Dye Removal from Aqueous Solution using Bio-Sorbents

K. Sreelakshmi¹, K. G. Harshan²

¹M. Tech. Student, Department of Civil Engineering, M. Dasan Institute of Technology, Calicut, India
²Associate Professor, Department of Mechanical Engineering, M. Dasan Institute of Technology, Calicut, India

Abstract: The use of cheap and eco-friendly adsorbents studied as an alternative substitution of activated carbon for removal of dyes from wastewater. Adsorbents prepared from Rice Husk, Orange Peel and Neem Leaf, were successfully used to remove the Methylene Blue and Methyl Orange from aqueous solution by batch adsorptions. Prepared bio-sorbents were used to adsorb MB and MO at varying dye concentrations, contact time, adsorbent dosage, pH and particle sizes. The dye adsorption capacity of bio-sorbents decreased in the order Orange Peel Powder > Neem Leaf Powder > Rice Husk Powder. The sorption data for Orange Peel Powder were then correlated with the Freundlich and the Langmuir adsorption isotherm models. The recovery of dye from the adsorbents and their regeneration capacities were also studied. Orange Peel showed high regeneration capacity in both Methylene Blue and Methyl Orange desorption study, than other adsorbents.

Keywords: Bio-sorbents, Methyl Orange, Methylene Blue, Rice Husk Powder, Orange Peel Powder, Neem Leaf Powder, Regeneration.

1. Introduction

Waste water from the textile industries contains moderate concentrations of dyestuffs which contribute significant contamination of aquatic ecosystem. Adsorption of dyes by activated carbon, is an effective method for color removal. But, the prohibitive costs of manufacture and regeneration of activated carbon limits its application in the field. The most economical way to treat the dye containing effluents is the use of low-cost adsorbents, as it is easily available and can be regenerated.

The present study was done to evaluate and compare efficiencies of as Rice Husk Powder(RHP), Orange Peel Powder(OPP) and Neem Leaf Powder(NLP) as adsorbents for the removal of MB and MO dyes from aqueous solutions. The effect of adsorption parameters such as initial dye concentration, contact time, adsorbent dose, pH and particle size has been studied.

2. Materials and Methods

A. Adsorbents

Rice Husk Powder (agricultural waste), Orange Peel Powder (domestic waste) and Neem Leaf Powder (natural material) are the adsorbents used in this study. They were collected and washed several times with distilled water to remove dust. Washed adsorbents were sun-dried and then pulverized to working size. The adsorbents were then sieved using 90µm, 150µm, 300µm and 600µm mesh.

B. Dyes

Methylene Blue (Cationic) and Methyl Orange (Anionic) are the dyes used as adsorbates in this study. Stock solutions of 1000 mg/l were prepared in double distilled water and the experimental solutions of the desired concentrations were obtained by successive dilutions.

C. Methodology

Absorbance of 100mg/l was determined at different wavelengths using UV-VIS Spectrophotometer 119 to obtain a plot of absorbance verses wavelength. Dominant wavelength corresponding to the maximum absorbance of MB ($\lambda_{max}$=664 nm) and MO ($\lambda_{max}$=464nm) as determined from the plot, was used for measuring the absorbance of residual concentrations of dyes. The efficiency of the adsorbents were evaluated by conducting batch mode experimental studies.

Percentage removal = \[
\frac{(C_o - C_e)}{C_o} \times 100
\]

Where, $C_o$ = Initial dye concentration (mg/l), $C_e$ = Final dye concentration (mg/l), $m$ = Mass of adsorbent (g/l)

1) Effect of Initial Dye Concentration and Contact Time

1g of adsorbent of ≥ 600 mesh size with 100ml of dye solutions were kept constant. Batch experiments for initial MB concentration of 100, 150, and 200 mg/l were performed at nearly 273K on a rotary shaker at 230 rpm, starting from 5 minutes up to attaining a constant absorbance, at pH = 7. The final absorbance was noted and the final concentrations were calculated. The breakthrough curve was plotted by calculating the percentage removal and the optimum contact time was identified for further batch study.

