Dye Removal from Aqueous Solution using Adsorption on Modified Coconut Shell

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ABSTRACT

This work presents a novel adsorbent consisting of coconut shell carbon was investigated for its efficiency in the removal of dye, namely methyl orange, from aqueous solution. Coconut shell was used to prepare activated carbon by physiochemical activation with phosphoric acid as the activating at 600 °C. Characterization includes ash and fixed carbon contents, pH and moisture of the adsorbents were also investigated. The adsorption studies of adsorbents were done using batch method. The effect of process parameters like adsorbent dose, pH, contact time and initial of concentration on the extent of methyl orange adsorption from solution has been investigated. Optimum conditions for methyl orange removal was found to be adsorbent dose 0.2 g, pH value 3.0, equilibrium time 60 minutes. The isotherm of methyl orange adsorption of the coconut shell-based activated carbon is tend to be Freundlich isotherm (R^2 = 0.9993), which indicated that the multilayer adsorption has occurred at specific sites within the adsorbent.

Keywords: *Batch adsorption; Dye; Isotherm; Modified coconut shell.*

1. INTRODUCTION

Dyestuffs are being used by a large number of industries to colour their products and make their appearance more attractive [1]. Textile, printing, and other related industries are facing problems of treatment and disposal of dye wastewater. Many countries discharge the effluent to surface water without any treatment because of technological and economical limitations [2]. There are various conventional methods for removing dyes including coagulation and flocculation [3], oxidation or ozonation [4] and membrane separation [5]. However, these methods are not widely used due to their high cost and economic disadvantage. Chemical oxidations are generally not feasible on large scale in industries. In contrast, an adsorption technique is a most versatile and widely used technique. Activated carbon is the most popular adsorbent for removal of dyestuffs from wastewater [6]. Activated carbon exhibits the best dye removal characteristics, recent research regarding adsorbents obtained from cellulosic residues has shown satisfactory results in the use of such materials as adsorbents [7]. The following are example of waste materials used in dye removal: rattan sawdust [8], cashew nut shell [6], *Luffa cylindrica* fibers [9], pineapple stem [10] and rice straw-derived char [11]. Many researches are concentrating on modified agricultural waste as adsorbent. The main aim of this study was the use of coconut shell as adsorbent material for removal of methyl orange (MO) from aqueous solution. The effects of adsorbent dose, pH, contact time and effect of concentration of MO were investigates.

2. MATERIALS AND METHODS

2.1 Dye

The dye under consideration is methyl orange (MO; $C_{14}H_{14}N_3NaO_3S$; Mol. Wt. 327.33) was from Fluka chemika and was used without further purification. The chemical structure of MO is shown in Fig. 1. The stock solution of 500 mg/L was prepared by dissolving the appropriate amount of MO in 1000 mL with distilled water. Different concentrations ranged between 50 and 350 mg/L of MO was prepared from the stock solution. The other reagents used in this study were of pure analytical grade.

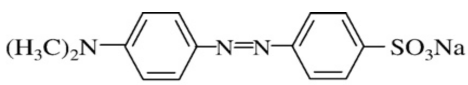

Fig. 1 *The structure of methyl orange.*

Measurements of pH of the solutions were carried out on a digital pH meter C830. All the adsorption experiments were carried out at room temperature (25±2 °C).

2.2 Adsorbent

The coconut shell was collected from Nong Saeng district, Udon Thani province. It was washed with water to remove the adhering dirt. They were cut with knife for reducing dimensions to 0.5 - 1.0 cm. and air-dired. After drying, coconut shell was pretreated with phosphoric acid (H_3PO_4) solution at 60 °C for 30 min. They were dried in oven at 110±2 °C for 30 min. The coconut shell was carbonized at 600 °C under nitrogen atmosphere for 2 h. The activated product was then cooled to room temperature. The dry carbon was crushed into powder, sieved to different particle size and then preserved in desiccators until use.

2.3 Method of adsorbent Characterization

Proximate analysis consist of moisture content, ash content, volatile matter and fixed carbon determined by put the selected sample to different range of the temperature, between 100°C to 950°C. The laboratory methods to measuring the proximate analysis of samples in this research were carried out based on ASTM standard. This standard determine the condition of lab analysis such moisture and volatile content [12].

2.4 Batch adsorption studies

Batch experiments were conducted to investigate the parametric effects of adsorbent dose, pH, contact time and initial adsorbate concentration for MO adsorption on the prepared carbon.

