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Biosorption of Methylene Blue Dye from Water on Leaf Biomass of *Neolamarckia cadamba* (Kadam)

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Abstract In this present work, the leaves of Kadam (*Neolamarckia cadamba*) were used as adsorbent for the removal of Methylene blue dye from aqueous solution. The adsorption characteristics of the dye on Kadam leaf powder was evaluated as function of pH, initial concentration of adsorbate, contact time and adsorbent dose. The effective adsorption was found to be in the conditions of pH 4, initial adsorbate concentration of 10 mg/L, contact time of 30 mins and adsorbent dose of 0.4 g at 120 rpm agitation speed at room temperature. The results reveal that maximum percentage adsorption of dye onto Kadam leaf powder was 95.1.

Keywords: *Kadam tree leaf powder, Methylene blue dye, adsorption, pH*

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1. Introduction

Fresh water is already a limiting resource in many parts of the world. In the next century, it will become even more limiting due to increased population, urbanization, and climate change. This limitation is caused not just by increased demand for water, but also by pollution in freshwater ecosystems. Pollution decreases the supply of usable water and increases the cost of purifying it. Some pollutants, such as heavy metals or chlorinated organic compounds, contaminate aquatic resources and affect food supplies.

Most of the industrial dyes are stable to light and oxidation and are resistant to aerobic digestion [3]. The presence of colour in the aquatic system reduces the solubility (because of high COD) and transparency of water besides causing potential ecological imbalance in the growth and development of aquatic species [7,8]. The discharged dye effluents into the water bodies create a risk of ecotoxicity and potential danger of bioaccumulation [2].

Table 1. Various dye removal methods from wastewater

Physical methods	Chemical methods	Biological methods
Adsorption	Fenton reagent technique	Aerobic degradation
Ion exchange	Ozonisation	Anaerobic degradation
Filtration	Photocatalytic methods	
Coagulation/ Flocculation		

The conventional wastewater treatment processes which depend on aerobic biodegradation are low in removal efficiency for reactive and other anionic soluble dyes. Hence due to inefficient biodegradation of dyes this may not be an ideal option for treatment of dyes in polluted water.

Physical and Chemical methods of dye removal from wastewater such as chemical oxidation, coagulation, or filtration and membrane separation are a bit expensive [4,5].

Biosorption is the concentration and accumulation of contaminants from aqueous solution by using biological matters. Biosorption has been established as a potential/ effective technology in dye removal from aqueous solution using inactive and dead biomass [1].

Methylene blue dye was chosen because it is widely used in textile, paper and carpet industries. In spite of being not strongly hazardous, it can cause some harmful effects, such as increase in heartbeat, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [9].

It is harmful when it is swallowed and it can be harmful if it is breathed and comes in contact with skin. It is a cationic dye which is toxic and may cause several health risks such as nausea, vomiting, eye injury and methemoglobinemia in humans upon exposure [6].

2. Methods

2.1. Preparation of the Biosorbent

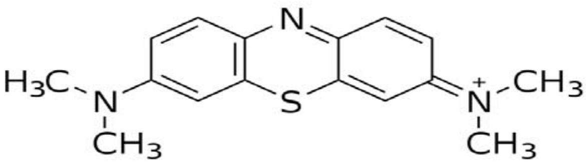
Kadam tree leaves were collected from the University campus. The leaves were at first washed with tap water repeatedly for 3-4 times and then with distilled water till the impurities were gone. These were then shade dried for 24 hours and then dried in a hot air oven at 105°C for

6 hours. The leaves were then ground to fine powder and boiled to remove tannins and lignins in it and dried again. After that the leaf powder was sieved to 100 μ size. The adsorbent thus prepared was then stored in plastic bottles in a dessicator for future use.

2.2. Preparation of Sorbate (Dye Solutions)

The dye stock solution having 1000 mg/L concentration was prepared through dissolving the required amount of Methylene blue dye powder in 1000 ml (1 L) distilled water. From this stock solution standard dye solutions of concentrations (10, 20, 30, 40, 50, 60 and 70) mg/L were prepared by serial dilution process.

C.I. number = 52015
C.I. name = Basic blue 9
λ_{max} = 665 nm
Empirical formula = $C_{16}H_{18}ClN_3S.3H_2O$
Structure,



3. Batch Adsorption Studies

Batch adsorption experiments were carried out in 250 ml Erlenmeyer flasks with 100 ml of working volume of the dye solution of different concentrations. The pH of the dye solution was adjusted with the addition of 1 N HCl and/ or NaOH. A predetermined amount of adsorbent, Kadam leaf powder (KLP) was accurately weighed and added to the solution. The flask solution was agitated at a desired speed using a shaker. Each of these parameters were varied keeping the other parameters constant, to study the influence of pH (2-10), initial dye concentration (10-70 mg/L), contact time (0-90 minutes) and KLP dosage (0.1-0.6 g). Samples were collected from the flasks at predetermined time intervals and filtered using Whatman filter paper no. 40. The filtrates were then centrifuged at 4000 rpm for 10 mins and finally the residual dye concentration in the solution was analyzed using a uv-visible spectrophotometer at particular wavelength corresponding to the λ_{max} value of the dye. All the experiments were performed in duplicates.

