



Removal of Methylene Blue from Wastewater using Un-Activated Rice Husk and Activated Rice Husk

Danish^[a], Abhishek^[b], Kulvinder^[c], Deepak kr^[d], Jatin^[e]

^{a,b} B.tech student, GNIT mullana, haryana

^c HOD in CED, GNIT mullana, haryana

^{d,e} Asst.. professor in CED, GNIT mullana, haryana

ABSTRACT

Dyes are used in almost every processing industry like textile, paper, printing, etc. Fifteen percent of the total world production of dyes is lost during the dyeing process and is released as textile effluent (Sohrabi et al., 2009). A large amount of these dyes are transferred to the water through washing or by other industrial operations. Dye is the most difficult to treat constituent of the wastewater. The presence of these dyes in wastewater is undesirable and it is essential to remove these dyes before discharging wastewater into the environment. Dyes may significantly affect photosynthetic activity in aquatic life because of reduced light penetration and may also be toxic organisms due to the presence of aromatics and metals, chlorides, etc. Dyes usually have synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade. The textile industry utilizes about 10,000 different dyes and pigments. The textile industry mainly discharges wastewater originating from the dyeing and finishing processes. Removal of hazardous dye from wastewater is one of the growing challenges. During the past three decades, several physical, chemical, and biological decolorization methods have been reported and attempted for the removal of pollutants from plastics, dyestuffs, textile, pulp, and paper effluents; few, however, have been accepted by these industries (Slokar et al., 1998).

1. Introduction

Among all wastewater treatments, the adsorption process has been recognized to be an effective and economical procedure for the removal of dyes from industrial effluents. The removal of colorant and other pollutants from the wastewater is considered an important application of the adsorption process using suitable adsorbents. Adsorption is a simple technique as compared to the other operations and also the availability of a wide range of adsorbents makes it more popular than the other operations. Moreover, the efficiency of this operation is higher. Adsorption onto sorbent materials is one of the most popular methods for the removal of pollutants from wastewater. Recently, numerous attempts have been made in finding inexpensive and effective adsorbents containing agricultural residues or natural polymers. Studies showed that many materials, such as peat, sawdust, chitosan, biomass, cyclodextrin, bark, wood, etc., could be used as adsorbents.

2.Objectives:-

Dye is the most 'difficult to treat' constituent of the wastewater.

Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade.

Among all wastewater treatment, the adsorption process has been recognized to be an effective and economical procedure for the removal of dyes from industrial effluents.

Adsorption onto sorbent material is one of the most popular methods for the removal of pollutants from wastewater.

2. Material and Method:-

Materials

The adsorbent used in this experiment was rice husk. The rice husk was collected from Rice Mills. Methylene blue (MB) a textile dye was purchased from S.D. Fine Chemicals Ltd. Dye solution was prepared in the laboratory as per the requirement. For Taguchi analysis, the software used was MINITAB 16. Citric acid used for activation of rice husk was purchased from S.D. Fine Chemicals Ltd.

Preparation of adsorbent

The rice husk collected was screened and washed with distilled water to remove dirt and was sun-dried for a day. Another fraction of the same size was activated using citric acid which was reported as follows: 100gm of rice husk was soaked in 0.6M citric acid for 2 hr at 20°C. The acid husk slurry was dried overnight at 50°C and the dried husk was then heated at 120°C. The reacted product was washed several times with distilled water to remove excess citric acid, oven drying overnight at 100°C. The final product was sieved to 250-500 um size.

Preparation of dye solution

Methylene blue (MB) was purchased from a market in its powdered form. The stock solution of dye was prepared by dissolving 10 g of methylene blue (MB) in 1000ml of distilled water. The working solutions were prepared by serial dilution of this stock solution. The working solution was used to prepare a calibration curve between the concentration and absorbance with the help of a spectrophotometer. Methylene blue (MB) is a heterocyclic aromatic chemical compound with the molecular formula: C₁₆H₁₈ClN₃S. It was chosen because of its known strong adsorption onto solids. The dye is regarded as acutely toxic, but it can have various harmful effects. The structure of methylene blue is as given below:

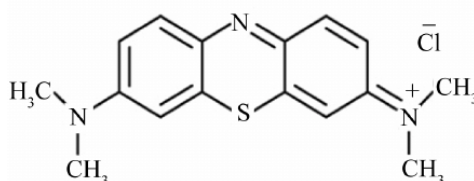


Fig. Structure of Methylene Blue (MB).

Batch adsorption experiment

During the batch experiment, the working solution of different concentrations were prepared by serial dilution of stock solution. All the experiments were carried out in a conical flask of 100ml. The factors varied in the experiment are pH, contact time, adsorbent dose, and initial concentration of dye. The stoppered conical flasks were used in the experiment for placing the samples in the mechanical shaker which was operated at 160 rpm. After the desired contact time the samples were filtered and the absorbance was calculated with the help of a spectrophotometer with an absorbance wavelength (max) of 664nm. The spectrophotometer (La Motte Company, USA) readings were recorded and used for further necessary calculations.

$$\text{Sorption Capacity (\%)} = (C_0 - C_e) / C_0 * 100$$

Where, C₀ and C_e are the initial and residual concentration (mg / L) respective

3. Result and Discussion

Calibration curve.

