Adsorption Studies of Activated Carbon Prepared From Rice Husk for Removal of Methylene Blue Dye from Aqueous Solution

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***Abstract*:**

Rapid increase in industrialisation has resulted in the generation of a variety of toxic pollutants such as detergents, acids, Agro-chemicals, heavy metals, dyes, etc. Dyes are an important class of pollutants which are extensively used in various industries. The presence of dyes in water largely affect the photosynthetic activities of aquatic plants by reducing the transmission of sunlight into the water bodies, toxic and even carcinogenic affecting the aquatic biota and human health. Due to their complex chemical structure of dye, the removal techniques are often expensive. In this study, activated carbons, prepared from low-cost rice husk by Thermal and Acid activation, were used as the adsorbent for the removal of methylene blue, from aqueous solutions. A batch experiments were carried out in order to investigate the effect of various parameters. UV-visible spectrometer was used for the analysis of final concentration of the solution. Experimental results have shown that, the amount of dye adsorption increased up to reaching equilibrium point with decreasing the initial concentration, adsorbent dosage, contact time and temperature. Over 99.9% removal efficiency were achieved for the given dosage, with respect pH increasing of basicity of solution will increases removal efficiency. Equilibrium adsorption and Kinetic data were studied using Langmuir, Freundlich Isotherms and by pseudo-first, second-order rate respectively.

Keywords: Adsorption, Activated carbon, Dye, Rice Husk, Methylene blue

1. INTRODUCTION

Colour has play important role for both aesthetics, social and market value item throughout the history of mankind. The first synthetic dye was discovered in 1856 by William Henry Perkin, since then, more than 10,000 different alternatives of synthetic dyes have been produced and are available commercially [5]. The production of dyes has increased many folds in the past decade, commercially synthetic dyes in the world with an annual production rate of over 7 × 105 to 1 × 106 tons [18]. The presence of coloured wastewater in the aquatic streams is hazardous to the environmental ecology affecting the aquatic life severely. About 10,000 types of dyes are used in various industries like textile, carpet, food and pharmaceutical [13]. Water contaminated with residual dyes is ultimately discharged in nearby water bodies, and this causes ecological disturbances [13]. Wastewater containing dyes are very hard to treat, since the dyes are organic molecules, resistant to biological degradation and are stable to light water pollution due to colour dyestuff industrial waste becomes a major concern. About 10- 15% of colored effluents are being disposed of from the industries into the environment after process completion [14]. Dyes can cause allergic dermatitis, skin irritation, cancer and mutations. Many physicochemical approaches have been tested, adsorption was considered to be superior to other techniques. This is credited to its low cost, easy availability, simplicity of design, high efficiency, easy operation, biodegradability and capacity to treat dyes [5]. Activated carbon adsorption process for the removal of dyes is an accepted practice especially if the adsorbent is inexpensive and readily available. The use of agricultural waste materials low cost eco-friendly and effective adsorbent material is looking as an alternative.

2. MATERIALS AND METHODS

2.1 CHEMICALS AND MATERIALS

Different Sophisticated laboratory instruments, materials and laboratory chemicals are used: Analytical grade Methylene blue Dye was used as adsorbate, Distilled water was used to prepare mother solution, Concentrated H_2SO_4 for activation of raw rice husk carbon, HCl, NaOH for pH adjustment were used. The required materials Beakers, PH meter, Oven, Muffle furnace, Grinding machine, Shaker, Meshes, Erlenmeyer flasks, Electronic weight balance, Spectrophotometer (UV/ Vis), Scanning Electron Microscope (SEM), The Fourier Transform Infrared spectroscopy (FTIR) was used.

2.2 SOLUTION PREPARATION

MB (supplied by Lab Chemicals P. Ltd., Chennai, India) was taken as the model adsorbate in this study. The stock dye solution was prepared by dissolving 1 g of MB in one liter distilled water. The pH of the experimental solutions was adjusted by addition of either dilute 0.1 M HCl or 0.1 M NaOH solutions. The pH measurements were performed using a Digital pH meter.

2.3 ADSORBENT PREPARATION

Rice husk (RH) is obtained from the local rice producing mill located in Avadi, Chennai, Tamil nadu India. The RH was washed with Double distilled water to remove all the impurities and air-dried for 24 hours. Carbonization was carried out in muffle furnace at 6000C for about half an hour to set complete carbonized carbon. Rice husk is activated with concentrated sulphuric acid (300 ml/kg) for 30 min and it is repeatedly washed with Distilled water. The activated mass filtered, dried and again thermally activated in hot air oven at 1100C for 2 hours and it was ground well and sieved to obtain desired particle size (150 µm).

