

# SURFACE ASSIMILATION STUDIES FOR THE REMOVAL OF DYES FROM SYNTHETIC WASTEWATER FROM THE BIOMASS OF AZADIRACHTA INDICA

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## ABSTRACT

Water, one of the essential resources for the survival of all living organisms, is not only limited to human beings alone but also for productive activities like agriculture, industrial activities, etc. Many industries have come up due to rapid industrialization which resulted in countless benefits as it plays a vital role in the economic development of underdeveloped and developing countries. Despite its benefits, the industrial sector is one of the global polluters as it consumes a large number of chemicals and fuels. Industries like plastic, paper, cosmetics, textile use dyes to color their products. The waste effluent from these industries leaves out the colored water, which, even at low concentrations is highly visible and undesirable. Adsorption, one of the effective methods for the removal of dyes from waste effluent, has an edge when compared to other methods due to its sludge-free clean operation. Activated charcoal is the most widely used adsorbent and in spite of its widespread use in various cleaning procedures, it remains expensive. The present study is aimed towards the development of an industrially viable, cost-effective, and environmentally compatible adsorbent for the removal of dyes from wastewater. The biomass of *Azadirachta Indica* (Neem) is used to prepare activated charcoal using NaOH as an activating agent. The prepared activated charcoal is tested for Batch studies with different parameters such as the effect of time, dosage, and pH. The removal efficiency and the adsorptive capacity are calculated. The prepared activated charcoal from *Azadirachta Indica* has shown the removal of Methylene blue dye to a maximum of 94.33% from synthetic wastewater. Adsorption kinetic studies were analyzed for the resulting data and it was found that the Pseudo second-order kinetic model was the best fit.

**Keyword:-** Adsorption, Activated charcoal, Methylene blue, *Azadirachta Indica*, Kinetic studies, Textile wastewater

## 1. INTRODUCTION

Water supports all forms of life on the planet. 70% of the earth's surface is made of water out of which only 3% of fresh water is for human consumption. Due to the rapid industrialization, a number of industries have come up which resulted in a numerous benefit as the industrial sector plays a major role in the economic development of the under developed and developing countries. Among the various industries, textile industry is one such industry which plays a vital role in the economy of Asian countries. Textile industry contributes 7% of the total world exports and employs around 35 million workers around the world [8]. In India, the textile industry contributed 7% to the industry output (by value) in 2018-2019. It contributed 2% to the GDP, 12% to the export earnings and held about 5% of the global trade in 2018-2019. Besides the benefits, the industrial sector is one of the biggest global polluters

[6]. Textile industry is responsible for a number of environmental impacts. The main damage caused by the textile industry is the discharge of untreated effluent into the water bodies [6]. The untreated effluent from the textile industry constitutes 80% of the total emissions produced by this industry [30]. The untreated effluent has relatively high levels of Biological Oxygen Demand and Chemical Oxygen Demand [28]. Textile industry is using more than 8000 chemicals in various processes of the textile manufacturing including printing and dyeing.

### **1.1 DYES**

Dyes are soluble organic compounds especially classified as acidic, basic, reactive, direct etc. A dye is generally applied in an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber. Earlier fabric used to be dyed with natural dyes obtained from fruits, vegetables, roots. Color is the main attraction of any fabric because if it is unsuitably colored, it is bound to be a failure as a commercial adsorbent. With the production of synthetic dyes, it gave a boost to textile industry as synthetic dyes offer a range of colors and brighter shades, which was a major setback in natural dyes. But the untreated colored water when released into the environment is a major problem for environmental management [9]. The color associated with the textile dyes not only causes aesthetic damage to water bodies but also prevents the penetration of light into the water. This leads to a reduction in the rate of photosynthesis and dissolved oxygen levels which affects the entire aquatic life [14].

### **1.2 AVAILABLE TREATMENT TECHNOLOGIES**

A wide range of methods have been formulated for the removal of dyes from the water and the wastewater to reduce their impact on the environment. The methods can be classified as Physical (Sedimentation, Filtration, Floatation, Coagulation, Reverse osmosis, Adsorption, Incineration, Distillation, Membrane treatment), Chemical (Neutralization, Reduction, Oxidation, Ion exchange, Electrolysis) and Biological (Stabilization, Aerated lagoons, trickling filters, Activated sludge, Fungal treatment, Flocculation). But these methods suffer from one or the other limitations and have their own constraints. Adsorption, due to its simple design, has an edge over other method.

### **1.3 ADSORPTION**

Adsorption is often described as a surface phenomenon where particles get attached to the top layer of the material. For the adsorption process, two components are required, Adsorbate, a substance that gets deposited on the surface of another substance and Adsorbent, the surface of the substance on which the adsorbate adsorbs.