2) Effect of Adsorbant Dosage and Initial Dye Concentration

Initial dye concentrations of 200, 250 and 300mg/l of MB and 100, 150 and 200mg/l of MO were used in conjunction with adsorbent dosages of 1, 2, and 3g. The parameters wavelength, optimum contact time, pH, agitation speed, temperature and particle size were kept constant.
3) **Effect of pH**

Initial pH of dye solutions were adjusted using HCl and NaOH to 5, 6, 7, 8 and 9 for 200 mg/l concentrations. Wavelength, optimum contact time, adsorbent dosage, agitation speed, temperature and particle size were kept constant.

4) **Effect of Particle size and Initial Dye Concentration**

Four different sized particles of ≥600µm, 300-600µm, 150-300µm and 90-150µm mesh were used in conjunction with 100, 150 and 200mg/l dye concentration. Wavelength, optimum contact time, adsorbent dosage, agitation speed, temperature and pH were kept constant.

From the above experiments, the optimum values of the parameters were obtained and bio-sorption experiments with these optimum parameters were carried out. The data required to plot the isotherms were calculated for the most efficient adsorbent and the data was fitted to two isotherms: Langmuir and Freundlich. Desorption of dyes from the adsorbents were studied by using distilled water and 0.5N Sulphuric Acid, conducting batch study. The desorption capacity of both were compared for all the three adsorbents and for the dyes MB and MO.

3. **Results and Discussion**

A. **Removal of Methylene Blue Dye**

1) **Effect of Initial Dye Concentration and Contact Time**

From the above experiments, the optimum values of the parameters were obtained and bio-sorption experiments with these optimum parameters were carried out. The data required to plot the isotherms were calculated for the most efficient adsorbent and the data was fitted to two isotherms: Langmuir and Freundlich. Desorption of dyes from the adsorbents were studied by using distilled water and 0.5N Sulphuric Acid, conducting batch study. The desorption capacity of both were compared for all the three adsorbents and for the dyes MB and MO.

2) **Effect of Adsorbant Dosage and Initial Dye Concentration**

As presented in Fig. 1, Fig. 2 and Fig. 3, uptake of MB was rapid in first 15 minutes and after a certain time, the amount of MB adsorbed was almost constant. Therefore, the optimum contact time for batch experiments of RHP, OPP and NLP were taken as 35min, 25min and 50min respectively. As initial dye concentration increased, % dye removal decreased, but as the contact time increased, the % dye removal also increased.

Fig. 1. Effect of initial dye concentration and contact time on adsorption of MB on RHP (Break-through Curve)

Fig. 2. Effect of initial dye concentration and contact time on adsorption of MB on OPP (Break-through Curve)

Fig. 3. Effect of initial dye concentration and contact time on adsorption of MB on NLP (Break-through Curve)

Fig. 4. Effect of adsorbent dosage on adsorption of MB on RHP

Fig. 5. Effect of adsorbent dosage on adsorption of MB on OPP
As presented in Fig. 4, Fig.5 and Fig.6, the amount of MB adsorption and percentage removal increased with increase in dosage of adsorbent. Percentage removal of MB decreased with increase in concentration. This is due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent.

3) Effect of pH

As pH of solution increased, % dye removal increased, Fig.7. Therefore, bio-sorption of MB is greater at alkaline condition. The basic dyes give positively charged ions when dissolved in water. Thus, in acidic medium positively charged surface of sorbent tends to oppose the adsorption of cationic sorbate species. When the pH of dye solution increase, the surface tends to acquire negative charge and thereby resulting in an increased adsorption of dyes.

