Camellia oleifera Abel shells as a new biosorbent to remove methylene blue from aqueous solutions
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ABSTRACT
This study aimed at investigating the feasibility of using Camellia oleifera Abel shell (COAS), an agriculture product in middle-west region in China, for the adsorption of methylene blue (MB), a cationic dye. Batch adsorption experiments were carried out to evaluate the effects of contact time, pH, adsorbent dosage, temperature and initial concentration on the adsorption of MB. Adsorption equilibrium studies showed that MB adsorption followed Langmuir model with a maximum adsorption capacity of 454.54 mg/g. The results demonstrated that the COAS is a promising adsorbent in the removal of MB from aqueous solutions.

Key words biological adsorption, Camellia oleifera Abel shell, methylene blue

INTRODUCTION
Dyes are used widely in many modern industries, such as food, paper, rubber, plastics, cosmetics and textile, in order to color their products. Removal of dyes by adsorption technologies is regarded as one of the competitive methods because of high efficiency, economic feasibility and simplicity of design/operation (Chen et al. 2010; Rafatullah et al. 2010). Activated carbons, because of their large surface area and relatively high adsorption capacity for a wide variety of dyes, have become the most promising and effective adsorbent (Ahmad et al. 2007; Deng et al. 2009). However, the high cost of activated carbon inhibits its large-scale use as adsorbent.

For these reasons, there is growing interest in using low-cost substances as alternative to costly activated carbons. Materials like kaolin (Tehrani-Bagha et al. 2011), rejected tea (Nasuha & Hameed 2011), silkworm exuviae (Chen et al. 2011), rice husk (Han et al. 2008), fly ash (Mane et al. 2007), yellow passion fruit peel (Pavan et al. 2008), wheat bran (Wang et al. 2008), broad bean peels (Hameed & El-Khairy 2008), neem leaf powder (Bhattacharyya & Sharma 2005), wheat shell (Bulut & Aydin 2006) and coffee husks (Oliveira et al. 2008) have been studied. Camellia oleifera Abel shells (COAS) is a genus of Camellia family which is widely distributed in the southern China. The annual production in 2008 was 262,500 tons and this production generates a huge amount of shells as waste material.

In this work, we demonstrated that COAS was an effective absorbent in the removal of methylene blue (MB) from aqueous solutions. The effects of contact time, pH, adsorbent dosage, temperature and initial concentration on the adsorption of dye were studied. The analysis of adsorption isotherms of MB over COAS was investigated as well.

EXPERIMENTAL
Materials
The Camellia oleifera Abel shells used in this study was obtained from a factory (Fujian Shenghua Agricultural Co. Ltd., Fujian, China). Raw materials were washed repeatedly with distilled water and air-dried in the sunlight. Then the Camellia oleifera Abel was milled to 30–120 mesh. These shells were pretreated in 34% formaldehyde solution for 2 h at 60 °C. The pretreated shells were dried at 343 K and stored in plastic bags ready for use, the specific surface area is about 2.4 m²/g.

Chemicals
Stock solution was prepared by dissolving 4.0 g of MB (MB content 82%) supplied by Shanghai Chemical Reagent Co., Ltd., China, in 1 L distilled water without further purification. The test solutions were prepared by diluting stock solution to the desired concentrations. 0.1 mol L⁻¹ HCl or
0.1 mol L$^{-1}$ NaOH was used to adjust the pH of the solution. All the chemicals used were AR grade and ion-free distilled water was used throughout for preparing solutions.

**Scanning electron microscopy**

Scanning electron microscopy (Nova NanoSEM 230, FEI) analysis was carried out on *Camellia oleifera* Abel shells to study its surface morphology.

**Batch mode adsorption studies**

In order to evaluate the feasibility of adsorption, laboratory batch studies were carried out using 250 mL conical flasks containing 50 mL of the test solutions at the desired initial MB concentration. A previously defined amount of the adsorbent material (COAS) was then added and the flasks were shaken at a fixed temperature, for different contact times.

