbents were used to eliminate methyl orange (MO) and acid green 25 (AG25), two kinds of anionic dyes, from aqueous solutions. The fundamental adsorption behaviors of modified straw for removal of both MO and AG25, including the pH effect, adsorption isotherms, kinetics, and column adsorption, were investigated, respectively.

Furthermore, after adsorption of dyes, regeneration and reuse of the used adsorbents is a problem. Conventionally, large amount of solvent is applied as eluent to wash and recover adsorbents for recycle use. However, the generated waste eluent usually requires further treatment to avoid the secondary pollution. Recently, a novel way to make use of used adsorbents has been raised in reported literatures. (Dai et al., 2011; Yan et al., 2011; Zhang et al., 2011) Since the surface structures of adsorbents have been changed after adsorption of some contaminant, the used adsorbents can be applied to adsorb other pollutants in suitable conditions. In this work, the final anionic dyes loaded adsorbents were tried to be removal of a cationic dye, methylene blue (MB). The adsorption mechanisms for various dyes onto different adsorbents were discussed in detail.

2. Methods

2.1. Materials

The wheat straw used in the present study was obtained from a farm in Changzhou, Jiangsu Province. MO, AG25, MB, 3-chloro-2-hydroxypropyl trimethylammonium chloride (CTA), hydrochloric acid (HCl), sodium hydrate (NaOH), ethanol, isopropanol and other reagents used in this work were all A.R. grade reagents. The deionized water was used in all experiments.

2.2. Preparation of biosorbents

The synthesis of cationic modified straw is summarized in Supporting Information Fig. S1. The straw materials were ground and screened through a set of sieves to obtain geometrical sizes of 60–150 μm. The sieved straw was then washed with ethanol and distilled water. The washed materials were dried in an oven at 353 K for 24 h. The straw material used in the current study was named WS.

A desired amount of WS was added in 30% NaOH solution under agitation at 293 K for 1 h to get the alkaline WS. After being washed and dried, the alkaline WS was dispersed in NaOH isopropanol-water solution. Then CTA was added dropwise into the mixture and left under agitation at 318 K for 3 h. The raw product was then washed by deionized water and dried at 353 K overnight. At last, it was ground and sifted to get the geometrical sizes (60–150 μm), named modified wheat straw (MWS), and used as the adsorbent in the following experiments.

2.3. Instrument analysis

The FTIR spectra of WS and MWS were obtained with a Bruker IFS 66/S IR Spectrophotometer. All samples were prepared as potassium bromide tablets, and the scanning range was 650–4000 cm^{-1}.

The surface morphologies of WS and MWS were observed directly with a scanning electron microscope (Type SSX-550; Shimadzu Co.; Japan). The electron micrographs were taken with an acceleration voltage of 15.0 kV.

The ζ potential data was acquired from a Malvern Nano-Z ζ potential recorder. The range of initial solution pH was 2.0–12.0.

The nitrogen content of MWS was obtained with an Elementar Vario EL II elemental analyzer.

2.4. Adsorption studies

2.4.1. Adsorption of anionic dyes at different initial solution pH

The influences of different initial solution pH on adsorption of MO and AG25 onto MWS and WS were conducted, respectively. The initial concentrations of MO and AG25 solutions were both approximately 1000 mg L^{-1}. The initial pH value of MO solution was between 5.0 and 12.0, since MO was stable at pH higher than 5.0. The pH range of AG25 solution was between 2.0 and 12.0. 0.03 g adsorbent was immerged into 30 mL dye solutions with different pH under continuous stirring at 293 K for 48 h to achieve adsorption equilibrium. The initial and final pH values of these solutions were all detected by a pH meter (Type PHS-3C; Jinmai Corp.; China). The initial and final MO and AG25 concentrations were determined using Vis spectrophotometer (Type 7200; Unico Corp.; China) at fixed wavelengths of 464 and 642 nm, respectively, since the wavelength and intensity of the maximal absorbance for various dyes could not be affected by pH in the measured pH ranges as shown in the Supporting Information TEXT S1 and Fig. S2.

The amount of adsorption in batch experiments, q (mg g^{-1}), was calculated according to the following equation:

$$q = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_0 and C_e (mg L^{-1}) are the initial and final concentrations of solute in solution, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent.

2.4.2. Adsorption equilibrium study

The adsorption equilibrium study was studied at different temperatures: 283, 293, 303, and 313 K, respectively. The concentration of MO aqueous solutions ranged from 100 to 2000 mg L^{-1}, whereas the concentration of AG25 aqueous solutions ranged from 150 to 3000 mg L^{-1}. 0.03 g MWS was dosed in each of the dye solutions under continuous stirring for 48 h at initial pH 7.0.