2.4 CHARACTERIZATION OF ADSORBENTS

Fourier Transform Infrared Spectroscopy, also known as FTIR Analysis or FTIR Spectroscopy, is an analytical technique used to identify organic, polymeric, and, in some cases, inorganic materials. The Fourier Transform Infrared spectroscopy (FTIR) was used to obtain the functional groups of the adsorbent. The surface morphology of adsorbent will be found by scanning electron microscopy (SEM). The surface morphology of untreated Rice Husk materials is different from the treated ones as the treatment may significantly alter the physicochemical properties and porosity of the materials.

2.5 ADSORPTION EXPERIMENT

Adsorption measurement was determined by batch experiments of known amount of the adsorbent with 50 ml of aqueous methylene blue MB solutions of known concentration in a series of 250 ml conical flasks. The mixture was shaken at a constant temperature of 30 °C using Orbital Shaker Incubator at 150 rpm for a period of 150 min. The residual dye concentration in the reaction mixture was analyzed by UV spectrophotometer. The amount of dye adsorbed onto Rice Husk at equilibrium is qe (mg/g) which was calculated by the following mass balance equation:

$$qe = (Co - Ce)/m * V$$

Where *C*o is the initial dye concentration (mg/l), *C*e is the concentration of dye at, *V* is the volume of solution (l) and *m* is the mass of Adsorbent in (g)

The percentage dye removal was calculated as:

$$\% R = (Co - Ce)/Co * 100$$

The controlling mechanisms of adsorption process chemical reaction controlling used to determine kinetic models.

2.6 ADSORPTION KINETIC MODELS

Pseudo-first-order Model

The pseudo-first-order model for adsorption kinetic equation describing the adsorption rate based on the adsorption capacity. The pseudo first-order kinetic equation is expressed as

$$\log(qe - qt) = log\ qe - \frac{k1}{2.303} * t$$

Where q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mg/g), and k1 is the rate constant for pseudo first order adsorption (min-1).

Pseudo-second-order Model

The adsorption kinetics may also be described by the pseudo-second-order model

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{1}{qe} * t$$

Where, K2 is the rate constant of adsorption (min-1) Plots of t/qt versus t gave linear graphs from which qe and k2 were estimated from the slopes and intercepts of the plot respectively.

3 RESULT AND DISCUSSION

3.1 CHARACTERIZATION OF ADSORBENT

The Fourier Transform Infrared spectroscopy (FTIR) was used to obtain the functional groups of the adsorbent. Therefore, Present study FTIR test results in Tables 3.1 and, in Figures 3.1 gives knowledge of surface functional groups and this provides insight to the adsorption capacity.

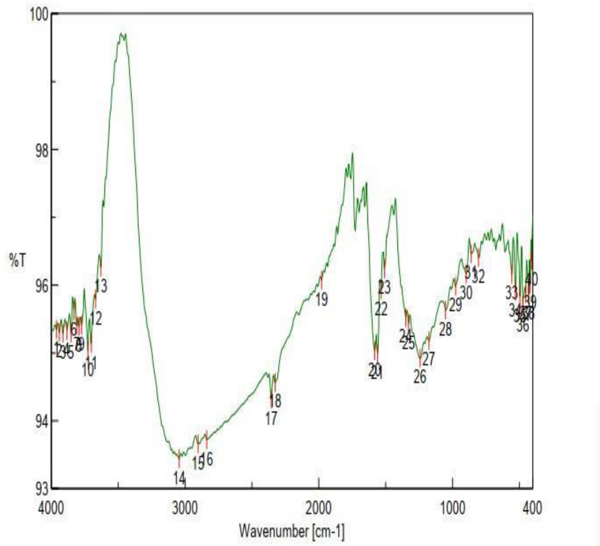


Figure 3. 1 FTIR spectra of treated Rice husk before Adsorption

Table 3. 1 FTIR spectra band assignment for Treated Rice husk

Assignment	Band position (cm
	Rice Husk
O–H stretching of hydroxyl group	3730–3298
C C stretching of alkyne group	2916–2341
C¼O stretching of lactones, ketones, and carboxylic anhydrides	1901–1736
C-O stretching vibrations in quinine structure	1647
C¼C of aromatic ring	1462
C–H stretching in alkanes or alkyl group	1361
C–O groups stretching in ester, ether or phenol group	1246–1169
C-N stretching of aliphatic primary amine	1049
–C C–H–C–H bend in functional group	895–667

