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Selective removal of cationic dye from aqueous solution by low-cost adsorbent using phytic acid modified wheat straw

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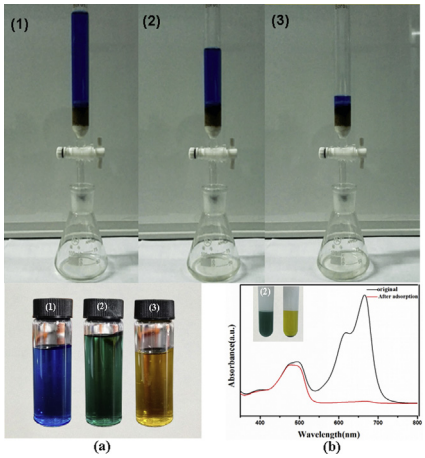
HIGHLIGHTS

- A low-cost adsorbent (PA-WS) was synthesized for methylene blue removal.
- Adsorption capacities of PA-WS achieve to 205.4 mg g^{-1} at pH 10.0.
- Adsorption mechanism of PA-WS for methylene blue was studied.
- PA-WS presented excellent selective adsorption and regeneration-reuse property.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the wheat straw (WS) was modified using phytic acid (PA) to improve adsorption capacity for selective removal of methylene blue dye (MB, cationic dye). The morphology, structure and surface state of the modofied wheat straw using phytic acid (PA-WS) were characterized using scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), respectively. The effects of pH, MB concentration, different temperatures and contact time on adsorption experiments were investigated. The maximum adsorption quantity of PA-WS for MB was up to 205.4 mg g^{-1} at 25 °C. Equilibrium adsorption isotherm data indicated a good fit to the Langmuir isotherm model and the adsorption kinetic was well-fitted by the pseudo-second-order model and the Elovich model. Regeneration study revealed that PA-WS can be reused effectively. These results indicated that PA-WS was a promising adsorbent for the removal of cationic dyes.

1. Introduction

Nowadays, water pollution is becoming more and more serious because large quantities of wastewater are discharged into

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the environment. Thus, removal of various pollutants from industrial effluents has become a critical issue. Dyes, as main pollutants in industrial sewage, are widely used in textile, leather, tanning, paper, food processing, plastics, cosmetics, rubber, and printing [1]. Most of dyes are harmful to ecosystem owing to the carcinogenic compounds produced during the process of degradation. Various methods such as adsorption [2], flocculation [3], oxidation [4] and electrolysis [5] have been used in the removal of dyes from wastewater. Among these techniques for dyes removal, adsorption is more efficient and economical way than the others [6].

To date, varieties of materials have been explored as the adsorbent for dyes removal [7–10]. Among these, biological materials, especially agricultural by-products or waste have been the most popular due to its low-cost, biodegradability, such as rice husk [11], bagasse [12] and peanut shell [13].

Wheat straw (WS) is an abundant agricultural by-product and has been used as an adsorbent to remove contaminant from wastewater [14]. However, the raw wheat straw is not an excellent adsorbent for removing ionic dyes because of the lack of functional groups [15]. In order to improve its adsorption capacity, it is effective to introduce ionic groups onto the surface of wheat straw [16–18].

Phytic acid (PA, known as inositol hexakisphosphate), was discovered in 1903 [19]. It is a non-toxic naturally occurring organic acid, and is biocompatible and environment friendly which widely exist in cereals and grains [20,21]. The six phosphate groups of PA provide a variety of viable cross-linking site [22]. Hence, PA can be used to modify the surface properties of many substrates [23].

The objectives of this study are: (1) to modify wheat straw by phytic acid (PA-WS) and apply it as an adsorbent for the removal of cationic dyes from aqueous solutions; (2) to study the effects of pH, temperature, contact time and further explore the possible adsorption mechanism according to adsorption equilibrium and kinetics; (3) to investigate the selective adsorption for cationic dyes and regeneration.

2. Materials and methods

2.1. Materials

The wheat straw used in this study was collected from local countryside, Chongqing, China. Methylene blue (MB), orange G (OG), urea, phytic acid (PA, 70 wt% in H_2O) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Dimethylformamide (DMF), hydrochloric acid (HCl) and sodium hydrate (NaOH) were purchased from commercial sources and used without further purification.

