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Application of longan shell as non-conventional low-cost adsorbent for the removal of cationic dye from aqueous solution

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ABSTRACT

With simple physical treatment, adsorption potential of longan shell for the methylene blue (MB) from aqueous solution was studied as a low-cost material under the conditions of adsorbent dosage (1–6 g/L), initial solution pH (2–12), contact time (5–180 min), temperature (293, 313, 313 K) and initial dye concentration (100–500 mg/L). The SEM images and FTIR spectra of longan shell before and after dye adsorption were analyzed to understand the adsorption process of MB onto longan shell. The kinetic data and the equilibrium data were simulated by different kinetic and isotherm models, respectively. The results showed that the adsorption process was well described by the pseudo-second-order kinetic model, and the experimental equilibrium data were better fit to Langmuir equation than Freundlich equation with the maximum adsorption capacity of 141.04 mg/g. In addition, main activation parameters (E_a, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$) and thermodynamic parameters (ΔG°, ΔH° and ΔS°) of the absorption process were also determined.

1. Introduction

Water shortage is a global problem that is further worsened by serious pollution caused by various chemicals including dyes [1]. It is well known that synthetic dyes are widely used in many fields, such as textile, paper, leather tanning, food processing, plastics, cosmetics, rubber, printing and dye manufacturing industries. According to the up-to-date data, the total dye consumption in the textile industry is more than 10,000 tons per year [2]. But the dyes cannot be completely combined to the materials, and their loss in wastewaters may vary from 2% to 50%, leading to severe contamination of surface and ground waters in the vicinity of dyeing industries [3]. Additionally, once they are discharged into the water it is hard to be disposed of, because the dyes have a complex molecular structure that makes them very stable and difficult to be biodegraded [4]. Methylene blue (MB), a cationic dye, is the most commonly used substance for different purposes because of its ease of applicability, durability, and good affinity to materials [5]. Although MB is not strongly hazardous, water containing MB could cause some negative effects, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [6]. Hence, focuses on specific methods and technologies to remove dyes from different kinds of wastewater streams are desired.

Today, the main treatment technologies for dyeing effluents are classified as physical methods (such as precipitation, adsorption and membrane processes), biological treatments, and chemical treatments (oxidative treatments including electrochemical processes and advanced oxidation processes) [7]. But these methods have some obvious limitations like process optimization, unsuitability for disperse dyes, being quite expensive, selective for particular dyes and longer acclimatization phase [8].

Among assorted available water treatment technologies, adsorption is considered to be better due to its convenience, flexibility and simplicity of design, ease of operation and insensitivity to poisonous pollutants. This method also does not result in the formation of hazardous substances [9]. Adsorption refers to the accumulation of a substance at the interface between two phases such as solid and gas or solid and liquid. Generally, the substance gathered at the interface is called 'adsorbate' and the solid on which adsorption occurs is known as 'adsorbent' [10]. Whether the method of adsorption is good or bad largely depends on the adsorbent, so low-cost and high-performance adsorbents are the ultimate goal of pursuit for many researchers. In recent years, a variety of natural adsorbents used to treat the dye wastewater received considerable attention from people, such as rice husk [11], grapefruit peel [12], wheat shells [13], sugarcane bagasse [14], fungi and yeast [15], pine sawdust [16], chitosan [17], coconut shell [18], corncob [19], vetiver roots [20]. It's worth noting that many natural adsorbents are waste materials that have little or no economic value and even present a disposal problem, so the development of those adsorbents is beneficial in reducing the cost of treating wastewater and protect our environment.

Longan, a plant of *Sapindaceae*, has been commercially cultivated in many warm regions of the word including China, Thailand, Vietnam, Australia, and Hawaii and Florida in the USA [21]. With 73.6% of the world's cultivated area and 59.7% of the world's total output of longan,

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China has become the largest country of longan growing and production in the world [22]. The fresh pulp of longan is juicy and sweet, with various nutritional components, and considered to have important edible and medical value. Although its flesh is widely used, the longan shell is often discarded as a by-product of the food industry without any reasonable utilization annually [23]. Plenty of cellulose, lignin, and a few flavonoids, the main components of longan shell, enable the longan shell to have excellent ability to remove the heavy metal ions from aqueous solutions, which is confirmed by the experiments of M.R. Huang et al. [24]. However, it is hard to find relevant coverage of the researches about longan shell as a novel adsorbent for the removal of synthetic dyes in literature.

Therefore, current study was undertaken to evaluate the application potential of the longan shell as an inexpensive and environment-friendly adsorbent in removing MB from aqueous solutions. The effects of some related factors such as adsorbent dosage, initial solution pH, contact time, temperature, and initial dye concentration were tested. Adsorption behavior of longan shell was investigated by means of different kinetic and isotherm models. In addition, the activation parameters and thermodynamic parameters of the adsorption process were also determined in this paper.

2. Materials and methods

2.1. Materials

Methylene blue (MB) purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), was used as adsorbate. The chemical formula and molecular weight of MB are $C_{16}H_{18}ClN_3S\cdot3H_2O$ and 373.9 g/mol, respectively. Solution pH, determined by a model PHSJ-4F pH-Meter (Shanghai REX, China), was adjusted to a given value using either HCl or NaOH as needed. A stock solution (500 mg/L) of MB was prepared in distilled water and diluted to obtain the desired concentration of dye. All other reagents employed were of analytical grade and used without any further purification.