A Calibration curve is a general method of determining the concentration of a substance in an unknown sample, comparing the unknown to a set of standard samples of known concentration. The calibration curve helps to convert the absorbance readings to concentration according to Beer-Lambert's law. To prepare the calibration curve, the absorbance readings were measured for the standard solutions of methylene blue (MB) at A_{max}=664 nm by using a spectrophotometer and are presented in Table 4.1

Table 4.1 Data of methylene blue for calibration curve.

Concentration (ppm)	Absorbance
0	0
0.1	0.0051
0.3	0.0235
0.5	0.0443
0.7	0.0639

0.9	0.0892
1.1	0.1113
1.3	0.1344
1.5	0.1535
1.7	0.1800
1.9	0.2084

Once the calibration curve is drawn, the concentration of an unknown sample may be determined by measuring the absorption of the sample at the same wavelength. The calibration curve, a plot of instrument response and concentration for methylene blue (MB) dye analyses, showed a good linear relationship whose equation and linear correlation coefficient (R) are presented in Figure 7.1.

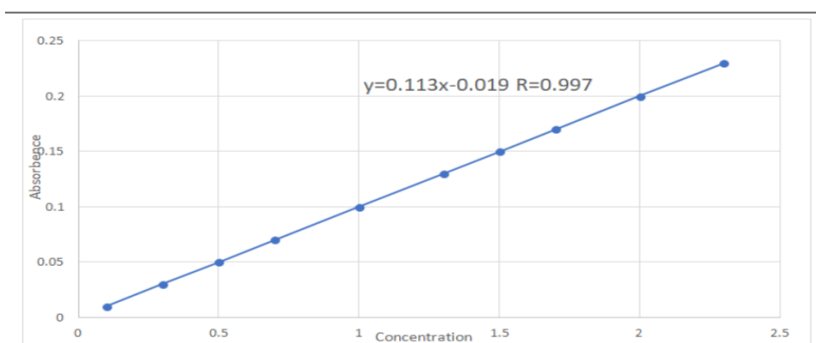


Fig 4.1 Calibration curve of methylene blue.

• **Adsorption behavior of rice husk towards methylene blue**

Batch studies were done to observe the adsorption behavior of methylene blue towards unactivated rice husk (URH) and activated rice husk (ARH) activated with citric acid. The influence of several parameters such as pH, contact time, adsorbent dose, and change in dye concentration on the sorption capacity of rice husk with respect to methylene blue was evaluated using batch studies. The low-cost adsorbent was compared on the basis of their sorption capacity towards pollutant. Adsorption isotherms, thermodynamics, and kinetics studies were performed in terms of sorption capacity.

• **pH Effects on sorption capacity**

The unactivated rice husk (URH) and activated rice husk (ARH) was used for the adsorption of methylene blue dye from an aqueous solution. Absorbance data were recorded after 1 h with the help of a spectrophotometer. The data for the adsorption of methylene blue dye was calculated and tabulated in Table 4.2. The sorption capacity of the rice husk at different pH was shown in Fig 4.2. It was observed that the sorption capacity of MB increased with the increase in pH and was maximum at pH 7 for both URH and ARH. This may be due to the fact that at higher pH values, the surface of the adsorbent becomes negative which enhances the adsorption of positively charged MB cationic dye through electrostatic force of attraction. At pH 9 there is a slight decrease in adsorption, which was due to repulsion between the adsorbent surface and the presence of partial negative charge on MB due to chloride ions. (Sharma et al., 2010) Results showed that the sorption capacity of activated rice husk (ARH) was 5.30% greater than that of unactivated rice husk (URH) at pH 7 which was due to an increase in surface active sites after activation.

Table 4.2: pH Effects on sorption capacity of URH and ARH towards MB

pH	Sorption capacity of MB on URH (%)	Sorption capacity of MB on ARH (%)
3	81.14	45.53
5	78.02	93.11
7	91.62	96.48
9	90.44	94.78
11	90.27	94.21

