

# COMPARATIVE ADSORPTION STUDIES BY USING LOW COST ADSORBENTS OF RICE HUSK AND RICE HUSK ASH ON METHYLENE BLUE DYE REMOVAL

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## ABSTRACT

*In this study, the rice husk (RH) and rice husk ash (RHA) were used as a low cost adsorbent to remove methylene blue (MB) from aqueous solution by batch sorption technique. Effects of initial dye concentration, solution pH, and adsorbent dose on sorption were studied. It was shown that the percent removal also increased when the adsorption capacity ( $q_e$ ) were increased. In the batch system, the adsorption capacity was increased when the parameters were increased until it achieved the equilibrium. The Langmuir and Freundlich's models were applied to the data related to adsorption isotherm. The optimal parameters for this experiment were 7.5ppm for initial concentration, 0.6g adsorbent dosage and pH 5.8. In the batch system, the adsorption capacity was increased when the parameters were increased until it achieved the equilibrium. The RHA could be employed as the more effective low cost adsorbent for removal of Methylene Blue Dye from aqueous solution.*

**KEYWORDS:** Rice husk ash; Rice husk; Dye removal; adsorption; Methylene blue

## 1.0 INTRODUCTION

Dyes are common constituents of effluent discharged by different industries, especially for the textile industry (Rajeshkannan et al.,

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2011). Among of these industries, textile industry used mostly dyes for fiber coloration. The conventional wastewater treatment, which rely on aerobic biodegradation have low removal efficiency for reactive and other anionic soluble dyes. However, it is not easy to remove dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems (Kargi & Ozmihci, 2004). It is usually treated with either by physical or chemical processes. However, these processes are very expensive. Currently, the liquid - phase adsorption technique is one of the most popular method for dyes removal from wastewater. It provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pretreatment step before its application (Rajeshkannan et al., 2011). The adsorption process is one of the effective methods for removal of dyes from the waste effluent.

Several methods for the treatment of dye wastewater are including filtration technology, chemical treatment, oxidation, sedimentation, adsorption and ion exchange. Dyes removal is effectively used physical and chemical methods but this method is highly expensive and has operational problems. Adsorption of the molecules onto various adsorbents is an ideal option for dye decolorization. Garg et al., (2003) had reported that the use of activated carbon as adsorbent is more widely and effectively but it needs high cost and plus the increased cost of adsorption system. However, production of activated carbon from agricultural by-products serves a valuable material and provides an efficient adsorbent material for the removal of organic pollutants from wastewater.

Adsorption is one of the processes, which besides being widely used for dye removal. The term adsorption refers to a process whereas a material is concentrated at a solid surface from its liquid or gaseous surroundings. One of the most important characteristics of an adsorbent is the quantity of adsorbate whereas it is usually calculated from the adsorption isotherms. The adsorption isotherms are constant-temperature equilibrium relationship between the quantity of adsorbate per unit of adsorbent ( $q_e$ ) and its equilibrium solution concentration ( $C_e$ ). A good adsorbent (Linsen, 1970; Tien, 1994) should generally possess a porous structure (resulting in high surface area) and the time taken for adsorption equilibrium to be established should be as small as possible so that it can be used to remove dye wastes in lesser time. Ion exchange is basically a reversible chemical process wherein an ion from solution is exchanged for a similarly charged ion attached to an

immobile solid particle (Gupta & Suhas, 2009). Ion exchange has been used for the removal of colors.

Natural materials that are available in large quantities, or certain waste product from industrial or agricultural processes, may have potential as inexpensive adsorbents. Rice husk waste can be used as an alternative and favorable adsorbent for dye removal. Plus, rice husk is discharged in large quantities at rice processing facilities but the recycling rate of the rice hulls is about 10.0% (Woon et al., 2006).

This research focus is to study the effectiveness of two low cost adsorbents, rice husk and rice husk ash for Methylene Blue Dye removal. The study has been extended by studying the effects of pH solution, the adsorbent dosage and the empirical study of applying the adsorption isotherm.

## **2.0 EXPERIMENTAL METHOD**

Bioadsorption experiments were carried out in a rotary shaker at 160rpm for 135 minutes at 30°C by using 250 mL shaking flasks containing 50 mL of dye solutions at different concentrations and initial pH values of dye solutions. After shaking the flasks for a predetermined time intervals, the samples were withdrawn from the flasks and the dye solutions were separated from the adsorbent by filtration in centrifugation. Dye concentrations in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of dye with a UV-Spectrophotometer.