Waste longan shell was collected from a fruit stall in Zhenjiang, China. It was washed repeatedly with tap water followed by distilled water to remove dust and soluble impurities, and then dried in an oven at 60 °C for 48 h. Dried longan shell was ground to power and sieved to obtain uniform size between 0–355 μm. The sieved samples were kept dry in a closed sealed bag until required. There were no further chemical or physical treatments prior to adsorption experiments.

2.2. Adsorption experiments

In our work, the effects of some important parameters like adsorbent dosage (1–6 g/L), initial pH (2–12), contact time (5–180 min), temperature (293, 313, 333 K), initial dye concentration (100–500 mg/L) on the removal of MB were studied by a series of batch adsorption experiments.

For example, the effect of adsorbent dosage on the adsorption performance was studied in the following conditions: without adjustment of initial pH, 0.05–0.30 g adsorbent was added to 50 mL of MB solution (150 mg/L) and stirred for 4 h at 288 K. After filter, the final dye concentrations were determined by measuring the absorbance values by means of a Shimadzu UV-2550 spectrophotometer at 666 nm. The percentage of MB removal and the adsorption capacity of adsorbent were calculated using the following equations:

$$R(\%) = (C_0 - C_t)/C_0 \times 100 \tag{1}$$

where R (%) is removal efficiency; C_0 (mg/L) is the initial concentration of MB and C_t (mg/L) is the concentration of MB at time t.

$$q_t = (C_0 - C_t)V/m \tag{2}$$

$$q_e = (C_0 - C_e)V/m \tag{3}$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium time and time t, respectively; C_0, C_t and C_e (mg/L) are the initial, time t and equilibrium concentrations of MB, respectively; and V (L) is the volume of the dye and m (g) is the mass of the adsorbent.

2.3. Characterization of the samples

FTIR spectra were measured on NEXUS 670 FTIR Spectrometer in KBr pellets to identify the chemical functional groups present on the longan shell samples before and after MB adsorption. And IR absorbance data were recorded for wave numbers in the range of 400–4000 cm^{-1}. Furthermore, the SEM micrographs were collected via scanning electron microscopy (S-3400N) to observe the surface morphology of the longan shell.

3. Results and discussion

3.1. Characterization of the longan shell

SEM, an important characterization technique, can be used for investigating the surface morphology of materials such as porosity, the particle shape and appropriate size distribution. The SEM images Fig. 1 display a highly porous morphology of raw longan shell with pores of more or less different shapes and sizes, which maybe a good explanation for great adsorption capacity of the adsorbent owing to the possibility for dyes to be trapped and adsorbed into these pores [25].

Since SEM images showed no information of the chemical functional groups on the longan shell, FTIR spectra for the adsorbent before and after MB adsorption were further observed (Fig. 2). Comparing Fig. 2(a) with Fig. 2(b), it can be found that two infrared spectra are similar. Before adsorption, the peaks around 3420 cm^{-1} and 1260 cm^{-1} might be assigned to stretching vibrations and deformation vibrations of –OH, respectively. The adsorption bands near the peaks at 2920 cm^{-1}, 1460 cm^{-1} and 1380 cm^{-1} may correspond to a series of C–H vibrations of $-CH_2-$ or $-CH_3$. The characteristic peaks observed at 1750 cm^{-1}, 1640 cm^{-1}, 1460 cm^{-1}, 1260 cm^{-1} and 1050 cm^{-1} can be attributable to stretching vibrations of C = O, C–O, or C–O–C. And the bands around 1640 cm^{-1} and 1460 cm^{-1} are also thought to be related with C = C vibrations. In sum, there are main groups of –OH and –COOH in longan shell. After adsorption, the bands at 1750 cm^{-1},1640 cm^{-1}, 1260 cm^{-1} and 1050 cm^{-1} all move to the direction of low wave numbers, and the band at 1460 cm^{-1} is unable to be detected, suggesting that the groups of –OH and –COOH in the adsorbent have play a significant role in the adsorption of MB onto longan shell [24–26].

3.2. Effect of adsorbent dosage on adsorption

The adsorbent dosage is one of important parameters that significantly affect the removal of MB from aqueous solution because adsorption capacity is connected with the number of adsorption sites [27]. Fig. 3 shows the influence of the adsorbent mass (1 g/L–6 g/L) on the sorption capacity under the conditions of 288 K, initial concentration of MB 150 mg/L and adsorption time 4 h. It can be seen that the increase in the adsorbent mass from 1 g/L to 3 g/L results in a rapid increase in the removal percentage of MB from 77.92% to 94.33%, which could be attributed to the increase of greater adsorbent surface area and availability of more adsorption sites. However, further increase in adsorbent amount from 3 g/L to 6 g/L did not significantly enhance the removal efficiency of dye (from 94.33% to 96.75%), which can be ascribed to the concentration of dye reached at equilibrium states between solid and solution phase. But the adsorption capacity of adsorbent was lower at a higher adsorbent dosage. So on the premise of the higher removal efficiency of dye, adsorbent dose should be reduced as much as possible from an economic perspective, and 3 g/L is an optimum adsorbent dosage for the adsorption process.