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ADSORPTION STUDIES OF METHYLENE BLUE DYE ON RICE HUSK AS A BIO-ADSORBENT AND VERIFICATION OF ADSORPTION ISOTHERMS

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ABSTRACT

The technological trend towards waste utilization and cost reduction in industrial processing has attracted use of Rice Husk as a value added material. Both rice husk (RH) and Rice Husk Ash (RHA) has been found suitable for wide range of domestic as well as industrial applications. The ability of rice husk to remove methylene blue from solution was investigated. Factors such as initial dye concentration, contact time, adsorbent dosage were studied. Results show that Langmuir isotherm and freindlich isotherm can be successfully applied to the methylene blue – rice husk. Rice husk has been used as a bio-sorbent for the removal of a MB dye from aqueous solutions. The process of removal has been optimized for different parameters like initial concentration of dye solution and contact time, adsorbent dose, and temperature. Elemental analysis of the adsorbent was carried out. Adsorption data were modeled by Langmuir and Freindlich isotherms. The data was better fitted in Freindlich isotherm model. The dye adsorption followed the pseudo second-order kinetics. Dye removal from industrial effluents is an important environmental concern. Various physical and chemical treatment methods can serve this purpose, of which the most economical and effective one is adsorption.. In this review, we look at the various adsorbents available and see how effectively they can be utilized to meet our requirements. The adsorption followed pseudo first order and/or pseudo second order kinetics. The dye removal process followed freindlich isotherm in most of the cases and in few investigations, it followed Langmuir isotherm also.

Keywords – *Adsorption, Rice- Husk, Methylene blue, freindlich isotherm. Langmuir isotherm*

1. INTRODUCTION

In 1990 ks low and ck lee[1] studied the adsorptive removal of methylene blue dye from aqueous solution by coconut husk and activated carbon-kinetic study and equilibrium isotherm analysis. Adsorption isotherm of the methylene blue (MB) on the activated carbon was determined and correlated with common isotherm equations. The equilibrium data for methylene blue adsorption well fitted to the Langmuir equation.

In 2013 Fahim Bin AbdurRahman, Maimuna Akter, M. Zainal Abedin[2] carried out batch adsorption studies for removal of dye from textile waste water using orange peels as bio adsorbent. Batch adsorption technique was used to study the effects of various important parameters such as amount of adsorbent, the contact time between the adsorbate and adsorbent. In general, experimental isotherm is useful for describing adsorption capacity to facilitate evolution of the feasibility of the process for a given application, for selection of most appropriate adsorbent and for p\preliminary determination of adsorbent dose requirements. The Langmuir isotherm is most

frequently used to represent the data of adsorption from solution. The isotherm studied was carried out for optimum condition, which was obtained. The Langmuir isotherm assumes that the adsorption take places as homogeneous sites, all sites are equivalent and there are no interactions between adsorbate molecule and adjacent sites. The adsorption data were analyzed according to the linear form of the Langmuir isotherm equation. In order to establish the maximum adsorption capacity, the Langmuir isotherm equation of the following linearized form was applied to the sorption equilibrium at different adsorbents doses. The isotherm is described by following equation.

$$\frac{1}{q_e} = \frac{1}{q_m K_a} \cdot \frac{1}{C_e} + \frac{1}{q_m}$$

where Ce represents the equilibrium dye concentration in solution (mg/L), qe is the adsorption capacities (amount of dye adsorbed per weight of adsorbent, mg/g) qm and Ka are Langmuir constant that can be determined from above Langmuir linear equitation. A graph of 1/qevs 1/Ce was plotted. The constant and KL can be evaluated from the intercept and slope of this linear plot. Figure.4 shows the Langmuir isotherm plot 1/qe versus 1/Ce. The slope of this plot is equivalent to (1/qm KL) when it intercepts 1/qm. Also, by comparing the correlation coefficient (R2 value) shown in table.1, the Langmuir isotherm model obtained a better fit of the experiment data.

In 2013[3] Azharul Arafath, Mobarak Hossain, S.S. Alam, Raihan Sourav Carried out Studies on Adsorption Efficiency and Kinetics of Dye Removal from Textile Effluent using some Natural Bio-adsorbent.