4) Effect of Particle size and Initial Dye Concentration

It can be observed from Fig.8, Fig.9 and Fig.10, that as the particle size increases the adsorption of dye decreases and hence the percentage removal of dye also decreases. Also, as initial dye concentration increased, % dye removal increased up to 150mg/l and then decreased. This is due to the decrease in available surface area. For larger particles, the diffusion resistance to mass transfer is high and most of the internal surface of the particle may not be utilized for adsorption and so the amount of dye adsorbed is small.

5) Bio-sorption of MB at optimum parameters

From the above experiments, the optimum values of the parameters were obtained as:
- Initial Dye concentration = 200mg/l,
- pH= 9,
- Adsorbent dosage =3g,
- Adsorbent size = 90-150µm and
- Time is the optimum contact time.

Table 1 shows the calculations of bio-sorption of MB at optimum parameters. It was observed from the experiments that, Orange Peel Powder is having more percentage dye adsorption capacity (78.29%) and high percentage of dye removal efficiency at less time (25min), when compared to Rice Husk Powder and Neem Leaf Powder. Therefore, it can be concluded that, Orange Peel Powder is more efficient in removal of MB dye from dye containing effluents.
B. Removal of Methyl Orange Dye

1) Effect of Initial Dye Concentration and Contact Time

As presented in Fig. 11, Fig. 12 and Fig. 13 the optimum contact time for batch experiments of RHP, OPP and NLP were taken as 15min, 40min and 60min respectively. As initial dye concentration increased, % dye removal decreased, but as the contact time increased, the % dye removal also increased.

2) Effect of Adsorbant Dosage and Initial Dye Concentration

As presented in Fig.14, Fig.15 and Fig.16, the amount of MO adsorption and percentage removal increased with increase in dosage of adsorbent. Percentage removal of MO decreased with increase in concentration. This is due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent.

Table 1
Calculations of bio-sorption of MB at optimum parameters

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Contact Time</th>
<th>Initial Absorbance</th>
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<th>Final Concentration (mg/l)</th>
<th>Adsorbed Concentration (mg/l)</th>
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<td>76.4705</td>
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<td>58.8235</td>
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<td>Orange Peel Powder</td>
<td>25min</td>
<td>0.714</td>
<td>0.155</td>
<td>43.4173</td>
<td>156.582</td>
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As pH of solution increased, % dye removal decreased, Fig. 17. Therefore, bio-sorption of MO is greater at acidic condition. When the pH value is low, the surface of adsorbent is positively charged by adsorbing H\(^+\) ions which is attractive to the anionic dye. With the pH increased to the alkaline condition, the adsorption decreased due to an electrostatic repulsion between MO and negative charges on the adsorbent surface.

**4) Effect of Particle size and Initial Dye Concentration**

It can be observed that as the particle size increases the adsorption of dye decreases and hence the percentage removal of dye also decreases. For larger particles, the diffusion resistance to mass transfer is high and most of the internal surface of the particle may not be utilized for adsorption and so the amount of dye adsorbed is small.

**5) Bio-sorption of MO at optimum parameters**

From the above experiments, the optimum values of the parameters were obtained as:
- Initial Dye concentration = 200mg/l,
- pH = 5,
- Adsorbent dosage = 3g,
- Adsorbent size = 90-150µm and
- Time is the optimum contact time.

Table 3 shows the calculations of bio-sorption of MB at optimum parameters. It was observed from the experiments that, Orange Peel Powder is having more percentage dye adsorption capacity (78.29%) and high percentage of dye removal efficiency at less time (25min), when compared to Rice Husk Powder and Neem Leaf Powder. Therefore, it can be concluded that, Orange Peel Powder is more efficient in removal of MB dye from dye containing effluents.