The suspensions were filtered through Whatman filter paper (No. 42) and the concentration of MB in the filtrate was measured on a UV/VIS spectrophotometer (Cary 50 Varian, America) at 665 nm, from which the amount of MB absorbed per unit mass of biosorbent (mg MB/g dry biosorbent) was determined.

Blank tests were conducted in two ways: (i) without adsorbent, to check for the retention of the MB at the filter paper surface and other possible losses, and (ii) without the MB (in pure water), to verify if any colored species present in the shells were water soluble and would contribute to the color of water, masking in the results.

MB losses at the filter paper surface were negligible and no significant color effect could be accounted for the COAS adsorbent. The maximum contact time (equilibrium) was established in appropriate tests and for the isotherms it was taken as 24 h.

The time dependency of batch experiments was examined by varying the contact time of adsorbents from 5 min to 24 h.

In order to study the effect of pH on MB adsorption, the pH of the solution was varied from 3 to 10. The batch procedure at each pH was followed as above described using an initial concentration of 600 mg L$^{-1}$. The pH of the solutions during adsorption was monitored using a MARTE MB-10 potentiometer with the glass electrode.

The influence of temperature on MB biosorption was determined by equilibrating the suspensions in solutions at 298, 313 and 333 K.

The concentration of COAS was varied between 20 and 200 g L$^{-1}$ to determine the ratio required for optimum biosorption.

According to the standard curve method, the adsorption capacity of COAS uptake at equilibrium, $Q$ (mg/g), and the strain away rate $R$ were calculated using the following equation:

$$Q = \frac{C_0 - C_e}{m} v,$$

$$R = \frac{C_0 - C_e}{C_0} \times 100\%$$

Where $C_0$ (mg/L) is the initial concentration of MB, $C_e$ (mg/L) is the concentration of MB at equilibrium, $v$ (mL) is the volume of the solution, and $m$ (mg) is the weight of COAS.

**RESULTS AND DISCUSSION**

**Characterization of COAS**

Figure 1 shows the SEM micrographs of COAS sample before and after MB adsorption. It can clearly be seen
that COAS has a large amount of heterogeneous layers which provide possible adsorption sites for dye to be adsorbed. After MB adsorption, the surface of adsorbent becomes pretty smooth. With naked-eyes, we are able to observe that color of the COAS turns to blue, this can ascribe to the coverage of the dye molecules.

**Effect of contact time**

The effect of contact time on the MB adsorption by COAS is shown in Figure 2. The removal of MB by adsorption on COAS is found to be rapid at the initial period of contact time and becomes slow with the increase of contact time. It implies that the removal of MB over COAS has two distinct stages: a relatively fast one followed by a slower one. This is due to the strong attractive forces between the dye molecules and the sorbent, fast diffusion onto the external surface resulting in rapid equilibrium (Akbal 2005).

**Effect of pH on adsorption**

Figure 3 shows the dependence of MB adsorption on pH. MB adsorption efficiency is greatly influenced by pH variation, the MB removal ratio was minimal at low pH (pH = 3), the MB removal amount increased with the increase in pH. The removal are 37.9 and 88.3% for pH = 3 and pH = 10, respectively. This can be interpreted by considering the electrostatic attraction. At low pH value, the H\(^+\) ion can be considered as competitor of MB cations for adsorption sites on COAS surface. As the pH of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases. The negatively charged sites favor the sorption of cationic dye due to electrostatic attraction. Similar phenomenon was observed for the adsorption of MB onto various carbons (Kannan & Sundaram 2001).