The most generally used adsorbent for industrial purpose is the Activated carbon due to its excellent adsorption capability. It can be made from many substances containing high carbon content such as coal, coconut shell, wood etc. but the raw material which is used to prepare, has a very large influence on the performance. Although, commercial activated carbon is a preferred adsorbent for the removal of color, its widespread use is limited due to its high cost and the cost of regeneration is also high because the desorption of the dye molecules is not easily achieved. This limitation has led to the development of an alternative, low-cost adsorbent. In recent years, there have been numerous studies focused on the development of cheaper materials such as fibers, hardwood, rice husk, orange peel, sawdust etc.

### **1.4 AZADIRACHTA INDICA**

Azadirachta Indica, commonly known as Neem is native to Indian sub-continent. The Latin name of Azadirachta Indica is derived from the Persian which refers to "The free tree of India" (Azad = free, dirakht = tree, i-hind = of Indian origin). This tree can thrive on the merest trickle of water, whatever may be the quality. So, it is noted for its drought resistance.

In the present study, the bark of Azadirachta Indica is used for the preparation of low cost activated carbon. The contents of Neem bark are shown in the table below.

**Table – 1:** Contents of Neem bark

Trunk bark	Stem bark
Nimbin (0.04%)	Tannins (12-16%)
Nimbinin (0.001%)	Non – tannins (8-11%)
Nimbidin (0.4%)	
Nimbosterol (0.03%)	
Essential oil (0.02%)	
Tannins (6%)	

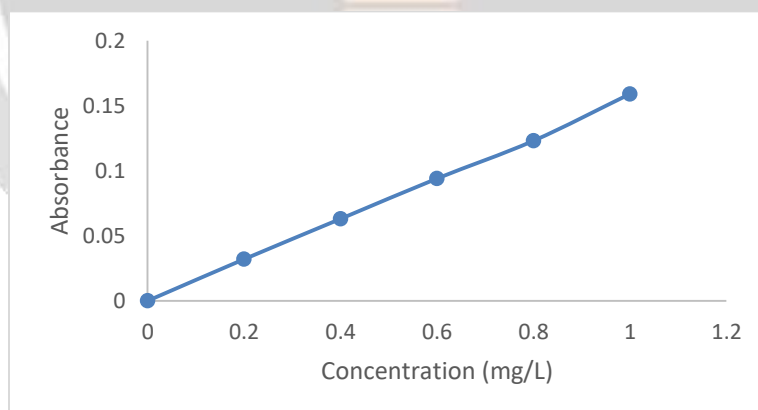
## 2 METHODOLOGY

### 2.1 Preparation of Activated Charcoal

The bark pieces of *Azadirachta Indica* are collected, washed with distilled water and dried at 100°C in a hot air oven for an hour. They are then placed in a muffle furnace at 500°C for an hour so that the bark pieces are turned into charcoal. It is made into a fine powder using mortar and pestle. The powder is sieved such that it passes through IS .425 M. M sieve and retains on IS .250 M. M sieve. Activation of charcoal is done using NaOH by taking charcoal powder and NaOH in 1:1 ratio and mixing it with 20 ml distilled water. 0.1 N HCl solution is added to maintain the pH between 6.5 and 7. The mixture is placed in a hot air oven at 100°C for an hour to obtain activated charcoal.

### 2.2 Preparation of Methylene blue solution

Stock solution of Methylene blue was prepared using 1 gm of Methylene blue diluted in 1000 ml of distilled water. Different dye concentrations of 0.2 gm/L, 0.4 gm/L, 0.6 gm/L, 0.8 gm/L and 1 gm/L were prepared and their percentage absorbance was found using UV Spectrophotometer at a maximum wavelength of 664 nm. Calibration curve is plotted with the obtained values.

**Chart - 1:** Calibration curve

### 2.3 Effect of contact time

The effect of contact time was studied by taking 0.6 gm of adsorbent in 100 mL of aqueous solution of Methylene blue at an initial concentration of 1 mg/L. The sample is collected at different time intervals like 15, 30, 45, 60 and 75 minutes. It is filtered and the removal efficiency was calculated.

## 2.4 Effect of adsorbent dosage

The effect of adsorbent dosage was studied by taking different dosage of adsorbent as 0.2 gm, 0.4 gm, 0.6 gm into 100 mL of aqueous solution of Methylene blue and by keeping the other conditions constant. The samples were collected for various time intervals of 15, 30, 45, 60, 75 minutes and absorbance values are obtained to find the optimum dosage.

