

REMOVAL OF METHYLENE BLUE IN AQUEOUS SOLUTION ONTO ACTIVATED RICE HUSK ASH BY MICROWAVE METHOD

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ABSTRACT

Nowadays, it is possible to use any plant biomass material, brought to the pyrolysis under anaerobic conditions to produce activated carbon, which can be residues of crops and wood waste, or different organic materials. Dyes produced by the textile, printing and paper industries can end up in waste waters and are therefore a potential source of pollution of rivers and waterways. In this research, rice husk, abandoned and available agriculture waste, were developed into activated carbon using microwave methods. The optimal experimental parameters such as pH, contact time, activated carbon dose, and temperature were investigated. The activated carbon was characterized by scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) analysis. The maximum adsorption capacities toward methylene blue was 6.13 mg g^{-1} . The experimental data fitted the Freundlich equation well, although the Langmuir equation could also describe them. The adsorption process follows the pseudo-second-order kinetic model compared to the pseudo-first-order kinetic model.

Keywords: *rice husk ash; agriculture waste; adsorption; activated carbon; methylene blue.*

1. INTRODUCTION

Textile and dyeing industrial manufacture are significantly concerned due to the large amount of effluent containing highly colored species. Pigments are threaten to human beings. [1, 2] Methylene blue (MB) is a cationic dye(.) having various applications in chemistry, biology, medical science and dyeing industries. Its long-term exposure can cause vomiting, nausea, anemia and hypertense. Conventional methods such as physical, chemical and biological methods, including adsorption, biosorption, coagulation/flocculation, advanced oxidation, ozonation, membrane filtration and liquid – liquid extraction have been widely used for the treatment of dye - bearing wastewater. The advantages and disadvantages of every removal technique have been extensively reviewed [2-4]. Adsorption is a very effective separation technique in terms of initial cost, simplicity of design, ease of operation and insensitive

to toxic substances. Activated carbon (powdered or granular) is the most efficient adsorbent used for dye removal. But it is expensive to produce and regenerate. Currently, a number of non-conventional, low cost adsorbent such as rice hull ash, sugarcane bagasse, sawdust, pine needle, eucalyptus bark, prawn shell activated carbon, and mango seed kernel powder have been used for the removal of dyes and heavy metal ions from aqueous solution. The rice husk was separated during the rice milling process. Rice husk contains about 75% of volatile organic compounds burned during burning and the remaining 25% converted to ash. Organic compounds contain mainly cellulose, lignin, and hemicellulose, as well as other ingredients such as nitrogen and inorganic compounds. In particular, lignin accounts for 25-30% and cellulose accounts for 35-40%.[5-7]. Rice husk was prepared into activated carbon by microwave radiation to enhance its adsorption capacities.[8, 9].

The main aim of this study was to evaluate the possibility of using a Rice husk to develop a new low cost activated carbon with microwave method and study its application to remove methylene blue dye from aqueous solution. Kinetics, thermodynamic studies and adsorption isotherm models were investigated to evaluate experimental data.

2. EXPERIMENTAL

2.1 Chemicals and materials

Methylene blue (C₁₆H₁₈N₃SCl₃H₂O) was obtained from E. Merck. The solution was prepared by dissolving the required amount of dye in distilled water. All other reagents used in this study were analytical grade.

Rice husks are collected from farms in the Mekong Delta area, Vietnam. Rice husk was soaked with tap water to eliminate dust and impurities and then cured under the sun for 3-4 days.

2.2 Microwave activated carbon rice husk preparation

Rice husk ash (RHA, 10 g) was mixed with 10 mL of 91% H₃PO₄ in a porcelain beaker. The mixture was put into a microwave model SHARP R-20A1(S)VN for 5 min at 500 W. The product was left to room temperature then centrifuged to wash until pH of solution was at 6.0-6.5. The final result was dried in oven at 80°C in 3 hours to obtain the activated rice husk ash (ARHA).[8-10]

2.3 Adsorption studies

The batch adsorption tests were carried out to evaluate the different parameters affected such as activated carbon dose, pH, agitated time, initial concentration of heavy metals on the removal efficiency of MB. The effect of pH parameter was studied with the initial pH from 3.0 to 8.0. The effect of contact time was carried out at 303 K and 200 rpm. ARHA (2 g L⁻¹) was stirred with a metal ions solution (100 mL). After been completely mixed by using a shaker

incubator (model LM-570RD) at 303 K and 200 rpm, the residual concentration of metal ions was measured using an UV spectrophotometric machine. Different concentrations of MB ranging from 10 - 250 mg L⁻¹ were examined under the optimal temperature, pH, agitation time and ARHA dose that have been found in the earlier tests.