Several peaks were observed from the spectra indicates that Treated Rice husk are composed of different functional groups which are responsible for adsorption of the cationic dye Methylene blue, The result shows that The presence of hydroxyl group, alkyne group, lactones, ketones, and carboxylic, alkanes or alkyl group, ester, ether or phenol group, aliphatic primary amine, bend in functional group. The surface morphology of adsorbent was found by scanning electron microscopy (SEM). The surface morphology of untreated Rice Husk materials is different from the treated ones as the treatment significantly alter the physicochemical properties and porosity of the materials. The treatment partially removes protective thin wax on surface. The availability of pores and internal surface is evidently presented in the SEM picture test results in Figure 3.2

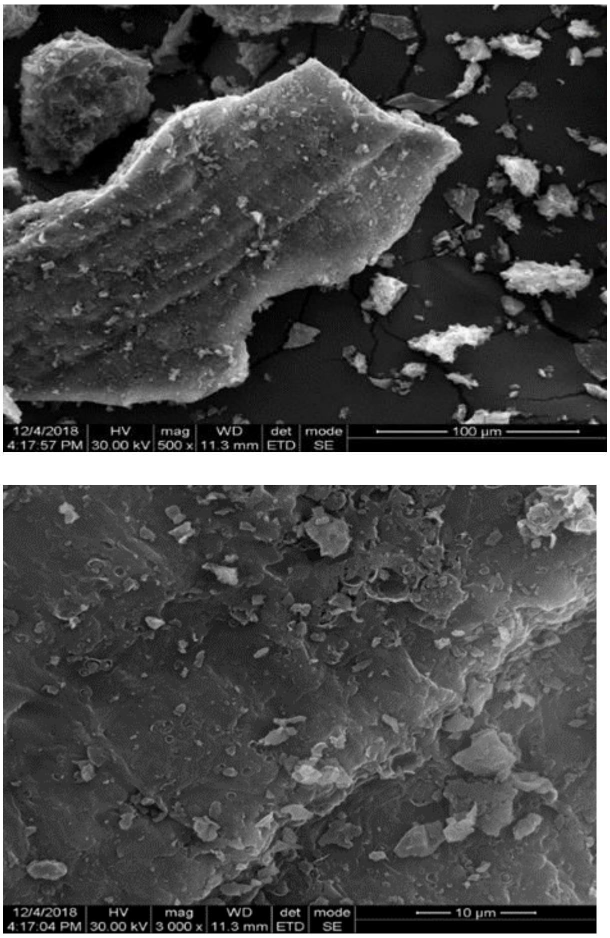


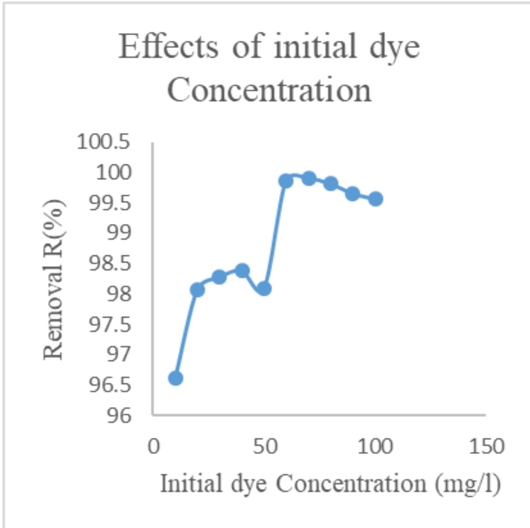
Figure 3.2 surface morphology of adsorbent

3.2 EFFECT OF OPERATING CONDITIONS

The experimental solutions were obtained by diluting the stock dye solution with deionized water to give the appropriate concentration range of experimental solutions. MB (supplied by Lab Chemicals P. Ltd., Chennai) was taken as the model adsorbate in this study. The concentration of the residual dye was measured using UV/visible spectrometer at a λmax corresponding to the maximum adsorption for the dye solution (λmax=668 nm) by withdrawing samples at fixed time intervals The influence of pH (2, 4, 6, 7, 8, and 10), contact time (30, 60, 90, 120, and 150 min) and initial Methylene blue concentration (10, 20, 30,40,50,60,70,80,90 and 100 mg/lit), in temperature (15^{0}C, 25^{0}C, 35^{0}C, 45^{0}C and 55^{0}C), adsorbent (0.20, 0.40, 0.60, 1, 1.20, and 1.40g), on the performance of the rice husk carbon evaluated.