## 2.5 Effect of pH

To determine the effect of pH, adsorbent dosage of 0.6 gm is taken and time interval is taken from 15 to 75 minutes. 0.1 HCl solution is used to reduce the pH to 2, 4, 6 and 0.1 N KOH solution is used to increase the pH to 8 and 10. The samples are collected and analyzed for the absorbance values.

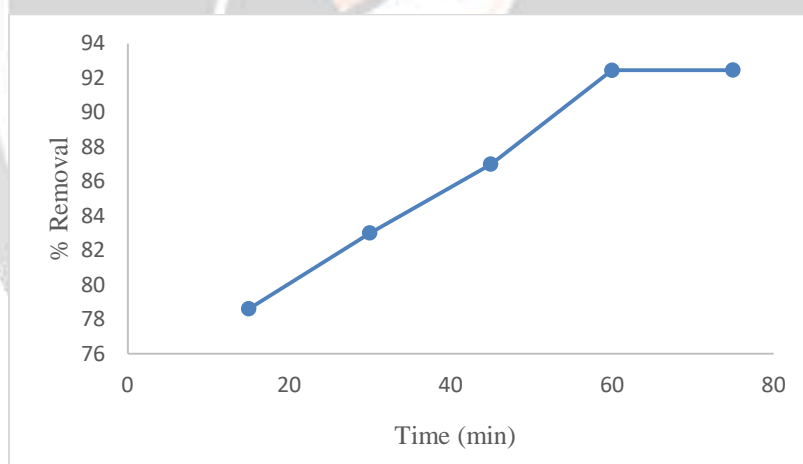
## 2.6 Adsorption kinetics

From the resulting data of the batch studies, adsorption kinetics, pseudo first order and pseudo second order, were plotted to find out the best fit kinetic model.

## 3 RESULTS AND DISCUSSION

### 3.1 Effect of contact time

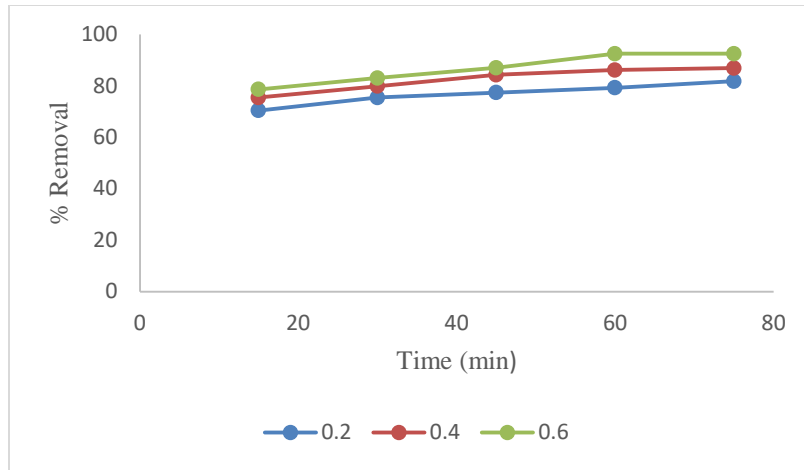
The percentage removal of Methylene blue increased with duration. Initially for the sample collected at 15 minutes, the removal percentage was 78.6% and it gradually went up to a maximum of 92.46% at 75 minutes. Further there was no adsorption observed due to the deposition of Methylene blue on the available sites of the adsorbent.



**Chart 2:** Effect of contact time

### 3.2 Effect of adsorbent dosage

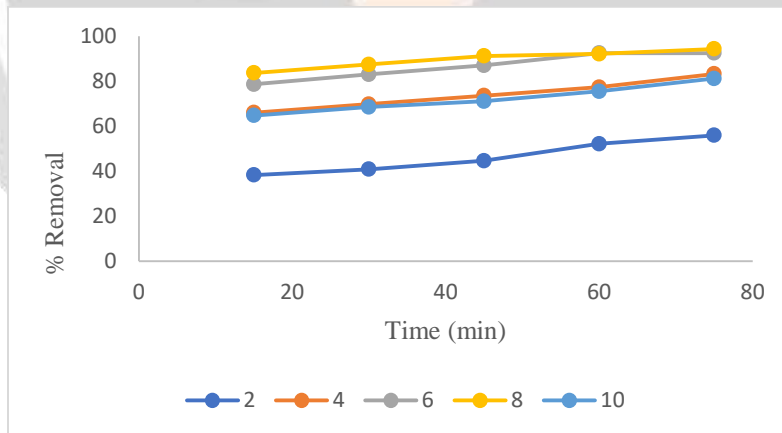
When the adsorbent dosage was increased from 0.2 to 0.6 gm, the removal percentage of Methylene blue also increased from 70.41% to 92.46%. It was observed that the maximum removal using 0.2 gm adsorbent was 81.74%, using 0.4 gm was 86.85% and using 0.6 gm it was 94.46%. The dye removal increased with an increase in adsorbent dosage and this might be due to the fact that at better dose of the adsorbent, extra sorbent and pore volume might be available for the adsorption interaction which results in percentage removal. The graph shows the variation of adsorbent dosage and removal percentage of Methylene blue.