### Table 2: Calculations of bio-sorption of MB at optimum parameters

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**Fig. 17.** Effect of pH on adsorption of MB on RHP, OPP and NLP

**Fig. 18.** Effect of particle sizes of RHP on adsorption of MO

**Fig. 19.** Effect of particle sizes of OPP on adsorption of MO

**Fig. 20.** Effect of particle sizes of OPP on adsorption of MO
C. Removal of Methyl Orange Dye

1) Effect of Initial Dye Concentration and Contact Time

As presented in Fig. 11, Fig. 12 and Fig. 13 the optimum contact time for batch experiments of RHP, OPP and NLP were taken as 15min, 40min and 60min respectively. As initial dye concentration increased, % dye removal decreased, but as the contact time increased, the % dye removal also increased.

2) Effect of Adsorbant Dosage and Initial Dye Concentration

As presented in Fig. 14, Fig. 15 and Fig. 16, the amount of MO adsorption and percentage removal increased with increase in dosage of adsorbent. Percentage removal of MO decreased with increase in concentration. This is due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent.

3) Effect of pH

As presented in Fig. 17, the effect of pH on adsorption of MB on RHP, OPP and NLP was observed.

Fig. 11. Effect of initial dye concentration and contact time on adsorption of MO on RHP (Break-through Curve)

Fig. 12. Effect of initial dye concentration and contact time on adsorption of MO on OPP (Break-through Curve)

Fig. 13. Effect of initial dye concentration and contact time on adsorption of MO on NLP (Break-through Curve)

Fig. 14. Effect of adsorbent dosage on adsorption of MO on RHP

Fig. 15. Effect of adsorbent dosage on adsorption of MO on OPP

Fig. 16. Effect of adsorbent dosage on adsorption of MO on NLP

Fig. 17. Effect of pH on adsorption of MB on RHP, OPP and NLP
As pH of solution increased, % dye removal decreased, Fig.17. Therefore, bio-sorption of MO is greater at acidic condition. When the pH value is low, the surface of adsorbent is positively charged by adsorbing H\(^+\) ions which is attractive to the anionic dye. With the pH increased to the alkaline condition, the adsorption decreased due to an electrostatic repulsion between MO and negative charges on the adsorbent surface.

4) **Effect of Particle size and Initial Dye Concentration**

It can be observed that as the particle size increases the adsorption of dye decreases and hence the percentage removal of dye also decreases. For larger particles, the diffusion resistance to mass transfer is high and most of the internal surface of the particle may not be utilized for adsorption and so the amount of dye adsorbed is small.

5) **Bio-sorption of MO at optimum parameters**

From the above experiments, the optimum values of the parameters were obtained as:
- Initial Dye concentration = 200mg/l,
- pH= 5,
- Adsorbent dosage =3g,
- Adsorbent size = 90-150µm and
- Time is the optimum contact time.

Table 2 shows the calculations of bio-sorption of MO at optimum parameters. It was observed from the graphs that, Orange Peel Powder is having more percentage dye adsorption capacity (86.845%) and high percentage of dye removal efficiency at comparatively less time (40min), when compared to Rice Husk Powder and Neem Leaf Powder. Therefore, it can be concluded from the experiments, that Orange Peel Powder is more efficient in removal of MO dye from dye containing effluents.

**D. Adsorption Isotherms**

1) **Isotherms for MB dye removal**

3g of Orange Peel Powder was taken for the initial dye concentrations of 100,150,200,250 and 300 mg/l MB dye solutions of 100ml each. The pH was adjusted to 9 and the agitation time was the optimum contact time 25min.

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<td>0.745</td>
<td>0.289</td>
<td>77.5838</td>
<td>122.416</td>
<td>61.208</td>
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<tr>
<td>Neem Leaf Powder</td>
<td>60min</td>
<td>0.745</td>
<td>0.228</td>
<td>61.208</td>
<td>138.791</td>
<td>69.3959</td>
</tr>
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<td>Orange Peel Powder</td>
<td>40min</td>
<td>0.745</td>
<td>0.098</td>
<td>26.3087</td>
<td>173.691</td>
<td>86.845</td>
</tr>
</tbody>
</table>
2) Isotherms for MO dye removal

