Experimental Investigations of the Removal of Methylene Blue from Waste Water using Agricultural Adsorbant

Manoj B. Mandake¹, Santosh Walke²*, Makarand Naniwadikar³, Ganesh Patil² and Sandhya D. Jadhav¹

¹Bharati Vidyapeeth College of Engineering (affiliated to University of Mumbai), Navi Mumbai, India
²Department of Mechanical and Industrial Engineering, College of Engineering, National University of Science and Technology, Oman
³AISSMS COE PUNE, Savitribai Phule Pune University, India

Abstract: The colored organic or inorganic chemical compounds which can impart colour to other substance are the Dyes which did significant applications in the most industrial sectors like the textile industry, leather industry, paper industry, plastic, foodstuff industry etc. to impart color to their products. Due to the large volume of dye use in these businesses, a significant quantity of wastewater containing colored organics is generated. Because of insufficient dye-fiber fixation, during the dyeing process, half of the dye is lost in the wastewater. Peanut and rice husk are used to absorb MB from water. Initial Methylene Blue concentration, Peanut and Rice Husk dose, and pH were monitored and compared to current adsorbents to identify the optimal removal conditions. The equilibrium amount of MB adsorbed at time t (min) for rice husk and peanut hull are obtained as 5.1 and 5.19 mg/g respectively. As part of the research, an intra-particle diffusion model was implemented to regulate the mass transfer model's rate-controlling step mechanism.

Keywords: Waste Water, Methylene Blue, Peanut Hull, Rice Husk, Adsorption.

1. INTRODUCTION

Dye in water, even in trace amounts, may be hazardous and very noticeable, making the elimination of color from waste effluents crucial for environmental reasons. Government regulations necessitating the treatment of textile wastewater highlight the ongoing need for an efficient procedure to remove these colors from wastewater, which is an environmental problem in and of itself [1-3]. In the past, dyes were decolorized in several ways. The adsorption method is best for removing dyes. Adsorption is a physical process that's cheap and fast [4].

Chemical, physical, and biological methods have all been considered in relation to the elimination of dyes from industrial effluents [5]. Adsorption is becoming more used as a technology for treating aqueous wastewater. Advantages of the adsorption process include its ability to renew cheaply, the use of common process equipment, the lack of sludge during operation, and the recovery of the sorbate [6]. Reducing waste in agriculture via recycling is crucial. Several types of agricultural byproducts are being investigated for their potential to filter out certain colours from water solutions under varying circumstances of use [7, 8]. For the purification process various techniques, like flocculation-coagulation, precipitation, photocatalytic degradation, biological oxidation, ion exchange, adsorption and membrane filtration, have been investigated [9]. According to their physicochemical properties and cheap cost, agricultural solid wastes may be suitable prospective adsorbents. Agricultural waste has little commercial value and is difficult to dispose of. Membrane filtration blocks passage of contaminants through physical obstruction, chemical adsorption, or a combination of both processes and can remove far more contaminants than any other purification method. Adsorption takes an important role in membrane filtration process [9]. Agricultural waste utilization is important. Several agricultural waste products are being explored for removing dyes from aqueous solutions. Industrial sources pollute water reservoirs with dyes. Textiles, paper, cosmetics, food, and polymers are sources. Adsorption using a membrane gets better adsorption capacity and a relatively faster time than granular form [10]. The most common adsorption materials are activated carbon, membrane, nanomaterial and carbon based materials and the aforementioned adsorbents, membrane has been found to be an excellent adsorbent due to its easy preparation, high porosity and interconnected pore structures [11]. The membranes were reused for more than three-four cycles across a wide pH range, demonstrating their viability as a dye removal substitute. The method is less costly than the commonly used membrane options [12]. Dye pollution in aquatic environments harms human health and the environment [13]. Most dyes are toxic, mutagenic, and
carcinogenic [14]. MB is an aromatic synthetic cationic dye used in the commercial dyeing of silk, wool, and cotton. MB is also carcinogenic. MB is not considered poisonous, however intake causes burning [15]. Before dumping industrial waste water into the environment, it must be treated. Solvent extraction and membrane [16]. The research gap identified in the previous research work is limited study of effect of operating parameters on equilibrium concentration, in the present work the wide range is selected and its effect on the MB removal is studied. The two agricultural based adsorbents are used for this study such as rice husk and peanut hull, and adsorption isotherms studies shows that for first order and second order ratio of time and q are directly proportional to time.

