

PREPARATION AND UTILIZATION OF MODIFIED RICE STRAW FOR REMOVAL OF METHYLENE BLUE

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ABSTRACT

In Thailand, rice straw is a huge lignocellulosic agricultural by-product of rice production. The smoke caused by open-field burning rice straw frequently results in serious air pollution. Hence, in this paper, a new economical technology for rice straw disposal and utilization was developed. The rice straw based adsorbent was prepared by thermochemically esterifying oxalic acid onto the rice straw and characterized by infrared spectroscopy and scanning electron microscope. The feasibility of modified product as the cationic dye adsorbent for removing methylene blue (MB) from aqueous solution was investigated. The effects of various experimental parameters (e.g. initial pH, sorbent dosage, dye concentration, and contact time) were examined conducting batch experiment system and optimum experimental condition was decided. For highly efficient adsorption of MB, pH should be properly controlled at $\text{pH} \geq 7$. The minimum sorbent dosage at 2.0 g/l could almost completely remove MB from 250 mg/l of dye solution. The sorption process could be described by the pseudo second order kinetic model. The results in the research showed that this environment friendly modified rice straw was an effective adsorbent as it could remove the basic dye with lower treatment cost.

Keywords: Rice straw; Adsorbent; Methylene blue; Wastewater treatment

INTRODUCTION

Dyes are important water pollutants which are generally present in the effluents of the textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals and foodstuff industries. Dye wastewater discharge into the environmental water bodies deteriorates the water quality and may cause a significant impact on human health due to mutagenesis, interatogenic or carcinogenic effects of some dyes or their metabolites. The water pollution with cationic dyes is becoming a huge environmental problem even very little concentrations of dyes (in ppm) because they can easily interact with negatively charged cell membrane surfaces, and can enter into cells and concentrate in cytoplasm [1].

Rice straw as a by-product of grain crops is a biological resource in the crop production system. It contains a high content of natural cellulose, hemicelluloses and lignin. However, this resource has not been properly used; except for a limited utilization as pulp, feed and other purposes. Rice straw is mostly

incinerated. It is not only a huge waste of natural resource, but also a serious pollution to the environment [2].

The objective of this work was to develop a new economical technology for rice straw exploitation and utilization as a rice straw based adsorbent. Methylene blue (MB) was used as a compound representative of the cationic contaminant to evaluate the feasibility of the modified rice straw for removing this basic dye from aqueous solution.

MATERIALS AND METHODS

Preparation of the modified rice straw adsorbent

"Jasmine" rice straw was collected from a local farm in Phitsanulok area. The collected samples were cut into segment of 10 cm length, washed with tap water to remove soil and dust, dried overnight at 50°C, ground and sieved to retain about 50 mesh fractions for further chemical modification.

The thermochemical modification of rice straw was performed according to the method by Vaughan et al. [3] with a slight modification. Ground rice straw was blended with 0.5 M oxalic acid at the ratio of 1:24 (straw:-acid; w/v) and stirred at 50°C. After 1 h the slurry was filtered and then transferred to place in a stainless steel tray. The thermo-chemical esterification between acid and straw was proceeded at 120°C for 90 min in a forced air oven. After cooling the oxalic acid-modified rice straw was washed with distilled water until the liquid did not turn turbid when 0.1 M CaCl₂ was dropped in. After filtration, the modified rice straw was suspended in 0.1 M NaOH at suitable ratio and stirred for 60 min, followed by washing thoroughly with distilled water to remove residual alkali, and then the wet modified rice straw was dried at 50°C for 24 h and preserved in a desiccator for further use as adsorbent.

Adsorption test of MB

The adsorption capacities of MB on modified rice straw were performed using batch equilibrium procedures according to the method by Dragan and Apopei [4]. The 0.01 g of modified rice straw was placed in a vial and contacted with 10 ml of aqueous solution of the dye with a certain concentration. After shaking at 25°C for 6 h, the adsorbent was filtered off and the residual concentration of the dye remained in the filtrate was measured by UV-Visible spectrophotometer at 665 nm. The experiments were conducted in triplicates and negative controls (with no adsorbent) were simultaneously carried out.

IR spectra study

The IR spectra of rice straw before and after esterification were examined on a Fourier Transform Infrared Spectrometer to elucidate the functional groups presenting in the rice straw by using KBr pellet technique for preparation samples.

Scanning electron microscope

SEM was used to characterize the morphology of crude rice straw and modified rice straw. The samples were cut, mounted on stub, gold coated by Sputter coating Sc-7620 and examined by a model Leo 1455 Vp scanning electron microscope.

RESULTS AND DISCUSSION

Characterization of modified rice straw

The IR spectra of crude rice straw and modified rice straw are compared in Fig. 1. It could be seen that there was an obvious characteristic stretching vibration absorption band of carboxyl group at 1737 cm⁻¹ in IR spectrum of modified rice straw. This result indicated the carbonyl functional group; hence it confirmed the occurrence of esterification reaction.