The load of MB adsorbed on the surface of the adsorbent at equilibrium and time, q_e and q_t respectively, in mg g⁻¹ were estimated based on the equations as follow:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

where C_0 , C_e , and C_t are the initial concentrations of MB, at equilibrium and at time t in mg L⁻¹, correspondingly, V represents the solution volume (L), and m symbolizes the adsorbent dose used (g).

3. RESULTS AND DISCUSSION

3.1 Biosorbent characteristics

FTIR Analysis

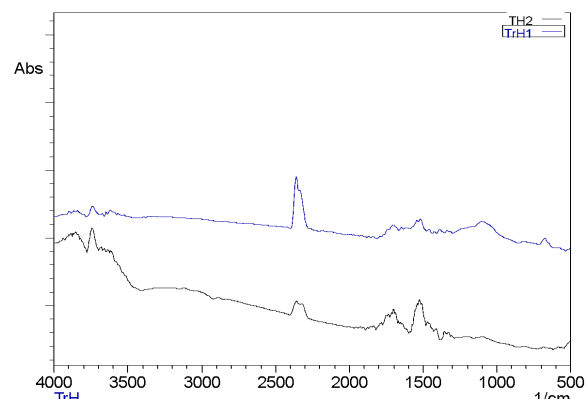
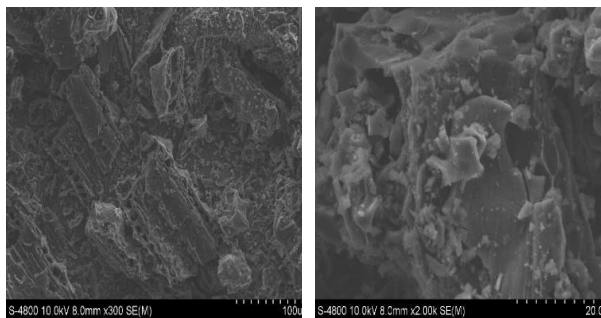


Figure 1. FTIR spectra of ARHA before and after adsorption of MB

The functional groups of activated carbon are closely related to the specific chemical properties, which affect their adsorption capacity. In this study, FTIR analysis was used to identify the functional groups, especially the amino moiety. The

peak at 670 cm^{-1} disappeared after an adsorption experiment, which may be due to the losing of Mn – O bond. New bands at 1510 and 1704 cm^{-1} may be due to the C=O stretching vibration from the carboxylic acid groups. A peak at 2348 cm^{-1} disappeared because of the absence of aliphatic groups such as CH, CH₂, CH₃. A strong peak was centered at 3736 cm^{-1} , which may be due to the hydroxyl stretching region.

SEM analysis



(a) (b)

Figure 2. SEM of rice husk ash before (a) and after (b) activated by microwave methods.

The SEM image after treatment and before adsorption reveals that the pores within the particles are highly heterogeneous and the activated carbon exhibits gaps of different sizes. The heterogeneous pores may provide a high possibility for dye and heavy metals to be trapped and adsorbed.

3.2 Effect of pH on MB removal

The pH factor has an important effect on dye adsorption since the pH of the medium will control the magnitude of the electrostatic charges which are imparted by ionized dye molecules. As a result, the rate of adsorption will vary with the pH of an aqueous medium.[9] The effect of pH on the removal of MB by ARHA was studied. It was observed from the Figure 3 that the adsorption was clearly dependent on the pH factor where adsorption was increased when pH increased and the capacity removal of MB was highest at a pH of 6 at $q = 4.3347 \text{ mg g}^{-1}$

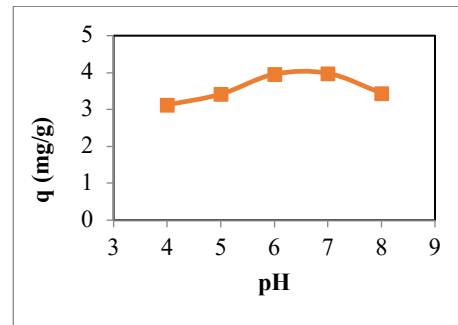


Figure 3. Effect of the initial pH on MB adsorption on ARHA in 180 mins

3.3 Effect of ARHA dosage on MB adsorption capacity

The percentage of color removal increases with increasing ARHA dosage. When the adsorbent dose increases, the number of sorption sites at the adsorbent surface will increase, as a result, increase the percentage of color removal from the solution. The effect of the adsorbent dose on the percentage of MB removal was studied at 30°C and it can be observed in Figure 4 and Figure 5 that the percentage of MB removal increased with the increase of adsorbent dose. However, when the dosage is increased too high, and the adsorption is saturated, MB is returned in solution.