**Effect of adsorbent dosage**

To investigate the effect of adsorbent dosage on the adsorption of MB, a series of adsorption experiments with initial MB concentration of 600 mg/L were carried out with different adsorbent dosages. The obtained results are shown in Figure 4. The removal ratio increased as the increase in the COAS dosage over the range of 0.1–1.0 g. This is a result of increased surface area and availability of more adsorption sites. The increase in MB removal ratio with increase in the adsorbent is agreement with the report of the adsorption of MB over jackfruit peel (Hameed 2009).

![Figure 2](https://iwaponline.com/wst/article-pdf/64/7/1566/444752/1566.pdf)  
**Figure 2** | Effect of the time on the adsorption to MB by COAS (conditions: C\(_0\) = 600 mg/L, T = 298 K, pH = 6, W/V = 0.2 g/50 mL).

![Figure 3](https://iwaponline.com/wst/article-pdf/64/7/1566/444752/1566.pdf)  
**Figure 3** | Effect of pH on the adsorption to MB by COAS (conditions: C\(_0\) = 600 mg/L, T = 298 K, W/V = 0.2 g/50 mL).

![Figure 4](https://iwaponline.com/wst/article-pdf/64/7/1566/444752/1566.pdf)  
**Figure 4** | Effect of dosage on the adsorption to MB by COAS (conditions: C\(_0\) = 600 mg/L, T = 298 K, pH = 6, t = 24 h).
Effect of temperature

Temperature is an important parameter in the adsorption process. To determine the effect of temperature, adsorption studies of MB were performed at three different temperatures (298, 313 and 333 K). The results shown in Figure 5 indicate that the removal of MB by adsorption on COAS was found to be accelerated from 298 to 333 K. The fact that the adsorption of dye is in favor of temperature indicates that the mobility of the dye molecule increases with a rise in the temperature, then the dye molecule interacts more effectively with the sorbent surface. The increase in adsorption capacity with increasing temperature suggests that the process of removal of the dye by COAS is endothermic in nature and activated process.

Effects of initial concentration of MB

To investigate the effect of initial concentration of MB, a series of adsorption experiments were carried out with different initial concentration of MB ranging from 100 to 2,000 mg/L. The results obtained are summarized in Figure 6. The adsorption of MB on COAS increased with increase in dye concentration although the removal ratio of MB decreased with increase in initial concentration of MB. The equilibrium adsorption capacity is increased from 24.52 to 420.10 mg/g as the MB concentration increased from 100 to 2,000 mg/L. MB onto bamboo-based activated carbon exhibited the similar trend (Hameed et al. 2007).

Isotherm analysis

To describe experimental data of adsorption isotherms, Langmuir and Freundlich models are used in this work. The linearized Langmuir and Freundlich isotherms for MB adsorption on COAS were obtained. The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms and their respective coefficients are summarized in Table 1. The value of Freundlich exponent \( n \) (1.84) is the range of \( n > 1 \), implying a favorable adsorption (Ho & McKay 1998). The \( R^2 \) value (0.9748) of Langmuir isotherm is higher than that of Freundlich isotherm, this indicates that the Langmuir isotherm provides a better fitness to the isotherm data. Based on the Langmuir isotherm, a maximum adsorption capacity of MB onto COAS is 454.54 mg/g. Table 2 compares the adsorption
capacity of COAS obtained in present study with that of the reported adsorbents. It can be seen that COAS has much higher adsorption capacity than many other adsorbents, suggesting that COAS have great potential application in dye removal from aqueous solution.

CONCLUSIONS

The adsorption of MB from aqueous solution onto COAS has been investigated. Adsorption tests were carried out as a function of contact time, pH, adsorbent dosage, temperature and initial concentration. The adsorption experiments indicated that COAS was effective in removal of MB from aqueous solution. The percentage of removal decreased with the increasing concentration of dye in the solution and increased with the increasing adsorbent dosage. Higher pH and temperature accelerated the MB adsorption onto COAS. The adsorption data was well described by the Langmuir isotherm equation. It can be concluded that COAS could be employed as an efficient adsorbent for the removal of color from water from this study.

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