Effects of Initial Dye Concentration

The effect of initial concentration on the removal efficiency of activated rice husk carbon was investigated over wide range of MB concentration (10, 20, 30,40,50,60,70,80,90 and 100 mg/lit). As it can be seen in the Figure (3.3 a, b), uptake of MB was rapid at lower concentration and as concentration reached at Equilibrium Concentration (70mg/l) the amount of MB adsorbed was High (99.9%). After Equilibrium reached Percentage sorption decreased but the amount of MB adsorbed per unit mass of adsorbent increased with increase in MB concentration



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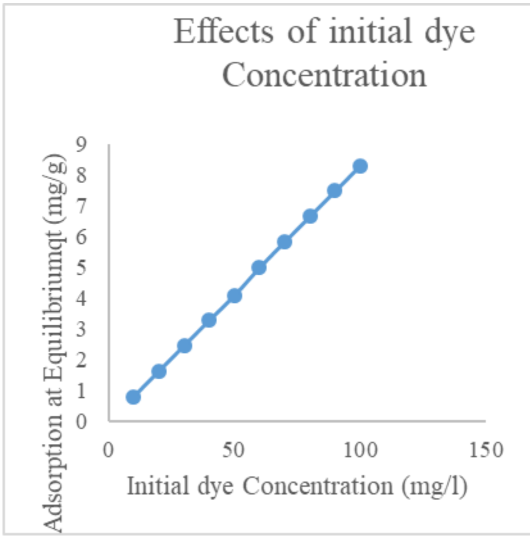

(b)

Figure 3.3. Effect of initial concentration on the adsorption efficiency of Methylene blue (a) Removal R(%),

(b) Adsorption at Equilibrium qt (mg/g) Conditions: pH = 6.4, t= 150 minutes, Adsorbent= 0.60g, and T= 30 ±2°C.

Effect of Adsorbent Dosage

The effect of adsorbent Dose (0.20, 0.40, 0.60, 1, 1.20, and 1.40g), in which the percentage sorption increased with the increased in adsorbent dosage it reaches the equilibrium dosage (1.40g). Figure (3.4 a, b) shows that after reaching equilibrium, the percentage removal is decreased with increasing the adsorbent dosage. Increasing of adsorbent dosage leads to increase of active sites for adsorption but this phenomenon may not lead to high adsorption capacity and adsorption efficiency of adsorbent due to the over load of the

(a)