The modified rice straw was also characterized by SEM. It was clearly elucidated that although the esterification reaction did not cause the severe morphology damage, it seem to be that the packed structure was less compact than that of the crude rice straw (Fig.2). This result might assist MB adsorption of modified rice straw.

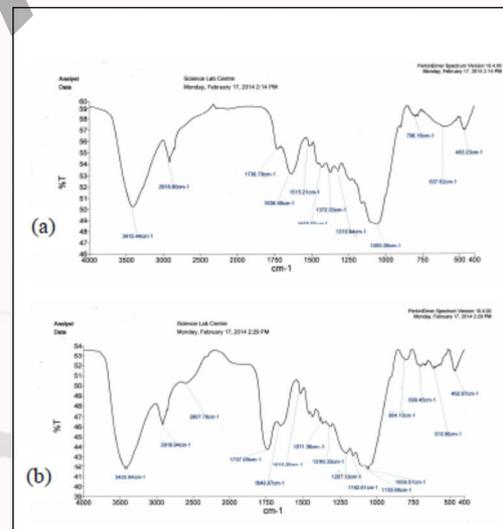


Fig. 1 IR spectra of (a) crude- and (b) modified rice straw

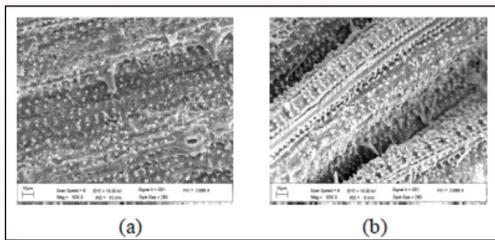


Fig. 2 SEM micrographs (500x) of (a) crude- and (b) modified rice straw

MB ADSORPTION CAPACITIES OF MODIFIED RICE STRAW

Effect of initial pH of MB solution

The initial pH of MB solution was performed over a range from 3 to 11. Fig. 3 shows that the maximum percentage of MB adsorbed was reached at pH 7 and kept basically unchangeable over basic range. It could explain that at a relative high initial dye solution pH, most of the carboxylic groups from oxalic acid attached onto the rice straw surface were ionized. They then interacted with the cationic dye molecules, thus increasing dye adsorption [5-6].

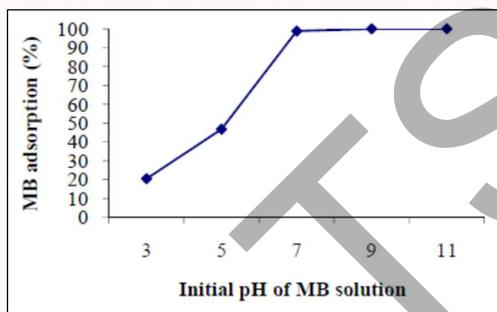


Fig. 3 Effect of initial pH of MB solution on adsorption capacities of modified rice straw (MB concentration 250 mg/l; adsorbent dose 2 g/l; contact time 6 h)

Effect of adsorbent dose

As seen in Fig.4, along with the increase of modified rice straw dosage from 0.5 to 3 g/l, the adsorption equilibrium was reached at 2.0 g/l and kept almost invariable above 2.0 g/l of adsorbent dose. Thus, it is interesting that using modified rice straw only 2.0 g could remove MB completely in solution containing 250 mg/l.

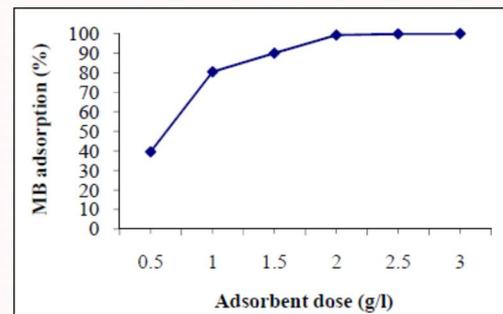


Fig. 4 Effect of modified rice straw dose on adsorption capacities of MB solution (MB concentration 250 mg/l; contact time 6 h; pH 7)

Effect of initial MB concentration

The influence of MB concentration on adsorption percentages of MB was estimated under the condition of 2.0 g/l adsorbent used. As shown in Fig. 5, the modified rice straw adsorbent could completely removed MB in aqueous solution at the concentration upto 250 mg/l. However, when the dye concentration increased to 500 mg/l, the percentages of MB adsorption only decreased slightly to 98.59% but with slower reaching equilibrium. Possible caused of slow attainment to equilibrium could be due to slow molecular diffusion into the micropores of modified rice straw adsorbent [7].