The removal efficiency was calculated by using the following formula:

$$Dye\ removal\ (\%) = (C_i - C_f)/C_i x100 \qquad (1)$$

Where, C_i = Initial Concentration (mg/L) and C_f = Final Concentration (mg/L).

3.1. Effect of Initial Dye Concentration

For this aliquots of stock Methylene blue solution (10 mg/L-70 mg/L) were taken in 250 ml Erlenmeyer flasks and 0.4 g of adsorbent was added to each flask. The flasks were shaken for 30 mins in a shaking incubator. After agitation the solutions were filtered and then centrifuged at 4000 pm for 10 mins. Then the absorbance of the supernatant was checked using an uv–vis spectrophotometer at 665 nm. The amount of Methylene blue dye adsorbed per unit weight of adsorbent was calculated as

$$Q = \left(\left(C_i - C_f\right)*V\right)/W)\ mg/g \qquad (2)$$

Where,
C_i = Initial concentration of dye (mg/L)
C_f = Final concentration of dye (mg/L)

3.2. Effect of Adsorbent Dose

For this 10 mg/l of stock Methylene blue dye solution were taken in five conical flasks and 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g of adsorbent was added to each flask. The flasks were kept in the shaker for 30 mins and agitated at 120 rpm. After that the solutions were filtered and then centrifuged at 4000 rpm for 10 mins. Finally the absorbances of the supertanatant solutions were estimated.

3.3. Effect of Time of Agitation

10 mg/l dye solution was taken in four conical flasks and 0.4 g of adsorbent was added in each of the flasks. The flasks were kept in the shaker for different time intervals 0, 30, 60 and 90 minutes. After agitation the solutions were filtered and then centrifuged at 4000 rpm for 10 minutes. The absorbance of the supernatant was found to estimate for the final dye concentration.

3.4. Effect of pH

10 mg/L dye solution was taken in five conical flasks and pH of the flasks were adjusted at 2, 4, 6, 8 and 10 respectively. 0.4 g of adsorbent was added to each of the flasks and then agitated for 30 mins in the shaker. After shaking the solutions were filtered and then centrifuged as described earlier. Finally the absorbances of the supernatants were estimated using the spectrophotometer.

4. Results and Discussion

4.1. Characterization of the Biosorbent

4.1.1. pH of the Biosorbent

The slurry obtained by mixing 10 g of powdered biosorbent with 100 mL of distilled water was tested for pH. The pH of the biosorbent was recorded at 4.69 which indicates that the Kadam leaf powder is slightly acidic in nature.

4.1.2. BET Surface Area, Pore Size and Pore Volume

Table 2. BET surface area, pore size and pore volume of Kadam leaf powder

Surface area (m^2/g)	Pore size (Å)	Pore volume (cc/g)
113.455	16.019	0.058

4.2. Biosorption Experiments

4.2.1. Effect of Initial Dye Concentration

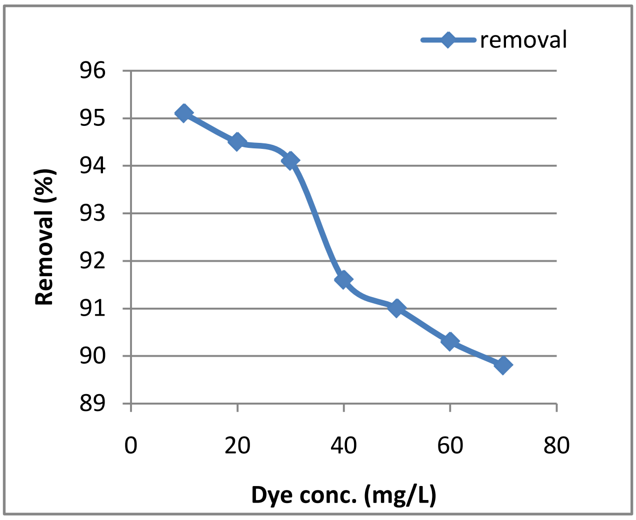


Figure 1. Effect of initial dye concentration on percentage adsorption of Methylene blue dye

Among all the dye solutions highest biosorption was seen to occur in 10 mg/L solutions. By changing the concentration at constant time intervals the difference in dye removal percentage was noted and it was plotted as graph. The graph shows that the percentage of adsorption gradually decreases as the initial dye concentration increases.