## **3.0 RESULT AND DISCUSSION**

### **3.1 Effect of pH Solution onto Adsorption of Methylene Blue**

Adsorption capacity ( $q_e$ ) defined as the quantity adsorbate absorbed per unit weight of adsorbent. It is paramount because it described the key economic in the adsorption process and also determines the direct cost in term of the rate of the adsorbent exhaustion (Slejko, 1985).

The optimal percentage removal for RHA is 98.3% which is slightly higher than RH, 96.9%. In addition, the percentage removal of methylene blue onto RHA adsorbent is higher compare to RH bioadsorbent in all pH dye solutions. This is because RHA has a large a number of functional groups (-CO-, -OH, -Si-OH, -Si-H, -C-OH, etc.) that may interact with dye molecules extremely compare to RH. Faust

& Aly (1997) were specified that the increasing length of side chain will increase the hydrophobicity of the molecule which results in greater adsorption. According to the functional group of RHA, there is the presence of both free and hydrogen bonded (hydroxyl) OH groups and Si-OH (hydroxyl group on silicon) groups on the surface. This stretching was due to both the silanol group (Si-OH) and adsorbed water on the surface (Abou Mesalam, 2003). The silanol groups (Si-OH) determined the chemical behavior of its surface, exercising an important function in the adsorption processes (Wood & Rabinovich, 1989). It is a weak acid & strongly interact with mainly with water, forming hydrogen bridges. However, at pH 6.0 and above, the adsorption capacity ( $q_e$ ) was decreased and achieved the equilibrium. Consequently, at low pH, the surface of bioadsorbents was getting protonated which result the repulsive force between cation and cause the functional group would be in dissociate form.

The effect of pH on methylene blue adsorbed by RHA was studied by Sarkar et al., (2010). They claimed that the adsorption at pH of 6.0 was better because of the better removal of methylene blue. Figure 1 demonstrates the percentage removal is optimally at pH 6.0. This graph in Figure 1 indicates that the percentage removal is increasing with the increasing of pH. This is because methylene blue dye is cationic dye that can achieve basicity at higher pH in the adsorption separation process by RHA and RH. This results contributed by the electrostatic interaction between the protonated groups of carbon and acidic dye and chemical reaction between adsorbate and adsorbent (Namasivayam & Kavitha, 2002). As the pH increased, the effect of competition of H<sup>+</sup> ions decreases and the positively charged ions takes their place on the surface while there is increasing of negative charges on the carbon surface. The negative charges are neutralized and may increase the protonation by dilution process and finally provides more active sites for the adsorbent (Santhi & Manonmani, 2009). As a conclusion, the higher the amount of exchangeable base cations, the more acidity can be neutralized in a short time perspective.

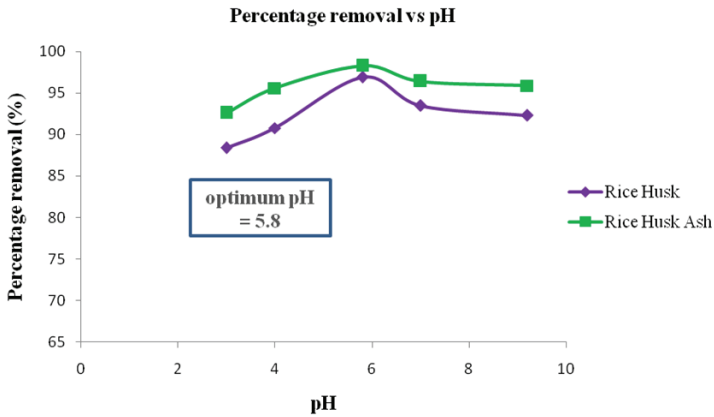


Figure 1. Effect of pH solution for methylene blue dye removal

### 3.2 Effect of Adsorbent Dosage onto Adsorption of Methylene Blue

The value of adsorption capacity ( $q_e$ ) decreased with the increase of adsorbent dosage. The  $q_e$  is decreased from 1.687 to 0.361 mg/g for RH and from 1.794 to 0.366 mg/g for RHA. The decrease of  $q_e$  may be caused by the aggregation of particles of the adsorbent that resulted in less binding sites for dyes (Safa & Bhatti, 2011). Furthermore, the  $q_e$  decremental also affected by the overlapping of adsorption sites as a result of overcrowding of adsorbent particles in the dye solution. Consequently, the adsorbent cannot perform simultaneously consistent to adsorb the adsorbate. These proved that as the adsorbent dosage is increased, the capability of  $q_e$  is also increased. According to theory, if the molecule is too large, adsorption will be hindered and adsorption capacity will decrease as very large molecules block or cannot penetrate pores or pathway within the adsorbent. In addition, the larger molecules will diffuse more slowly from solution and therefore will require longer times for full equilibrium adsorption capacity to be realized (Slejko, 1985).