The esterification method was used by the authors to study the reactive distillation of ethyl acetate. The decanter is used to separate the product’s wastewater from that of the product, and there are various methods for treating that wastewater [17-19]. The methods for producing biogas from palm waste were investigated by the authors in Oman, and the biogas energy can be used for wastewater treatment [20]. Our research team used polyethersulfone and copper oxide-graphene oxide (Cu2O-GO) to create a noble fouling-resistant membrane. The prepared mixed matrix membranes’ performance in terms of wastewater treatment and fouling resistance was also investigated [21, 22]. Using two renewable technologies, Saravanan et al. conducted an experimental study to purify underground water in remote areas of Oman, generating enough electricity to operate the reverse water purification system and water purification system at the lowest possible cost [23]. Cellulose nanofibers obtained from agricultural waste have gained popularity as an alternative to traditional wastewater treatment materials. Shabib et al. studied their isolation and characterization [24]. According to Saravanan et al., one of the main sources of wastewater treatment is bloom energy [25].

2. MATERIALS AND METHODS

2.1. Methylene Blue

Methylene Blue was selected because of its high solid adsorption.

![Methylene blue structures.](image)

Although the cationic dye methylene blue isn't considered to be immediately dangerous, it does cause a number of problems for humans and animals [26]. Short bursts of fast or difficult breathing may result from inhalation, whereas issues with nausea, vomiting, and gastritis may result from oral consumption [27, 28].

2.2. Materials

Peanut and rice husk are obtained from local farmers. The gathered material is washed with distilled water to eliminate dirt. Continue washing until water is clear. After being properly cleaned, the materials were dried in an 8-hour hot air oven cycle at 85°C [29,30]. The powdered combination of the dry ingredients was made in a kitchen blender and then sieved through a 100 Mesh screen. Later, this combination was preserved in a glass container [31].

2.2.1. Equilibrium Studies

Adsorption at equilibrium can be calculated using Equation (1).

\[
q_e = \frac{(C_0 - C_e) V}{W}
\]

(1)

Co and Ce are the initial and final dye concentrations in the liquid phase, measured in milligrams per liter, respectively [11].

Equation for estimating dye removal is given as

\[
Adsorption\ Percent\ (%) = \frac{C_0 - C}{C_0} \times 100
\]

(2)

Here C (mg/L) is the concentration in the liquid phase at time t.

2.2.2. Effect of PH

Various pH levels were tested for their influence on color removal (i.e. 4, 7 and 10). Both 1 N NaOH and 1 N HCl solutions were used to achieve the desired pH level. Agitation for 4 hours is adequate to attain equilibrium at a steady pace [32]. After centrifuge the samples are tested for COD.

2.2.3. Isotherm

The Langmuir model is often expressed in the well-known form of

\[
q_e = \frac{q_{max} K C_e}{1 + K C_e}
\]

(3)
Where, \( q_e \) is the amount of MB adsorbed at equilibrium (\( e \)), \( C_e \) is the equilibrium solution concentration, and \( q_{\text{max}} \) is the maximum adsorption capacity.

\[
\frac{C_e}{q_e} = \frac{1}{k q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]  \hspace{1cm} (4)

Freundlich equation is given in the following form:

\[
Q_e = K_F C_e^{1/n}
\]  \hspace{1cm} (5)

Adsorption capacity is represented by \( K_F \), while \( n \) is a measure of adsorption strength.

\[
\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln C_{eq}
\]  \hspace{1cm} (6)

The values for adsorption capacity and \( 1/n \) are calculated from the scatter plot of \( \ln(q_{eq}) \) vs \( \ln(C_{eq}) \).

2.2.4. Adsorption Kinetics

In order to ascertain the mechanism, kinetic models have been presented. Lagergren has presented first and second order kinetic models which are pseudo in nature, for dissecting the process of MB onto DPH [33, 34].

\[
\ln(q_e - q) = \ln(q_e) - k_1 t
\]  \hspace{1cm} (7)

Here we have the rate equation for first order adsorption: where \( q \) is the equilibrium adsorption capacity, \( q_e \) is the adsorption capacity at time \( t \) (min), and \( k_1 \) is the rate constant [35].

2.2.5. Model: Pseudo-Second Order

The rate of adsorption may be thought of as a pseudo-second order process. Eq (8) demonstrates the linear integration version of this model, and (9)

\[
\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  \hspace{1cm} (8)

\[ q = f\left(\frac{q_e}{k_2t}\right)^{1/2} = k_2t^{1/2}
\]  \hspace{1cm} (9)

Here \( K_i \) is the intra-particle diffusion rate.

3. RESULTS

3.1. Initiation of Fluctuation in Dye Concentration

Figure 3.1 presents the COD reduction % vs contact time.

3.2. Variable Adsorbent Dose

The methylene blue adsorption results are shown in Figure 3.3.

The dyes uptake reduces with increasing adsorbent dose in peanut husk is illustrated in Figure 3.4.
Figure 3.4: Adsorbent Mass and MB Adsorption on Peanut Hull (100 mg/L, 100 mL at 25 degrees Celsius).