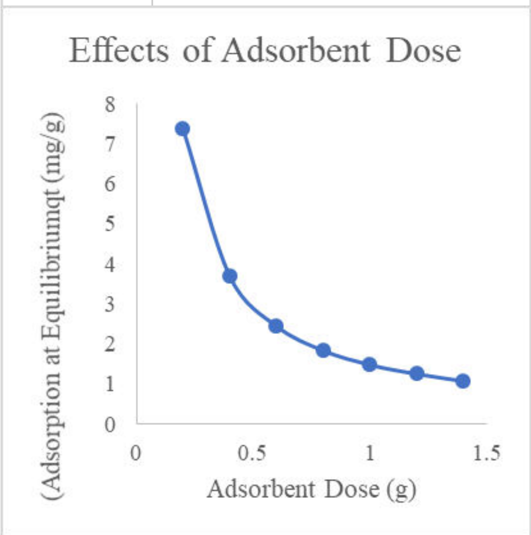

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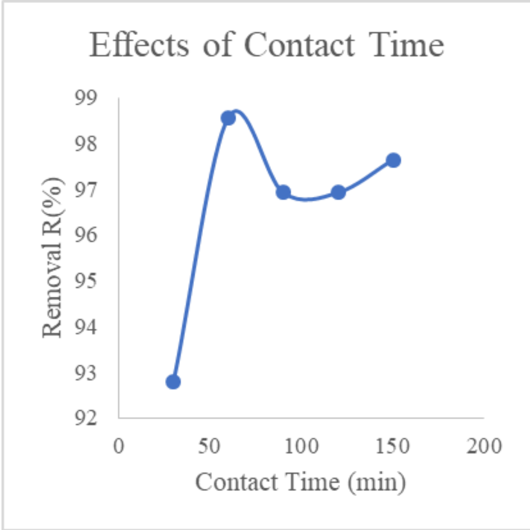
Figure 3.4: Effect of adsorbent dosage on the adsorption efficiency of Methylene blue (a) Removal R(%), (b) Adsorption at Equilibrium qt (mg/g), at Co=30mg/l. pH = 6.4, t=150 min, T= 30 ±2°C.

Effect of Contact Time

The effect of contact time (30, 60, 90, 120, and 150 min) on the amount of dye adsorbed on the Adsorbent was investigated the result obtained is presented in Figure. 3.5 (a, b) As it can be seen a rapid adsorption of Methylene blue dye on Adsorbent was observed at the initial stages of the adsorption and equilibrium is attained within about 60 min.



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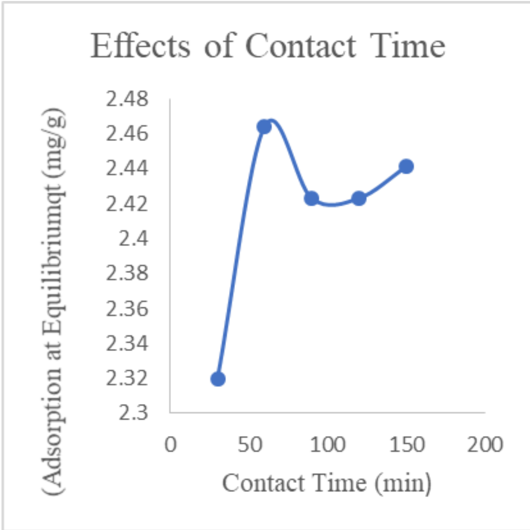

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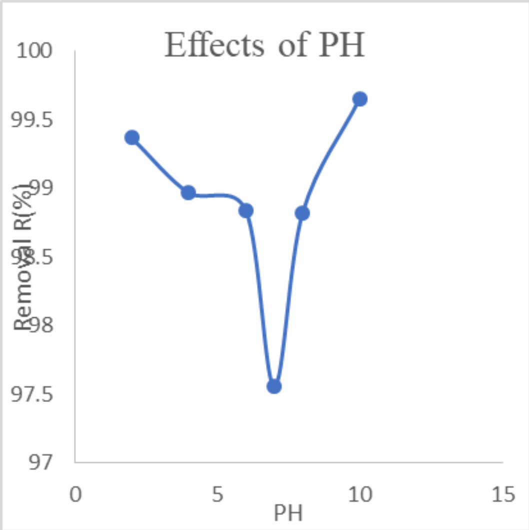
Figure 3.5. Effect of contact time on the adsorption efficiency of Methylene blue (a) Removal R(%), (b) Adsorption at Equilibrium qt (mg/g): C0=30 mg/l, pH =6.4, T= 30 ±2°C, Adsorbent 0.60g

Effect of pH

Studies were carried out to see the effect of pH on adsorption MB on Adsorbent the influence of pH (2, 4, 6, 7, 8, and 10), result obtained as it can be seen in Figure (3.6 a, b), the removal of Methylene blue increased with increasing of pH in basic solution. Lower adsorption of Methylene blue is observed at Neutral pH is due to the Absence of H+ ions and OH -. The high Absorption observed on when Acidic and Basic solution but The Higher Adsorption Reached in basic solution at pH-10.