Referring to Figure 2 indicates that the percentage removal of adsorbent RH is increased from 89.9 to 98.3% (for 0.2 to 0.8 g) and decreased to 96.2% after addition of 1.0 g of RH. It is caused by high adsorbent dosage giving the surface sites to be limited sorption due to limited space for the adsorbent to adsorb the methylene blue ions. After a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. Meanwhile, the percentage removal of RHA is increased from 95.7 to 99.3% and after addition of 0.6 g of RHA, the percentage is decreased

to 98.1 and 97.5%. In comparing these two low cost adsorbents, RH needs larger quantities than the amount of RHA in order to adsorb methylene blue. The optimum adsorbent dosage was found to be 0.8 g for rice husk ash and 0.6g for rice husk. This is because RHA is highly porous and lightweight and 99% of its' pore area caused by mesopore. The surface area is one of the principal characteristics affecting the adsorptive capacity of an adsorbent. In conclusion, the quantities of RHA that use for methylene blue removal is less compared by using the RH.

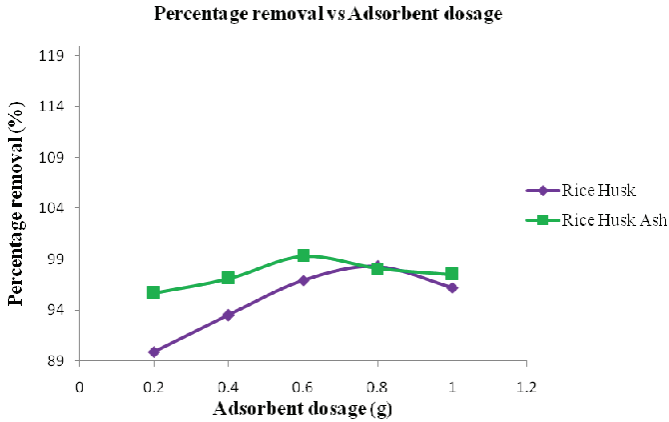


Figure 2. Effect of adsorbent dosage on the percentage removal of methylene blue

### 3.3 Effect of Initial Concentration Solution onto Adsorption of Methylene Blue

The  $q_e$  is increasing with the increasing of the initial concentration of solution. According to Figure 3, for RH, the  $q_e$  is increased from 0.1143 to 0.5920 mg/g with the increasing of the initial concentration. While for the RHA,  $q_e$  also increased from 0.1153 to 0.6009 mg/g. This result was concluded that the methylene blue molecules preferably adsorbed into the porous structure RHA rather than RH.

The percentage color removal of methylene blue for RH and RHA were increased due to the initial concentration was increased. Interestingly, the percentage removal of methylene blue by using RHA is higher compare to RH. The percentage removal is increased from 91.4 to 94.7% with 1.5 to 7.5 ppm of RH. Meanwhile, the percentage removal is increased from 92.2 to 96.1% with 1.5 to 7.5 ppm of RHA. This demonstrates that the higher initial concentration provides more necessary driving force to overcome the resistances to the mass transfer of iron between the aqueous phase and the solid phase and enhances

the adsorption uptake of methylene blue solution. This adsorption is involved in physical adsorption where the molecules are attracted by van der Waals forces, and attach themselves to the surface of the solid. The molecules remain intact, and can be freed easily (the forces are small, and short-range). Plus, there is more migration of methylene blue from solution to the surface of RHA. It is because more intra-particle diffusion of dye into the interior pores of the RHA particle (Safa & Bhatti, 2011).