**Chart 3:** Effect of adsorbent dosage

### 3.3 Effect of pH

The removal percentage of Methylene blue was lowest at pH 2 and maximum removal of was observed at a pH 8. From the graph, it clearly shows that with the increase in pH, the percentage removal increases but after reaching a maximum removal at pH 8, it removal percentage of Methylene blue decreases at pH 10.



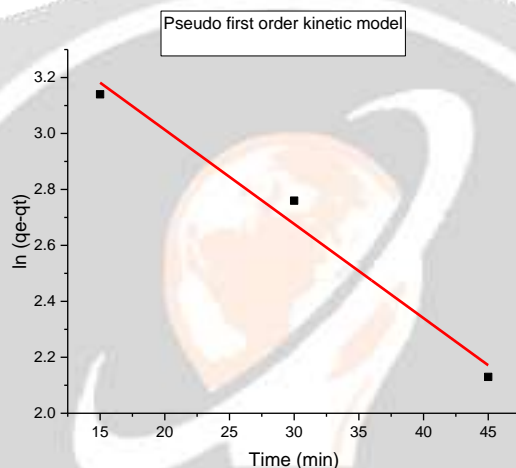
**Chart 4:** Effect of pH

### 3.4 Adsorption Kinetics

Pseudo first order kinetics is a plot between Time (min) on X-axis and  $\ln (q_e - q_t)$  on Y-axis. The experimental adsorption capacity and theoretical adsorption capacity are compared and R2 value is known. The graph for pseudo first order kinetics is shown below.

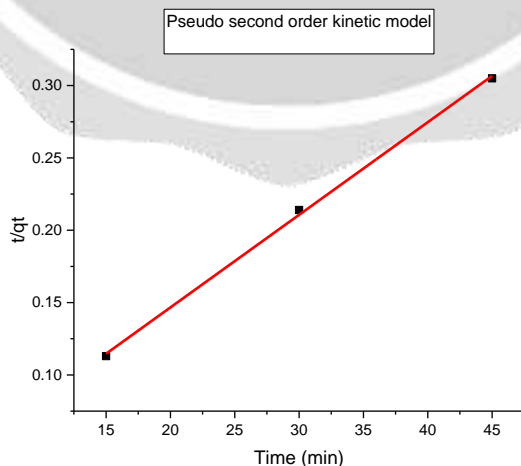
**Table 2:** Pseudo first-order and second-order kinetics

S. No.	Time (min)	$\ln (q_e - q_t)$	$t/q_t$
1	15	3.15	0.11
2	30	2.76	0.214
3	45	2.13	0.305



**Chart 5:** Pseudo first-order kinetic model.

Pseudo second order kinetics is a plot between Time (min) and  $t/q_t$ . The graph for the pseudo second order is shown below.



**Chart 6:** Pseudo second-order kinetic model

**Table 3:** Pseudo first-order and second-order kinetics

Order of Kinetics	Experimental adsorption capacity, $q_e^{exp}$ (mg/g)	Theoretical adsorption capacity, $q_e^{theo}$ (mg/g)	Rate constant 1/min		Correlation coefficient, $R^2$
			$K_1$	$K_2$	
1	155.9	39.9172	-0.00075	-----	0.95997
2	155.9	156.25	-----	0.002194	0.99819

With reference to the above table, the experimental adsorption capacity of the pseudo second-order was very much nearer to the theoretical adsorption capacity when compared to that of the pseudo first-order values. The Correlation coefficient of the pseudo second-order model is greater than the correlation coefficient of pseudo first-order model and is also near to 1. It can be concluded that the pseudo second-order kinetic model is the best fit.

#### 4. CONCLUSIONS

The study entailed the degradation of methylene blue dye in synthetic waste water using Azadirachta Indica bark. The results showed that Azadirachta Indica bark proved to be a effective bio sorbent for the removal of methylene blue dye. The performance is strongly affected by the parameters such as contact time, adsorbent dosage and pH. The maximum removal of methylene blue, 94.33% was observed at pH 8, adsorbent dosage of 0.6 gm and a contact time of 75 minutes. In neutral solution, the maximum removal observed was 92.46%. When the adsorption kinetics was applied, pseudo second-order kinetic model was the best fit.

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