In 2015 Koninika Tanzim and M. Zainal Abedin[4] studied Removal of Methyl Red from Aqueous Solutions by using pomelo peels as bio adsorbent they reported potential of Pomelo Peel, an agricultural waste material to be an effective bio-adsorbent for removal Methyl Red from aqueous solution. Equilibrium data are in well agreement with Langmuir adsorption isotherm model at 25°C. The adsorption capacity was found to be maximum at pH 6.5 and at adsorbent mass of 1g/100ml dye concentration within 80 minutes of physical adsorption. The major advantage of using bio-adsorbents for removing dues is due to their highly selective nature of adsorption. Preliminary results indicate that Pomelo Peel is a good bio-adsorbent for removing dyes from textile wastewater.

In 2010 Rahman Muhammad Bozlur, Shinichi Shibata, C Siddiqua Farah Diba and Magali Uono[5] studied the utilization of Acid activated saw dust as Low-Cost Adsorbent for the Removal of Lurazol Brown PH.

Dyes from an initial concentration of 300 mg/l of 40 ml solution. The adsorption obeyed both Langmuir and Freindlich isotherms. The values of rate constants found in the present investigation is encouraging for using acid activated sawdust as an adsorbent for treating dye waste water.

In 2012 Ibtissam Maghri, Fatiha Amegrissi, Mohamed Elkouali, Abdelkbir Kenz, Omar Tanane, Mohamed Talbi & M. Salouhi carried out Comparison of Adsorption of Dye Onto Low-Cost Adsorbents. The adsorption of methylene blue onto Mytilus Edulis shells and corn stalks was studied under various conditions such as concentration of adsorbate, adsorbent dosage and granulometry. Batch adsorption experiments were conducted and the result showed that the adsorption was dependent to granulometry and adsorbate concentration, but was partly dependent on the adsorbent dosage. It was rapid, stable and occurs in less than 60 minutes. The objectives of this work were to compare the process of adsorption of methylene blue with rice husk absorbent and to use isotherms (Langmuir and Freindlich) for modeling adsorption process. Results showed that rice Husk adsorbent is suitable for the adsorption of methylene blue dye and could be used as a low cost effective adsorbent in the treatment of the industrial wastewater[6].

2. MATERIALS AND METHOD

2.1 Preparation of Adsorbent

Rice husk is widely available in villages where rice is cultivated. After threshing of rice, rice husk accumulate in huge amount of quantity which is of no commercial use for farmers. These rice husks can be used as adsorbent for removal of dyes. Rice husk

where collected from farmer. Initially rice husk where grinded into fine particles then treated in microwave at 80 C. It was then sieved using a mesh of micron.

2.2 Preparation of Adsorbate

The methylene blue dye is a basic cationic dye, heterocyclic aromatic chemical compound with molecular formula: C16H18N3SCl, Molecular Weight=319.85. λ_{max} = 663nm. Stock solution of methylene blue dye was prepared by dissolving 0.1gm of dye in 1 liter distilled water. Later 100 ml solution where taken from mother solution for adsorption studies.

2.3 Batch Adsorption Studies

In this experiment, a batch adsorption technique was used. To study the effects of various parameters such as amount of adsorbent, the contact time between the adsorbate and adsorbent. 100 ml of dye solution was taken from 1000ml volumetric flask. A desired amount of adsorbent then added to the sample. This experiment was carried out at room temperature. The solutions were then subjected to magnetic stirrer for proper adsorption. Then the adsorbents were separated from the sample by using filter paper. The absorbance was measured for supernatant solution using UV Spectrophotometer. The final concentration of dye was estimated with the help of these absorbance data.

Table 1: Adsorption of MB dye on rice husk adsorbent

Adsorbent	conc. of dye	Absorption before contact	Absorption after contact	Ce	X/m	log (X/M)	log Ce	Ce/X/M
1	0.005	1.02	0.66	0.0032	0.00024	3.6197	2.5850	17.777
1	0.010	1.93	1.57	0.0082	0.00018	3.504	2.0861	28.461
1	0.015	2.98	2.21	0.0111	0.00039	3.4089	1.9546	45.555

3. RESULTS AND DISCUSSION

3.1 Effect of Amount of Adsorbent

Figure.1 illustrates that the adsorption capacity was increased with the increment of adsorbent dosage. The removal of dye increases with the increase in dosage of adsorbent. The adsorbent dosages were increased from 0.5g to 2g for 100 ml solution. With the increase in amount of adsorbent dosage adsorption increases.