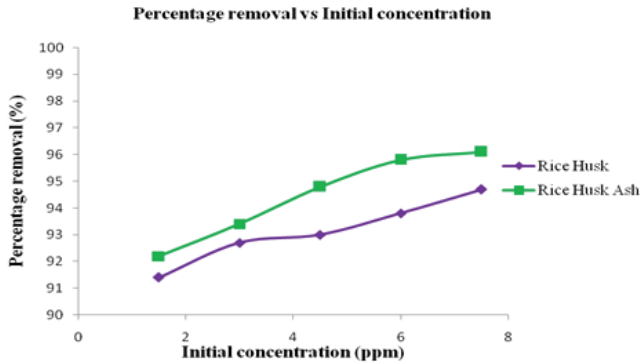
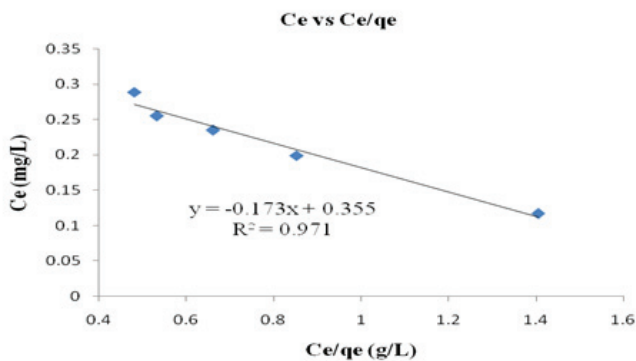


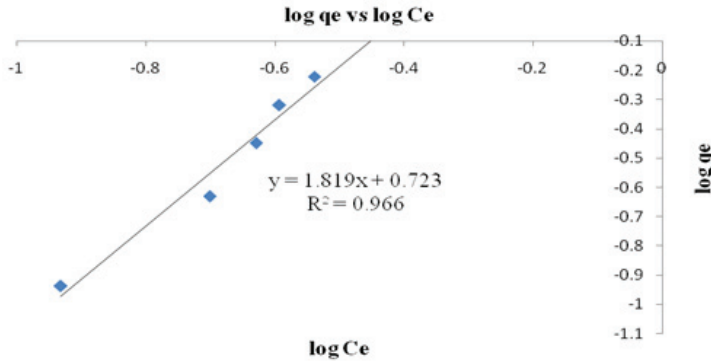
Figure 3. Effect of initial concentration on the percentage removal of methylene blue

### 3.4 Adsorption Isotherm

Adsorption data fitted well with the isotherm models such as Langmuir and Freundlich. The isotherm is important to determine the amount of adsorbent. This isotherm is a constant temperature equilibrium relationship between the quantities of the adsorbate per unit of adsorbent ( $q_e$ ) and its equilibrium solution concentration ( $C_e$ ) (Gupta & Suhas, 2009).



(a) Langmuir isotherm



(b) Freundlich isotherm

Figure 4. Linearized plots of (a) Langmuir and (b) Freundlich isotherm for adsorption of methylene blue onto rice husk at pH 5.8 and 0.6g adsorbent dosage for rice husk ash

According to the Langmuir isotherm shown in Figure 4(a), the values of  $Q_0$  and  $b$  calculated from the Langmuir isotherm.  $Q_0$  is the total adsorption capacity of the adsorbent and the value is 1.5748mg/g for RH and 5.7803mg/g for RHA. Meanwhile,  $b$  is related to the free energy of adsorption and the value is 0.7488L/mg for RH 0.4873L/mg for RHA. These values determined that the RHA has a higher adsorption capacity compare to RH.

The Freundlich constant,  $K_F$  is used as a relative measure of adsorption capacity and  $n$  is related to the intensity of adsorption. Referring to Figure 4(b), the value of  $K_F$  is 1.2310(mg/g)(L/mg)<sup>1/n</sup> for and the value of  $n$  is 0.0257 for RH. However for RHA, the value of  $K_F$  is 0.3243 (mg/g) (L/mg)<sup>1/n</sup>. Freundlich isotherm attempted to attach rigorous physical significance to the parameters  $K_F$  and  $1/n$ .  $K_F$  and  $n$  are constants for a given adsorbate and adsorbent at a particular temperature.

The application of Langmuir and Freundlich isotherms presented that the Freundlich and Langmuir isotherm models provided excellent satisfactory with the highest  $R^2$  value. The  $R^2$  value for both RH and RHA are 0.919 and 0.971 correspondingly for Langmuir isotherm. Langmuir–Freundlich models were found to best represent the equilibrium data, suggesting surface adsorption of methylene blue on RHA and RH. According to Langmuir model assumption through its’ derivation, this methylene blue adsorption is a reversible process and the enthalpy of adsorption is the same for all molecules independently of how many have RH or RHA have been adsorbed.



## 4.0 CONCLUSIONS

The batch adsorption was investigated by using two different adsorbents (Rice Husk And Rice Husk Ash) at three different parameters; effects of initial dye concentration, solution pH, and adsorbent on sorption were studied. The result confirmed the Rice Husk Ash (RHA) is the more effective – efficient low cost adsorbent compared to Rice Husk (RH) in methylene blue dye removal.

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