4.2.2. Effect of Adsorbent Dose

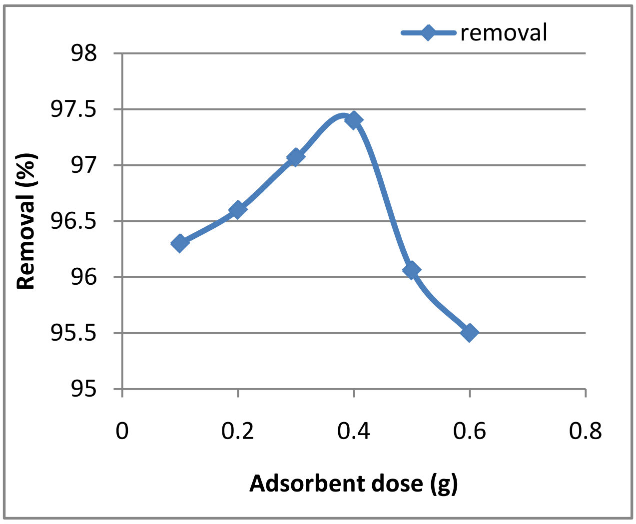


Figure 2. Effect of adsorbent dose on percentage adsorption of Methylene blue dye

Adsorption increased with increased adsorbent dose and reached peak at dose of 0.4 g. However, further increase in adsorbent dose exhibited lesser adsorption capacity. Percentage dye removal was found to be highest at an adsorbent dose of 0.4 g. At low adsorption doses, dye removal was also low which increased alongwith the increase in adsorbent dose and reached maximum at 0.4 g dose. Further increase in the adsorbent dose however showed decline in the dye removal percentage.

4.2.3. Effect of Contact Time

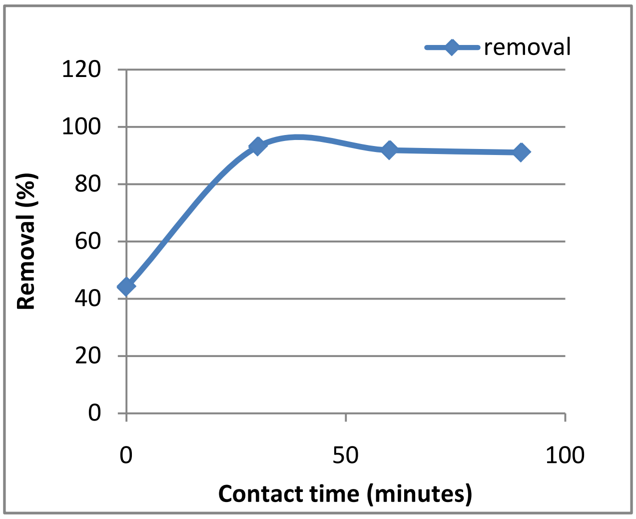


Figure 3. Effect of contact time on percentage adsorption of Methylene blue dye

Adsorption increased as contact duration increased showing highest adsorption at 30 minutes while with further increase in time, adsorption did not increase significantly. The reason behind this may be due to non-availabitity of binding sites of the adsorbent.

4.2.4. Effect of pH

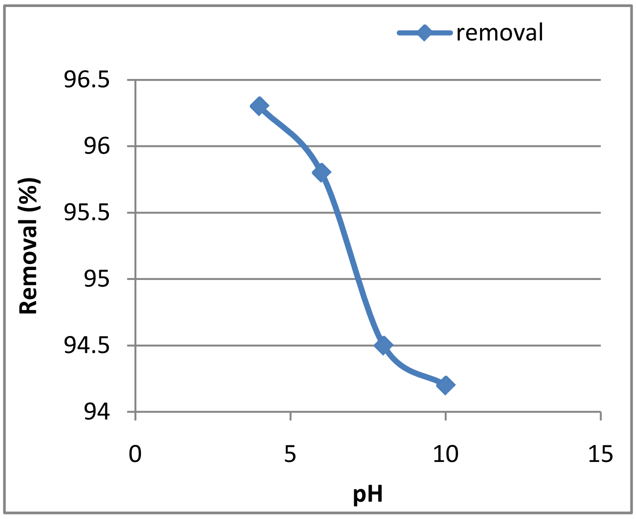


Figure 4. Effect of pH on percentage adsorption of Methylene blue dye

Varying pH of the dye solutions showed varied adsorption with maximum adsorption at pH 4. Beyond pH 4, adsorption percentage seemed to be decreased.

In case of Methylene blue, highest adsorption percentage of 95.1 was observed under conditions of 10 mg/L initial dye concentration, pH 4, contact duration of 30 minutes, adsorbent dose of 0.4 g and agitation speed of 120 rpm. Though it was seen that adsorption increased with increasing dose of adsorbent yet beyond 0.4 g dose the adsorption percentage was seen to be declined. Highest adsorption occurred at pH 4 and with further increase in pH, adsorption decreased. Contact time of 30 minutes was found to be more favourable while with increased contact time adsorption decreased.

5. Conclusion

In India and Asian continent, the Kadam trees are very commonly found. The experiments carried out in the study so far proved that the leaves of Kadam tree can act as an effective adsorbent for removal of a few dyes from aqueous solutions. As far as my study is concerned, the maximum removal efficiency was found to be 95.1 % for Methylene blue dye.

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