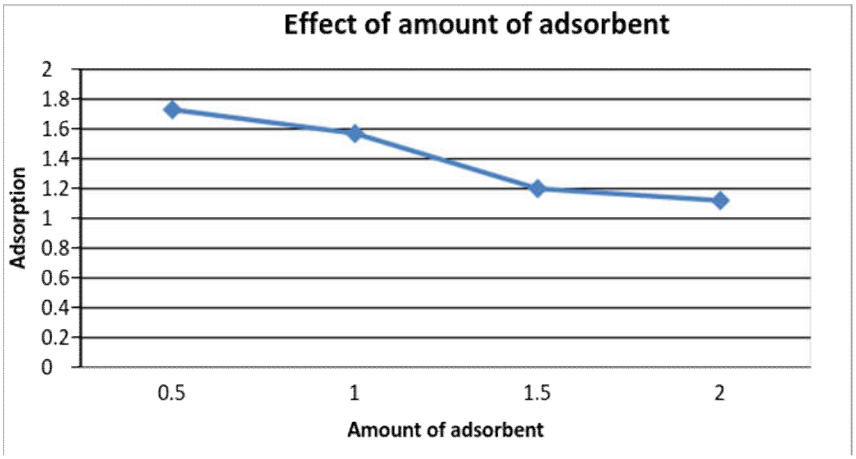

Figure 1: Effect of amount of adsorbent on adsorption

3.2 Effect of Dye Concentration on adsorption

Figure 2 illustrates comparison between absorption before and after contact time of adsorbent and adsorbate. Adsorbent weight was kept constant 1 gm. and concentration of dye was varied from 0.005, 0.010, 0.015 gm.

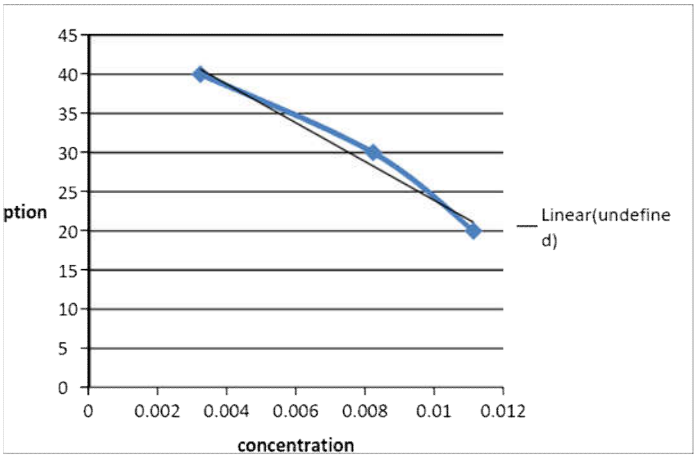

Figure 2: Percent adsorption of MB dye

3.3 Adsorption isotherm

In general, experimental isotherm is useful for describing adsorption capacity and how the adsorption molecules distribute between the liquid phase and solid phase. The adsorption isotherm s study like, freindlich and Langmuir were carried out. The Langmuir isotherm is most frequently used to represent the data of adsorption from solution. The isotherm studied was carried out for optimum condition, which was obtained. The Langmuir isotherm assumes that the adsorption take places as homogeneous sites, all sites are equivalent and there are no interactions between adsorbate molecule and adjacent sites. The adsorption data were analyzed according to the linear form of the Langmuir isotherm equation[7]. Effect of dye-adsorbent contact time: 150 ml of dye solution with dye concentration (50mg/L) is to be prepared in a conical flask with adsorbent concentration (0.5g/150ml) and kept inside the shaker. Dye concentration to be estimated spectrophotometrically [8] at the wavelength corresponding to maximum absorbance, λ_{max}, using a spectrophotometer (JASCO UV/Vis-550). The samples to be withdrawn from the shaker at predetermined time intervals and the dye solution should be separated from the adsorbent by the help of filter paper. The absorbance of solution is then measured. The dye concentration is to be measured after 30, 60, 90, minutes. A graph is to be plotted with qe vs time.[9]

3.4 Effect of contact time on adsorption

Fig 5 shoes that methylene blue dye adsorption were carried out at different contact time, adsorption increases with time. It is evident that the activated charcoal obtained from rice husk is efficient to adsorb methylene blue from aqueous solution.