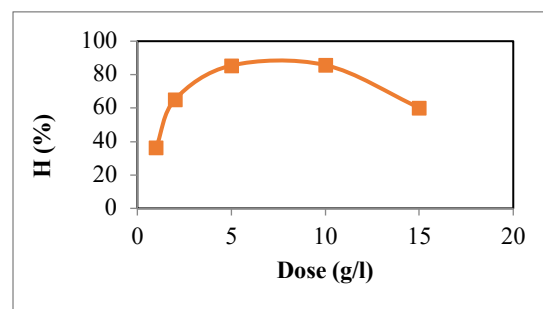


Figure 4. Percentage of MB removal in the study effect of activated carbon dose

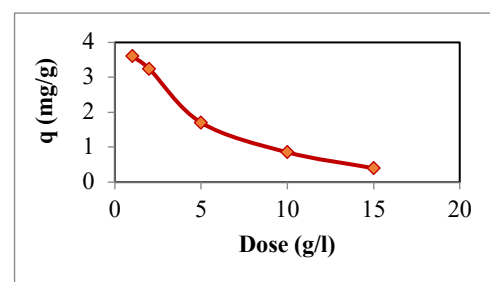


Figure 5. Effect of activated carbon dose on MB removal

3.4 Adsorption isotherms

As shown in Figure 6 and Table 1, the RMSE calculated by the Freundlich model is smaller than the RMSE calculated in the Langmuir model. This suggests that the Freundlich research model accurately reflects the process of adsorption of MB by ARHA at 303K. The nonlinear adsorption isotherm of ARHA for MB at 303 K follows the Langmuir adsorption model as well.

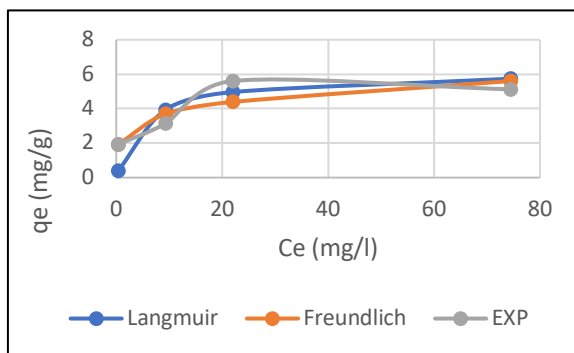


Figure 6. Non-linear isotherm models of MB adsorption by ARHA at 303 K

Table 1. Parameters of the Langmuir and Freundlich adsorption processes of ARHA for MB adsorption at 303 K

Materials	Langmuir			Freundlich		
	RMSE	KL	qmax (mg g ⁻¹)	RMSE	Kf	1/n
ARHA	0.8826	0.1921	6.1387	0.6346	2.3676	0.1999

3.5 Adsorption kinetics

From the value of the parameters of the second-order kinetic equation and the graph shows that the coefficient of determination of R^2 is very high reaching $0.9997 \div 0.9999$. In addition, the adsorption value required by the

kinetic equations is closer to the experimental value than the first-order adsorbent kinetics, showing that adsorption of ARHA follows the second-order quadratic dynamics. When the concentration of the adsorbed material is increased, the second rate constant decreases, correspondingly the initial adsorption rate of the solid phase increases. Accordingly, the response in the system depends on the concentration of Pb^{2+} on the contact surface between the two phases.

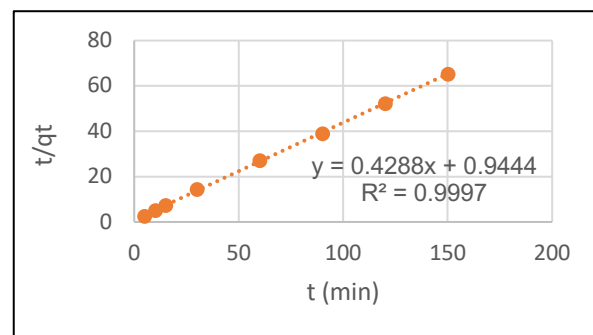


Figure 7. Pseudo-second order kinetic model for MB adsorption onto ARHA

4. CONCLUSION

The rice husk waste was successfully activated by microwave method to facilitate the adsorption of Methylene Blue from aqueous solutions. The maximum adsorption was observed at pH 6 within 180 min. A pseudo-second order model and intraparticle diffusion model adequately describe the kinetics of adsorption process. The equilibrium biosorption data fit better with the Freundlich equation than Langmuir model. The activated rice husk ash waste will be a promising, alternative, economical, and effective sorbent for the removal of methylene blue from wastewater.

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