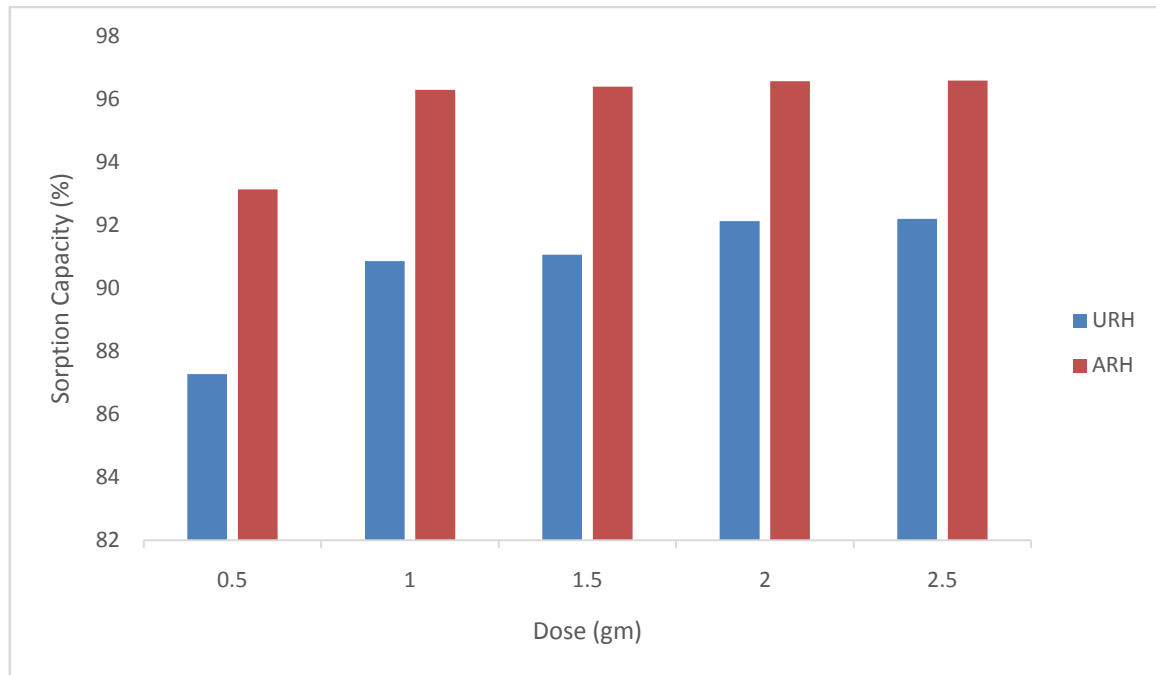


Fig. Effects of pH on the sorption capacity of MB

- **Effect of adsorbent dose on the sorption capacity of MB on ARH and URH**

The effect of adsorbent dose on the sorption capacity of rice husk towards methylene blue using a contact time of 1 hr is shown in Fig. Table shows the data recorded for the effect of adsorbent dose on the sorption capacity of MB on unactivated rice husk (URH) and activated rice husk (ARH). The molar concentration of methylene blue (MB) was kept constant and the quantity of rice husk was varied between 0.5g to 2.5g. The absorbance data was recorded for adsorbent dose 0.5, 1.0, 1.5, 2.0, 2.5 Fig. also reveals that the dye removal increases with an increase in adsorbent dosage. An increase in the adsorption with adsorbent dosage can be attributed to greater surface area and the availability of more adsorption sites. The result showed that the sorption capacity of MB was maximum at an adsorbent dose of 1.0 gm for both URH and ARH.

Table: Influence of the adsorbent dose on the sorption capacity of MB on URH and ARH

Dose of adsorbent (gm)	Sorption Capacity of MB on URH (%)	Sorption Capacity of MB on ARH (%)
0.5	87.28	93.14
1.0	90.86	96.30
1.5	91.07	96.40
2.0	92.13	96.58
2.5	92.21	96.60

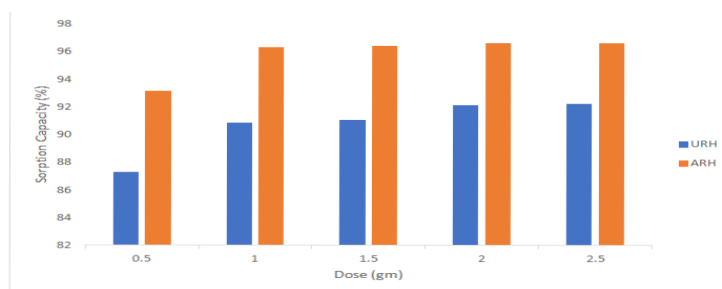


Fig. Effects of adsorbent dose on adsorption capacity of MB on URH and ARH.

4. Conclusion

1. Results of sorption experiments showed that the activated rice husk exhibited high sorption capacities towards methylene blue as compared to the unactivated rice husk.
2. Higher sorption capacities for removal of methylene blue with ARH in adsorption treatment were achieved at pH 7.
3. Experimental data of methylene blue fitted better to the Freundlich model than the Langmuir model when R^2 values are compared.
4. The negative value of AG at the experimental temperatures indicates that the adsorption of methylene blue on ARH was spontaneous. The positive value of AH and AS exhibits that the adsorption of methylene blue on ARH was endothermic.
5. The kinetics of methylene blue adsorption onto rice husk was examined using pseudo-first-order and pseudo-second-order kinetic models. The result indicated that the pseudo-second-order equation provided the best correlation of the adsorption data.

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