Batch adsorption experiments of MO were carried out in a 250 mL stoppered bottle at a constant temperature (25±2 °C) using a shaking thermostat machine at a speed of 150 r/min. The effect of pH on the adsorption of MO was examined by mixing 0.2 g of modified coconut shell (MCS) with 50 mL of MO (100 mg/L) solution with the pH ranging from 3.0 to 9.0. In kinetics studies, 0.2 g of MCS was mixed with 50 mL of MO solution with varied initial concentrations at 50, 100, 150, 200, 250 and 300 mg/L. The concentrations of MO in the supernatant liquor were determined by using standard curve. The absorbance of MO in aqueous solutions was measured by using UV-vis Spectrophotometer-Spectro SC at 466 nm. The quartz cell had a path length of 1.0 cm. The standard curve was obtained by plotting absorbance versus concentration of MO. The amount of MO adsorbed (q_e) was determined by using the following equation:

$$q_e = \frac{\left(C_0 - C_e\right)}{M}V$$

where C_0 and C_e represent the initial and equilibrium MO concentrations (mg/L), respectively; V is the volume of the MO solution (L) and m is the amount (g) of MCS.

3. RESULTS AND DISCUSSION

3.1 Characterization of adsorbents

The physicochemical properties of the adsorbent as obtained in this work after their characterization are shown in Table 1.

Table 1 *Obtained results from proximate analysis of MCS.*

Parameters	MCS
Moisture content (%)	7.79
Ash content (%)	10.80
Volatile matter (%)	39.22
Fixed carbon (%)	49.98
pzc	3.17

The moisture content is measure with the amount of water lost from materials upon drying to a constant weight. It is directly affected by physical and chemical properties of material which enable it to absorb the exiting water in the environment [13]. Based on laboratory analysis result, Modified coconut shell with 7.79 percent, had the low moisture content. Fixed carbon is the carbon remaining on surface as charcoal. The high percentage of the fixed carbon in MCS (49.98%) shows that this element requires a longer detention time on the surface of the furnace to achieve complete combustion compared to paper waste, food waste or even textile that has low fixed carbon load. Volatile matter is that portion of the wastes which is converted into the gas phases during the heating process (950°C).

3.2 Effect of adsorbent dosage

Fig. 2 shows the adsorbent dosage versus the adsorbed amount of MO on MCS. The adsorbent dosage was varied from 0.2 to 1.0 g. It indicated that the adsorbent dosage decreased with the increased of the adsorption capacity, which was probably related with the higher dose causes particles to aggregate, overlapping and overcrowding, resulting in a decrease of the availability of the surface area as well as decrease of the sorption capacity [14].

3.3 Effect of pH

pH is one of the most important factors affecting the adsorption process. Adsorption experiments were conducted with the pH ranging from 3.0 to 9.0. The effect of pH on adsorption kinetics of MO onto MCS at 25±2 °C is shown in Fig. 3, where the initial dye concentration was 100 mg/L. The amount of MO decreased from 21604±0.47 ug/g to 14756±0.55 ug/g, when pH was increased from 3.0 to 9.0. Colour removal due to pH change alone may be due to the structural changes being affected in the dye-molecules [15].

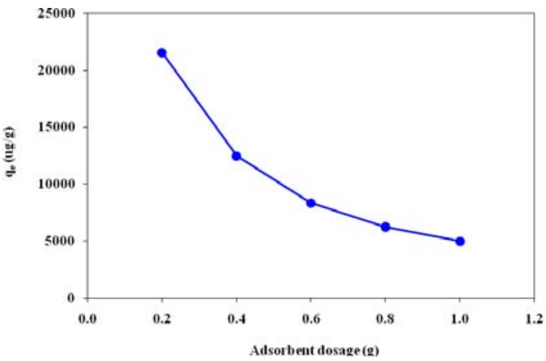

Fig. 2 *Effect of adsorbent dosage for the adsorption of MO on the MCS.*

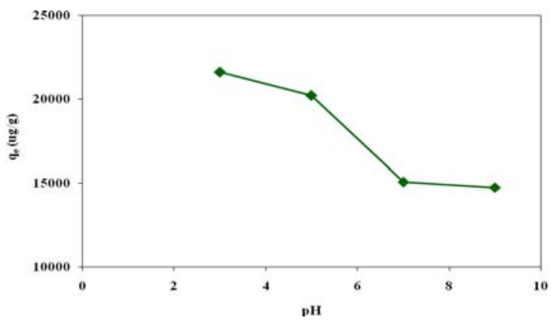

Fig. 3 *Effect of pH for the adsorption of MO on the MCS.*

3.4 Effect of contact time

Fig. 4 presents the effect of the contact time. The adsorbed amount of MO increased with an increase in contact time and reached equilibrium after 10 min for the initial MO concentrations of 100 mg/L at 25± 2 °C used in this study. This was due to the fact that, at the initial stage the number of free adsorption sites was higher, and the slow adsorption rate in the later stage was due to slower diffusion of solute into the interior of the adsorbent [16]. The maximum adsorption occurred after 10 min and there was almost no adsorption beyond this time because the equilibrium is attained.