3g of Orange Peel Powder was taken for the initial dye concentrations of 100, 150, 200, 250 and 300 mg/l MO dye solutions of 100 ml each. The pH was adjusted to 5 and the agitation time was the optimum contact time 40 min.

| Table 5 | Parameters obtained for Langmuir and Freundlich equations for MB dye |
|-----------------|-----------------|-------------|-------------|
| Langmuir Isotherm | Freundlich Isotherm |
| \( q_{mon} \) (mg/g) | \( K_L \) (l/mg) | \( R^2 \) | \( K_F \) (mg/g) | \( R^2 \) |
| 13.888 | 0.01305 | 0.953 | 1.8057 | 0.919 |

From Table 5 and Table 6 it is clear that, in the cases of both MB and MO dye adsorptions, the Langmuir isotherm is having the highest regression value and hence the best fit. From the values of \( R_L \) obtained from the Langmuir plot of MB and MO dye, it is observed 0<\( R_L <1 \) and therefore it can be concluded that adsorption shows a favourable nature. From the values of 1/n obtained from the Freundlich plot of MB and MO dyes, it is observed 1/n <1 and therefore it indicates a normal adsorption. Smaller the value of 1/n, greater is the expected heterogeneity. Therefore, more heterogeneity is seen in the adsorption of MO dye. Also, the value of n lies between one and ten, and this indicates a favorable sorption process.

E. Regeneration

The adsorbents Rice Husk Powder, Orange Peel Powder and Neem Leaf Powder after the adsorption experiments at optimum parameters of MB and MO dye removal were used for the regeneration experiments with distilled water and 0.5N H\(_2\)SO\(_4\). 0.5N H\(_2\)SO\(_4\) seems to be more efficient in desorbing the MB and MO dye than compared to distilled water. It is also seen that, the recovery of dye is more from the orange peel powder than other adsorbents and therefore the regeneration of Orange Peel Powder is much easier and effective by using 0.5N H\(_2\)SO\(_4\).

| Table 7 | Percentage dye desorption of distilled water |
|-----------------|-----------------|-------------|
| Adsorbents | MB % desorption | MO % desorption |
| RHP | 10.909 | 13.1868 |
| NLP | 57.0576 | 51.356 |
| OPP | 74.3727 | 73.993 |

| Table 8 | Percentage dye desorption of 0.5N H\(_2\)SO\(_4\) |
|-----------------|-----------------|-------------|
| Adsorbents | MB % desorption | MO % desorption |
| RHP | 54.772 | 60.00 |
| NLP | 84.294 | 94.5736 |
| OPP | 92.1146 | 98.6068 |

4. Conclusion

In this study, bio-sorption of dyes from the aqueous solutions was studied by batch adsorption experiments and also the regeneration capacities of the adsorbents were studied. Dye removal efficiencies of low-cost adsorbents were studied on acidic and basic dyes. The color removal efficiencies of the adsorbents have a break through curve, in which there shows no further color removal after a particular time, which gives the optimum contact time. From the comparative results, it is clearly known that, the effect of duration plays a very important role in adsorption process of color removal. From the study, it is able to conclude that bio-sorption is a very effective method from the treatment of dye containing effluents, mainly the textile industry effluents and the adsorbents can be recycled effectively in a very eco-friendly manner.
Among the bio-sorbents studied, the MB dye and MO dye removal efficiency is like: Orange Peel Powder > Neem Leaf Powder > Rice Husk Powder. Both the Langmuir and Freundlich isotherms showed normal adsorption characteristics, in the cases of MB and MO dyes Dye recovery is greater from Orange Peel Powder for both distilled water and H2SO4. 0.5N H2SO4 could desorb 92.11% of MB dye and 98.6% of MO dye from Orange Peel Powder, while distilled water could only desorb 74.37% of MB dye and 73.99% of MO dye from Orange Peel Powder.

References