2.2. Preparation of adsorbent

The wheat straw (WS) was grated and sieved to produce particles of 140–160 mesh. The sieved WS was then dried at 80 °C for 24 h. The modified wheat straw using phytic acid (PA-WS) was synthesized *via* esterification as shown in Scheme 1. A certain amount of WS powder was immersed in DMF and the mixture was ultrasonically dispersed for 30 min. Then, a finite amount of PA and urea were added to the mixture under stirring at 60 °C for 3 h. After cooling, the obtained PA-WS was filtered, washed thoroughly with deionized water and ethanol three times, respectively. Finally, PA-WS powder was dried at 60 °C for 24 h.

2.3. Characterization of adsorbent

The morphologies of WS and PA-WS were observed using a JSM-6510LV scanning electron microscopy (SEM) at an accelerating voltage of 15KV. Fourier transform infrared (FTIR) spectrum of sample was obtained as KBr disks on a Thermo Nexus 470 FTIR spectrometer. X-ray Photoelectron Spectroscopy (XPS) was performed using 200 W monochromated Al Kα radiation (Thermo Scientic ESCALAB 250Xi). The binding energies were calibrated based on the graphite C1 s peak at 284.8 eV. The concentration of dyes in aqueous solution was measured by UV–vis spectroscopy (UV-2550, Shimadzu Corporation).

2.4. Batch adsorption equilibrium and kinetics experiments

2.4.1. Preparation of methylene blue (MB) solution

Stock solution (1000 mg L^{-1}) was prepared by dissolving MB in distilled water. MB solutions with different concentrations were obtained by diluting the stock solution with distilled water.

2.4.2. Effect of pH

The effect of pH was studied by varying pH of MB solutions in the range of 2.0–10.0. The solution pH was adjusted by 0.1 M HCl or NaOH. Accordingly, adsorption experiments were measured by adding the PA-WS (0.05 g) and MB solutions (50 mL, C_0 = 300 mg L^{-1}) to 100 mL conical flask. And then, the mixture was shaked constantly at 30 °C for 12 h. After reaching the adsorption equilibrium, the MB dye solutions were filtered using syringe filters. Then, the filtrate was analyzed by UV–vis spectra, which was detected at wavelength of 664 nm. The adsorption quantity at equilibrium q_e (mg g^{-1}) was calculated using the following equation:

$$qe = \frac{(C0 - Ce)V}{m} \quad (1)$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of MB, respectively; V (L) is the volume of MB solution and m (g) is the dried weight of the adsorbent.

2.4.3. Equilibrium isotherms and kinetics

The adsorption equilibrium study of PA-WS was conducted at different dye solution temperatures: 25 °C, 35 °C and 45 °C, respectively. MB solutions (50 mL) with different initial concentration ranging from 100 to 900 mg L^{-1} were separately pipette into 100 mL conical flask, which contained PA-WS (0.05 g) powder. The MB solutions pH was adjusted to 10.0. After shaken for 12 h, the MB dye solutions were filtered by using syringe filters. The analysis method is similar with mentioned above. The adsorption quantity was calculated based on Eq. (1).

The kinetics of adsorption was also conducted at different temperatures: 25 °C, 35 °C and 45 °C, respectively. PA-WS (0.2 g) powder and MB dye solutions (200 mL, pH = 10.0; C_0 = 300 mg L^{-1}) were added into a 500 mL conical flask. Under shaking in a constant temperature oscillator, 3 mL of the sample solutions was taken out at desired intervals to trace the current dye solutions concentration. Meanwhile, 3 mL of distilled water was added into the bulk solution to keep the volume constant. The adsorption quantity $q_{(}t_{i)}$ (mg g^{-1}) at time t_i was calculated by using the following equation:

$$q(ti) = \frac{(C_0 - C_{ti})V_0 - \Sigma_2^{i-1} C_{t(i-1)} V_s}{m} \quad (2)$$

where C_0 and Ct_i (mg L^{-1}) are the dye initial concentration and dye concentration at time *ti*, respectively. V_0 (L) is the volume of the dye solution. V_s (L) is the volume of the sample solution taken out each time, which equal to 0.003L in this equation. And m (g) is the mass of adsorbent.

2.5. Selective adsorption

The selective adsorption experiment was carried out according to a reported method in the literature [24]. Concentrations of MB