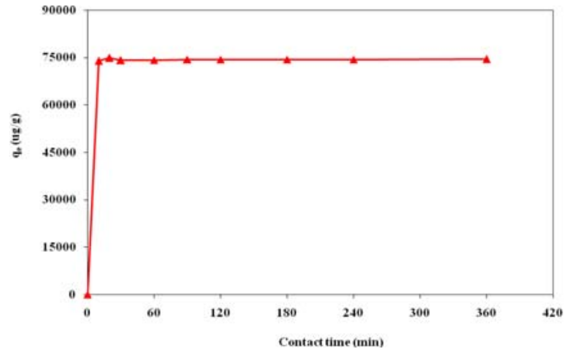

Fig. 4 *Effect of contact time for the adsorption of MO on the MCS.*

3.5 Adsorption isotherm

Adsorption isotherms describe how adsorbates interact with adsorbents and so are critical in optimizing the use of adsorbents. Thus, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems [17]. The Langmuir and Freundlich isotherm models were applied to the experimental equilibrium data for MO adsorption at different temperatures. The isotherm constants were determined by using linear regression analysis.

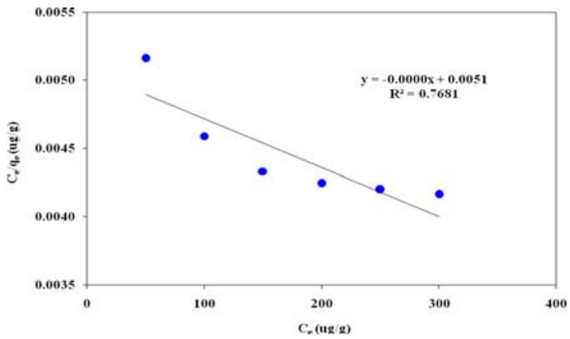

Fig. 5 *Langmuir isotherm for MO onto MCS.*

From the study of Langmuir and Freundlich adsorption isotherms, the isotherms demonstrated that the adsorption behavior both of planting materials was not a monolayer type but a multilayer type. From the Langmuir plots in Fig.5, it can be concluded that the adsorption behavior on the MCS showed non-linear lines. Therefore the types of adsorption behavior of MO on MCS do not correspond with the Langmuir isotherm. According to Freundlich adsorption isotherm, as shown in Fig. 6 and Table 2, R^2 values of MCS are close to 1 (R^2 = 0.9994) when compared with linearized Langmuir plotted (Fig. 5, R^2 = 0.7681). The results according to the linearized Freundlich isotherm showed that the interaction forces not limited to a monomolecular layer, but could continue until a multimolecular layer of adsorbed covered the adsorbent surface.

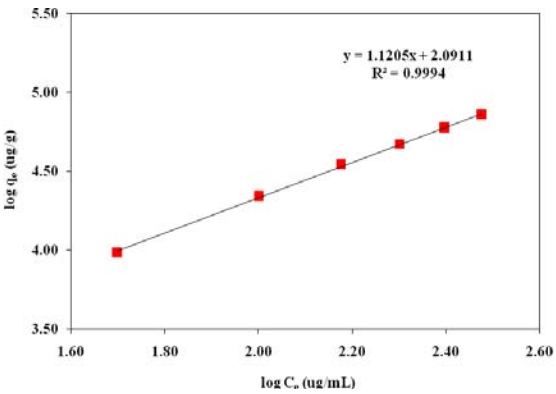

Fig. 6 *Freundlich isotherm for MO onto MCS.*

Table 2 *Adsorption isotherm and kinetic data for adsorbed of MO onto MCS.*

Isotherm model	MCS
Fruendlich	
1/n	1.1205
n	0.8924
K_f (mg/g)	123.3389
R^2	0.9994

where K_f is the adsorption capacity, n is the adsorption intensity and R^2 is the correlation coefficients.

4. CONCLUSIONS

Batch experiments showed that the adsorbent dosage, the pH of aqueous solutions, the contact time and the initial dye concentration significantly affect the adsorbed amounts of dye MO on the MCS. Equilibrium data were fitted to Langmuir and Fruendlich isotherms. The equilibrium data were best described by the Fruendlich isotherm model, with maximum adsorption capacity of 123.34 mg/g at 25±2 °C. Activated coconut shell increased the removal efficiency of MO from aqueous solution as a result of the increased internal surface area. Based on the results of this study, it can be concluded that the activated coconut shell adsorbent is an effective and alternative adsorbent for removal of MO from aqueous solution because of its considerable adsorption capacity, being of its abundance and low-cost.

5. ACKNOWLEDGEMENTS

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