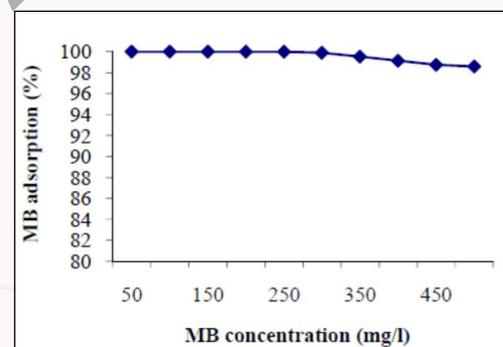


Fig. 5 Effect of MB concentration on adsorption capacity of modified rice straw dose (adsorbent dose 2g/l; contact time 6 h; pH 7)

Mb adsorption kinetics

The Mb adsorption kinetics on the modified rice straw is presented in Fig. 6. The adsorption rate of MB was very rapid at the initial stage of adsorption. It was caused by the fast diffusion and adsorption of MB molecules onto the external surface attached with oxalic acid of the modified rice straw adsorbent. After a very rapid adsorption, dye uptake rate slowly declined with lapse of time and reach equilibrium value at about 120 min. This

process was controlled by the pore diffusion velocities of dyes into the intraparticle matrix of adsorbent [8].

A pseudo-second order kinetics model [9] was used to explore the mechanism of dye adsorption. The kinetics data of the first 120 min in Fig. 6 was treated with the Eq.(1):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad \dots(1)$$

Where q_e (mg/g) is the adsorption capacity at equilibrium; K_2 (min⁻¹) is the rate constant of the pseudo-second order model. After definite integration by applying the boundary condition $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, Eq. (1) becomes the following linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \dots(2)$$

The experimental data in Fig.7 was linearly regressed using Eq. (2) that K_2 and q_e can be determined from the slope and intercept of the plot of t/q_t versus t . The high value of correlation coefficient showed that the data fitted well to the pseudo-second order rate kinetics model.

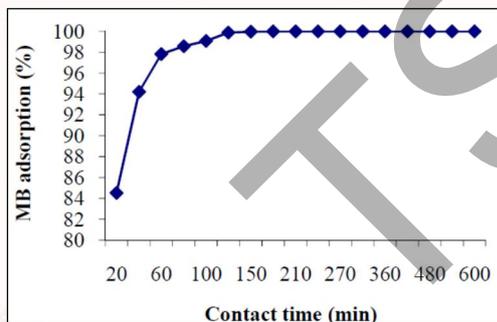


Fig. 6 Adsorption kinetics of MB by modified rice straw (MB concentration 250 mg/l; adsorbent dose 2g/l; pH 7)

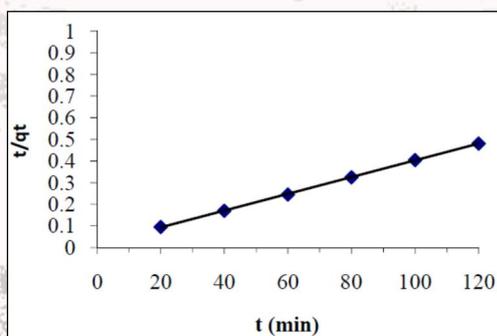


Fig. 7 The pseudo-second order kinetics model plot of MB adsorbed by modified rice straw (MB

concentration 250 mg/l; adsorbent dose 2g/l; pH 7.0)

The amount of the MB adsorbed on the modified rice straw was calculated as the adsorption capacity by using the following equation:

$$\text{Adsorption capacity} \left(\frac{mg}{g} \right) = \frac{\{(C_0 - C)V\} \times MD \times 10^3}{W}$$

Where C_0 and C are the concentration of MB in aqueous solution (M) before and after the interaction with the modified rice straw respectively, V is the volume of MB in aqueous solution (L), W is the amount of the modified rice straw (g), and MD is the molar mass of dye (MB = 319.85 g/mol).

Thus, when using the adsorption condition as MB concentration 250 mg/l; adsorbent dose 2g/l; pH 7; contact time 2 h; the adsorption capacity of the modified rice straw for MB removal was 124.86 mg MB/g modified rice straw. Anywise, as mention above (Fig. 5), it clearly notes that the adsorption capacity could significantly improve almost 2 times with longer contact time of higher MB concentration.

Although it has been known that activated carbon is quite effective for removal of dyes, its use is restricted in developing countries due to its higher cost [10]. Hence, these results introduce a chance to reduce the cost of wastewater treatment by using the modified rice straw as adsorbent for the cationic dye removal.

CONCLUSIONS

This study confirmed that the modified rice straw was an excellent adsorbent for removal of MB dye from aqueous solution with high adsorption capacity at short contact time. It can be used on the condition with the wide range of initial pH of MB solution ($pH \geq 7$) which might be suitable for various industrial wastewater treatments. The optimum condition using 2.0 g/l adsorbent could completely remove MB from 250 mg/l of MB solution at 2 h contact time resulted the adsorption capacity of 124.86 mg MB/g modified rice straw. The adsorption process could be described by the pseudo-second order kinetics model. These findings can conclude that the modified rice straw might be an alternative low-cost-adsorbent for effective

removal of the catio-nic dyes in wastewater treatment.

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