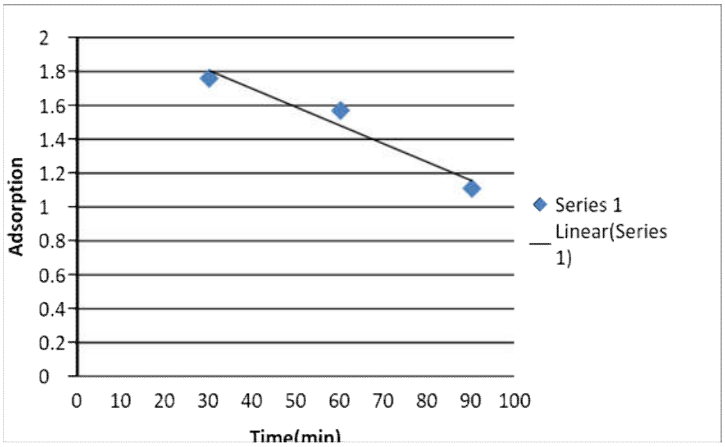

Figure 3: Plot time in min vs. adsorption of MB dye

In our work we have tried to determine adsorption of methylene blue dye on activated rice husk as a bio-adsorbent Figure.1 illustrates that the adsorption capacity was increased with the increment of adsorbent dosage [10]. The removal percentage is rises from 30% to

60% while the adsorbent dosages were increased from 0.5g to 2g for 100 ml solution. This result indicated that more surface area was made due to increased mass of adsorbent. Therefore, total number of sites increases.

Effect of contact time on adsorption was studied and results are shown in figure 5. Figure shows that, increase in removal efficiency with increase in contact time between adsorbate and adsorbent [11]. It can be attributed to the fact that more time becomes available for the dye to make an attraction complex with rice husk. The graph shows that, initial removal occurs rapidly as soon as the dye and rice husk in contact but after that when some of the easily available active sites engaged, dye needs time to find out more active sites for building. So, removal percentage is increased steadily over the period of experiment. It is concluded that dye and rice husk should be in contact for 90 minutes in order to get maximum removal percentage[12].

The Langmuir isotherm is most frequently used to represent the data of adsorption from solution [13]. The isotherm studied was carried out for optimum condition, which was obtained. The Langmuir isotherm assumes that the adsorption take places as homogeneous sites, all sites are equivalent and there are no interactions between adsorbate molecule and adjacent sites. The adsorption data were analyzed according to the linear form of the Langmuir isotherm equation [14]. In order to establish the maximum adsorption capacity, the Langmuir isotherm equation of the following linearized form was applied to the sorption equilibrium at different adsorbents doses. The isotherm is described by following equation [15]

$$\frac{1}{q_e} = \frac{1}{q_m K_a} \cdot \frac{1}{C_e} + \frac{1}{q_m}$$

where Ce represents the equilibrium dye concentration in solution (mg/L), qe is the adsorption capacities (amount of dye adsorbed per weight of adsorbent, mg/g) qm and Kaare Langmuir constant that can be determined from above Langmuir linear equitation. A graph of 1/qe vs 1/Ce was plotted.

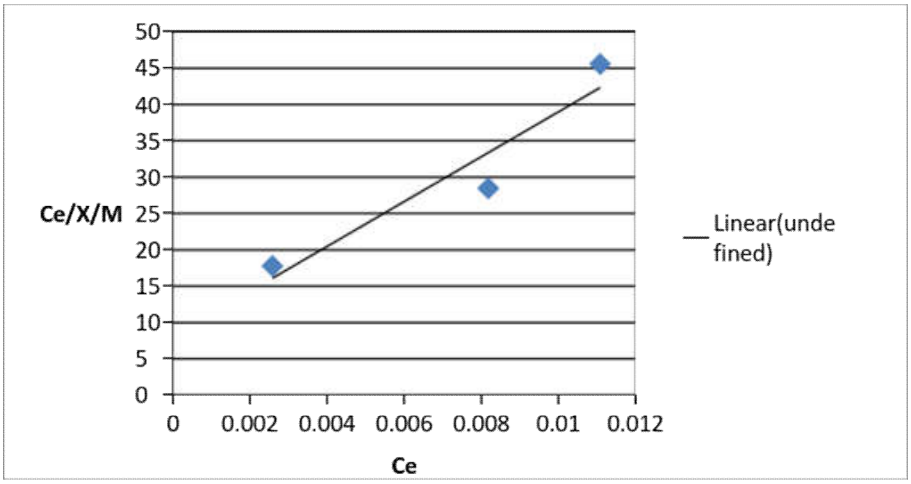

Figure 4: Langmuir Isotherm

The constant and KL can be evaluated from the intercept and slope of this linear plot [16] Figure.4 shows the Langmuir isotherm plot Ce/x/m versus Ce. The slope of this plot is equivalent to (1/qm KL) when it intercepts 1/qm. Also, by comparing the correlation coefficient (R2 value) the Langmuir isotherm model obtained a better fit of the experiment data.