3.3. Adsorption Isotherms Studies

The Langmuir or Freundlich adsorption isotherm at constant temperature is presented below.

$$q_e = \frac{q_{max} K C_e}{1 + K C_e} \quad (10)$$

$$\frac{C_e}{q_e} = \frac{1}{k q_{max}} + \frac{C_e}{q_{max}} \quad (11)$$

Langmuir isotherms are described by the dimensionless constant separation factor $R_L$ using Eq. (12),

$$R_L = \frac{1}{1 + b C_0} \quad (12)$$

The initial adsorbent concentration $C_0$ (mg/L), $R_L$ denotes the isotherm's shape.

The MB adsorption and constants and correlations are presented for Rice husk and Peanut hull in Table 3.1.

Table 3.1: MB Adsorption and Adsorbent Constants and Correlations

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Rice Husk</th>
<th>Peanut Hull</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{max}$ (mg/g)</td>
<td>36.1</td>
<td>55.2</td>
</tr>
<tr>
<td>$b$ (l/mg)</td>
<td>0.0025</td>
<td>0.0018</td>
</tr>
<tr>
<td>$R_2$</td>
<td>0.98</td>
<td>0.99</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.78</td>
<td>0.82</td>
</tr>
</tbody>
</table>

$$q_e = K_F C^{1/n} \quad (13)$$

Where $K_F$ indicates adsorption capacity and $n$ intensity. This equation's logarithm is:

$$ln(q_e) = ln K_F + \frac{1}{n} ln C_e \quad (14)$$

Figure 3.5: Analysis of MB adsorption onto rice husk and peanut hull using Langmuir isotherms.

Figure 3.6: Analysis of MB adsorption onto rice husk and peanut hull using Freundlich isotherms.

Model: Pseudo-First Order

$$ln (q_e - q) = ln(q_e) - k_1 t \quad (15)$$

The pseudo-first order adsorption rate constant, $k_1$, is defined as follows: where $q$ is the equilibrium amount of

Figure 3.7: Methylene Blue Adsorption Kinetics at Room Temperature (Pseudo-First Order).
MB adsorbed at time \( t \) (min), and \( q \) and \( q_e \) are the time \( t \) (min) values.

**Model: Pseudo-Second order**

This model may be expressed in a linear integrated form, which is

\[
\frac{t}{q} = \frac{1}{K_2 q_e} + \frac{t}{q_e}
\]

(16)

At first, the solute molecules were quickly adsorbed onto the outside of the adsorbent particles. This adsorption process eventually reached its maximum, meaning the molecules had to diffuse through the pores of the adsorbent in order to continue being adsorbed. This caused the rate of adsorption to decrease [36]. Figure 3.2 below shows the outcomes for using peanut hull as an adsorbent.

When the adsorption of the exterior surface reached saturation, the molecules will need to diffuse through the pores of the adsorbent into the interior surface of the particle, a similar observation was previously reported for the treatment of pulp and paper mill wastewaters with poly aluminium chloride and bagasse fly ash. The results are in line with the M. Rafatullah [37].

### 5. CONCLUSIONS

Since government regulations mandate the treatment of textile wastewater and dye removal from wastewater is seen as an environmental concern, there is a continuing demand for an efficient method to remove these colours. In the recent past, a variety of processes were used to decolorize dyes. The most effective method for removing dyes from them all is adsorption. It is generally acknowledged that adsorption is a physical process that costs less money and takes short time. The research indicates that rice husk and peanut hull, an agricultural waste biomaterial, can remove methylene blue from aqueous solutions. Dye absorption (mg/g) increases with solution concentration and pH and decreases with adsorbent dose. In the first stages of dye uptake, intra-particle diffusion is the governing force. Dye absorption (mg/g) increases with solution concentration and pH and decreases with adsorbent dose. Equilibrium observations corresponded well with Langmuir isotherm model with 36.1 mg/g for rice husk and 55.2 mg/g for peanut hull at room temperature. Early dye absorption is governed by external mass transfer and later by intraparticle diffusion. Adsorption Isotherms investigations demonstrate that for First order and second order ratio of time and \( q \) is linearly proportional to time, and the two agricultural adsorbents employed in this research are rice husk and peanut hull.

### REFERENCES


https://doi.org/10.1016/j.jhazmat.2005.01.029


[33] MS. Mia, P. Yao, X. Zhu, X. Lei, T. Xing, and G. Chen, "Degradation of textile dyes from aqueous solution using tea-


Received on 11-10-2022 Accepted on 08-01-2023 Published on 19-01-2023

DOI: https://doi.org/10.15379/2410-1869.2023.10.01.01

© 2023 Mandake et al.; Licensee Cosmos Scholars Publishing House. This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/), which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.