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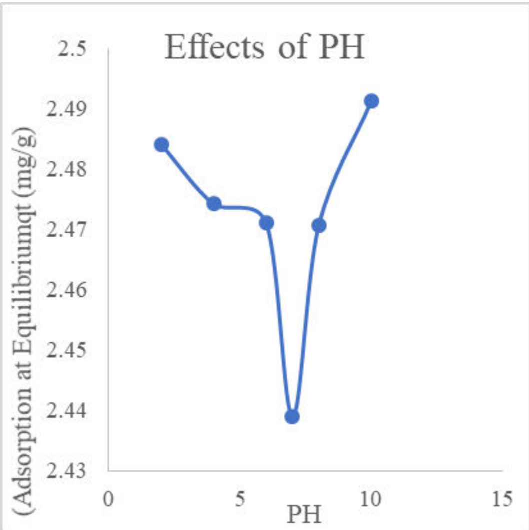
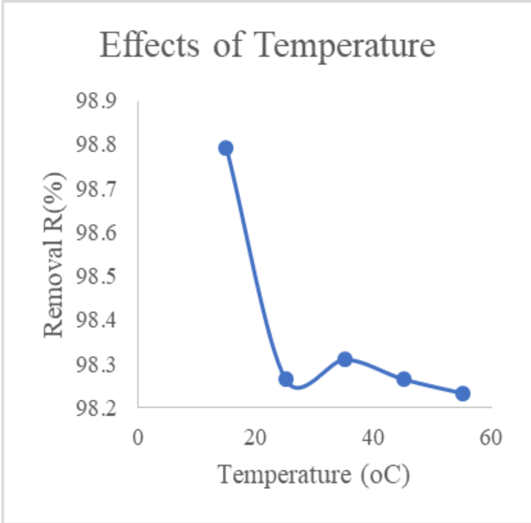


(b)

Figure 3.6. Effect of pH on the adsorption efficiency of Methylene blue (a) Removal R(%), (b) Adsorption at Equilibrium qt (mg/g): C0=30 mg/l, pH =6.4, T= 30 ±2°C, Adsorbent 0.60g

Effect of Temperature

The adsorption of dye onto RHCs. As it can be seen, removal of MB decreases with increasing temperature. The effect of temperature on the adsorption of dye over rice husk experiments were performed in temperature (15^0C, 25^0C, 35^0C, 45^0C and 55^0C). Figure (3.7 a, b) presents the influence of temperature



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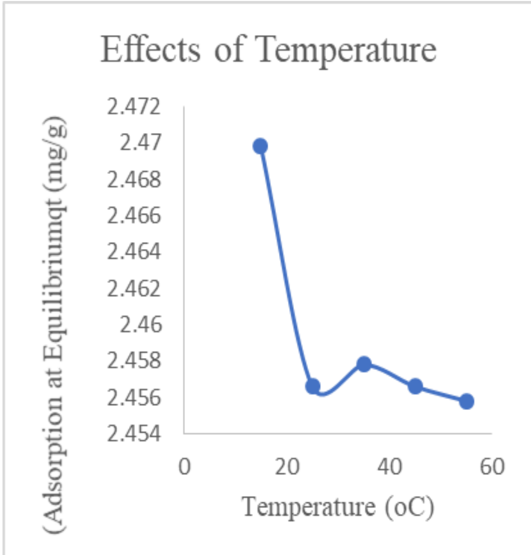

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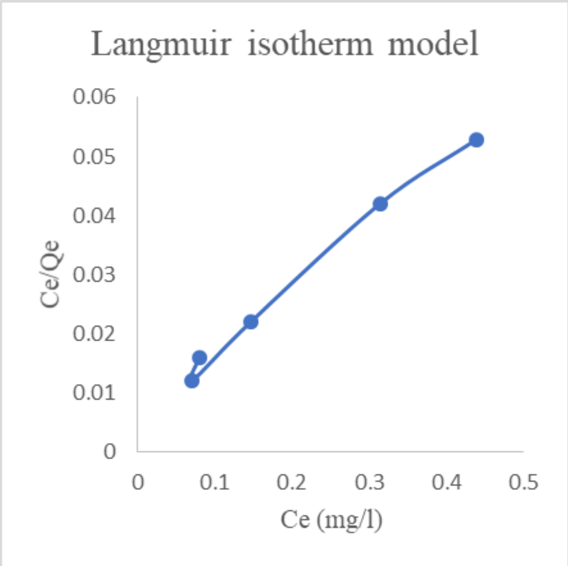
Figure 3.7. Effect of Temperature on the adsorption efficiency of Methylene blue (a) Removal R(%), (b) Adsorption at Equilibrium qt (mg/g): C0=30 mg, pH =6.4, T= 15-55 ° C, Adsorbent 0.60g

3.3 ADSORPTION ISOTHERMS

The Langmuir isotherm is based on the assumption that the adsorption process takes place at specific homogeneous sites, Freundlich isotherm is for multilayer adsorption. As shown in, Figure 3.8 (a, b) It leads to an empirical equation which describes a heterogeneous system RL = 0.006 which was found between (0 < RL < 1) and R2 = 0.9934. From these two values indicated that Langmuir isotherm gives a best fit