The Freindlich isotherm is an empirical equation used to describe heterogeneous systems. The Freindlich isotherm is given in logarithmic form as [17]

Log q e=log kf + (1/n) log Ce

where kf is a Freindlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g)(L/mg)1/n and 1/n is the adsorption intensity[18]. kf and 1/n can be determined from the linear plot of log qe vs. log Ce. , by comparing the correlation coefficient (R2 value) the Freindlich isotherm model can also fit to the experiment data.

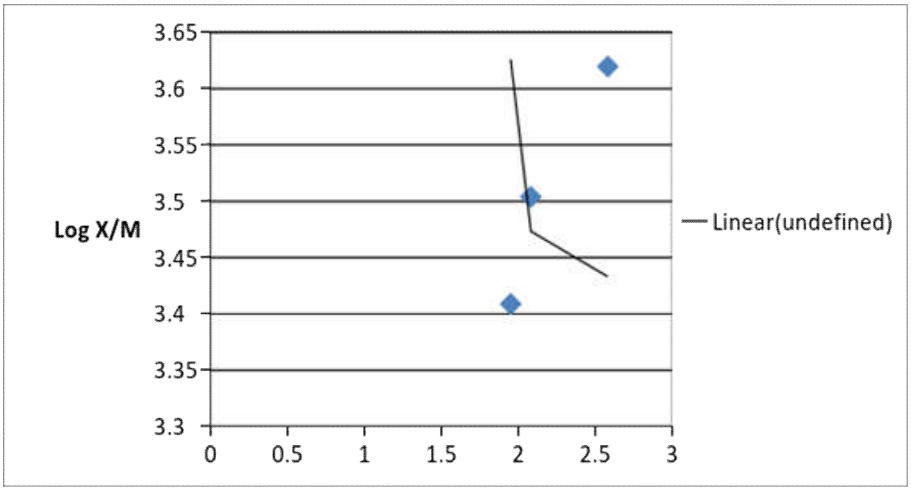

Figure 5: Freindlich Adsorption Isotherm

The straight line graph qe i.e log of x/m vs log of Ce was observed. This indicates the freindlich adsorption isotherm is verified for adsorption of methylene blue dye on rice husk as an adsorbent. From this graph (R) 2 values also confirm the straight line in the freindlich adsorption isotherm.

Comparative adsorption before and after was determined. This graph shows there is increase in adsorption with respect to amount of adsorbents.

Adsorption isotherm constants for methylene blue.

Freindlich isotherm	**Langmuir isotherm**
1/n = 0.361	qe = 3085.3
Ce = 2.8349	K = 8.0727
R2 = 0.9282	R2 = 0.9048

From the above values of freindlich isotherm 1/n & R2 values 0.9298 > 0.7 indicate favor the isotherm.

Similarly from Langmuir Kl and R2 values 0.9848> 0.7 favors the adsorption of methylene blue on rice husk adsorbent.

4. CONCLUSION

From this study, it may be concluded that the removal of Methylene Blue dye from standard solution of MB dye by adsorption on Rice Husk has been found to be useful for controlling water pollution due to dyes. From this experiment it is clear that, the adsorption of dyes onto rice husk is influenced by amount of adsorbents and contact time. Also, the adsorption of dyes onto rice husk follows the Langmuir isotherm model and Freindlich isotherm model. In the review the efficiency of rice husk as an adsorbent has been studied. For higher removal of dyes from stock solution adsorbent dose of 1 g was favorable. The uptake of the dye increased with increasing contact time. From this research work it can be concluded that, the experimental data are well described by Langmuir isotherm model and Freindlich isotherm model. Thus full utilization of agro-waste and treatment of textile wastewater is one of the good prospective for good environment. The rice husk can be proved as good, effective and eco-friendly adsorbent. With this cheap and environment friendly adsorbent considerable dye removal can be achieved. So it can be substituting other expensive bio-adsorbents. With the

experimental data obtained in this study, it is possible to design and optimize an economical treatment process for the dye removal from industrial effluents.

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