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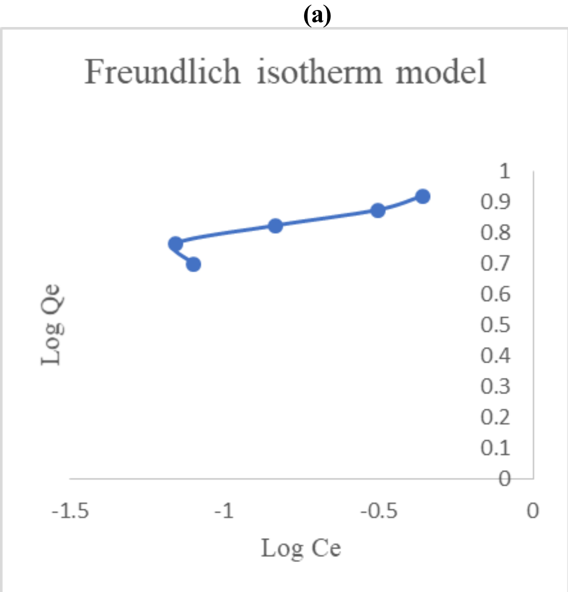


(b)

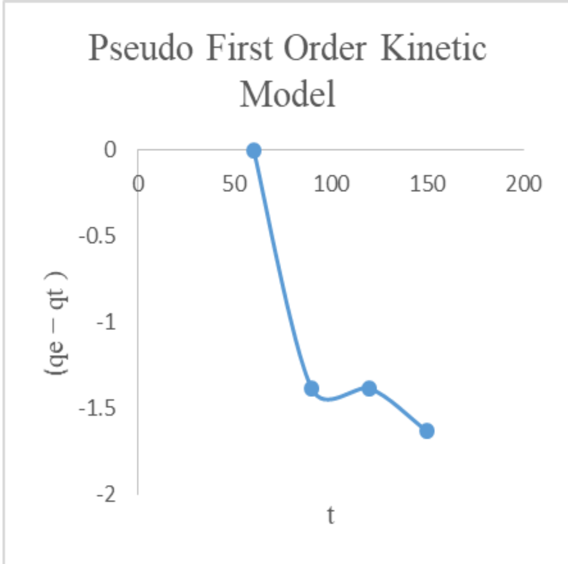
Figure 3.8: (a) Langmuir Isotherm (b) Freundlich isotherm for the MB adsorption data 50 - 100 mg/l concentration

Table 3.2. Langmuir and Freundlich isotherm for Methylene Blue Adsorption

Adsorbent	Langmuir Isotherm				Freundlich Isotherm		
	qm (mg/g)	KL (L/mg)	R2	RL	KF (mg/g)	n (g/l)	R2
Rice husks (RH)	9.1491	18.2167	0.9934	0.006	10.0347	4.3308	0.8794

3.4 KINETIC MODEL STUDY

The kinetic study is important in determining the efficiency of adsorption. Kinetic models have been exploited to test the experimental data and to determine the mechanism of adsorption. Figure (3.9 a, b) shows Pseudo first-order and pseudo second-order kinetics models were used. It was found that the experimental data fitted well to the second-order kinetics than that of Pseudo first-order kinetics model.



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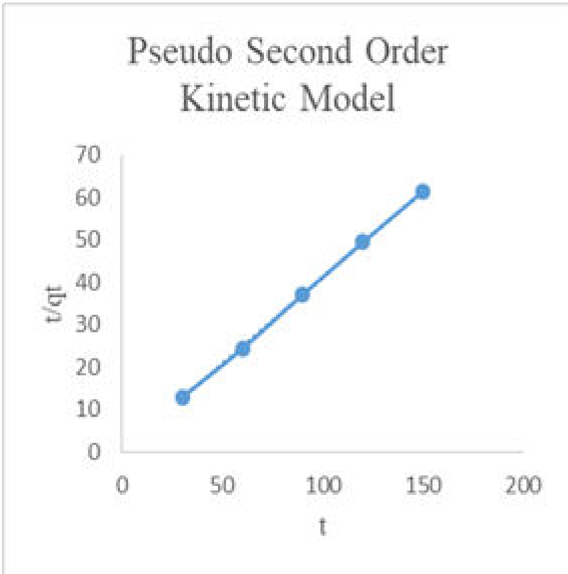


(b)

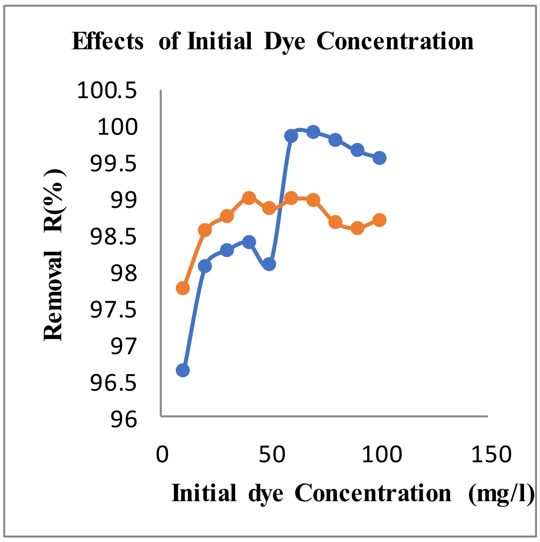
Figure 3.9 (a) Pseudo First Order Kinetic Model (b) Pseudo Second Order Kinetic Model

Table 3.3. Pseudo-First Order and Pseudo-Second Kinetics Parameters for Methylene Blue Adsorption

Adsorbent	qe,exp (mg/g)	qe,cal (mg/g)	K1 (min-1)	K2 (gmin-1mg-1)	R^2
Pseudo-First Order					
Rice Husk	2.4642	2.4436	0.0375		0.725
Pseudo-Second Order					
Rice Husk	2.4642	2.4545		0.3965	0.9997

COMPARISON WITH RAW AND MODIFIED RICE HUSK ADSORBENT

The effect of initial concentration on the removal efficiency of Activated rice husk carbon and Raw Rice Husk was investigated over wide range of MB concentration. As it can be seen in the Figure (3.9 a, b), After Equilibrium reached Percentage sorption decreased but the amount of MB adsorbed per unit mass of adsorbent increased with increase in MB concentration. The effect of Adsorbent Dose on the removal efficiency in which the percentage sorption increased with the increased in adsorbent dosage until reaches the equilibrium dosage. After reaching equilibrium, the percentage removal is decreased with increasing the adsorbent dosage. From the result Modified Activated Rice Husk shows better result when compared to Raw Rice Husk on Adsorption of MB.



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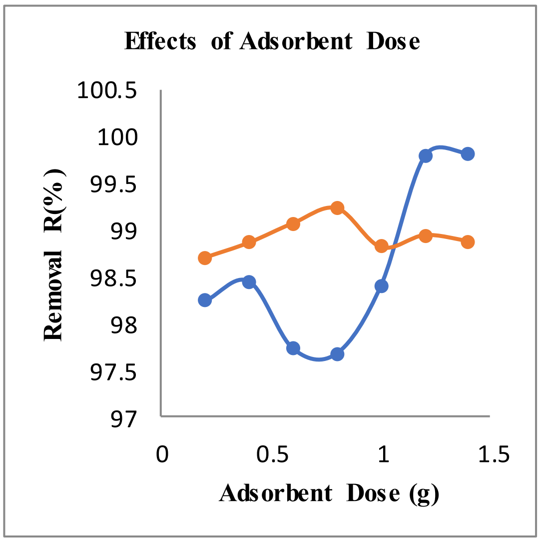

(b)

Modified Rice Husk Raw Rice Husk

Figure 3.9 Comparison with Raw and Modified Rice Husk Adsorbent, Removal R (%)

CONCLUSION

In this study, Activated Rice Husk was tested and evaluated as adsorbent for removal of Methylene blue dye from its aqueous solution in a batch adsorption experiment. The adsorption experiments were conducted for a wide range of solution pH, adsorbent dosage, temperature, initial concentration and contact time. Experimental results have shown that, the amount of dye adsorption increased up to reaching equilibrium point with decreasing the initial concentration, adsorbent dosage, contact time and temperature. with respect pH increasing of basicity of solution will increases removal efficiency. Equilibrium adsorption and Kinetic data were fitted with Langmuir, Isotherms and by pseudo-second-order rate respectively.

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