# Removal of Methylene Blue Dye by Using Activated Carbon Derived From Walnuts Shells

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**Abstract:**
**In this study, activated carbon was developed from Walnut shell (AACWS). The experiments were carried out to removal of methylene blue by using ACWS. In this research, parameters factors are study such as pH, adsorbent dose, contact time and initial dye concentration . Also adsorbent ACWS was studied for characterization using SEM and FTIR. The experiments result show that walnut shell activated carbon can be successfully used as an inexpensive alternative to commercially available activated charcoal for removal of dyes from wastewater.**

**Keywords: Walnut Shell ; Activated carbon ; Methylene Blue dye, Adsorption.**

## INTRODUCTION

“The term "colourant" refers to pigments and dyes. A dye is a material that dissolves in water.” [1] “One of the dyes is methylene blue. Mainly those dyes are used to meals industries, cosmetic & private care, pharmaceutical business enterprise, printing, leather, plastic and fabric business enterprise. Most of that methylene blue is utilized in fabric business enterprise for colouring the cotton, wool, silk, nylon and polyester. The methylene blue is water soluble dye so that after using in textile this dye is polluted water. After their used in industries, this methylene blue soluble water is realized in lake, pond, river and sea. This dye water is harmful for humans, plants and animals. Long-term exposure to it can result in anaemia, hypertension, nausea, and vomiting” [2][3].

It is important to remove this dye from wastewater. “There are different method is used to remove these dyes such as physical, chemical and biological. They are including ion exchange, ozonation, liquid extraction, coagulation and adsorption. The benefits and drawbacks of each removal approach have been thoroughly analysed” [4]. From these, adsorption process is most effective technique for the treatment of dye from waste water. Researchers and environmentalists continue to be concerned about the cost-effective removal of dyes. “Most researchers have tried adsorption from aqueous solution utilizing different agricultural-based biosorbents, like tangerine peels” [5], green marine macro algae, Caulerpa scalpelliformis [6]; orange, pineapple and pomegranate peels[7]; sunflower, potato, canola and walnut shell residues[8]; almond shell [9]; walnut shell [10]; potato peel, lemon peel, orange peel, watermelon peel, tomato peel, coffee waste, apple peel, banana peel, decaf coffee waste, eggplant peel, carob peel and grape waste[11]; orange peel [12]. Adsorption is a highly effective separation technique due to its low starting cost, simplicity of design, ease of operation, and insensitivity to harmful compounds. Activated carbon, whether in powder or granular form, is the best material for removing dyes. However, it is expensive to produce and rejuvenate [13]. During the last decade, a number of non-conventional, low-cost adsorbents such as rice hull ash, sugarcane bagasse, sawdust, pine needle, eucalyptus bark, prawn shell activated carbon, and mango seed kernel powder was used to take out dyes and heavy metal ions from water solutions [14]. The current work studies for removal of MB dye using activated carbon material prepared from walnut shell. The self-prepared adsorbent was characterized by SEM and FTIR analysis. Batch experiment was used at room temperature to observe the efficacy of adsorbent for adsorption of MB dye from test solution. Batch experiments were performed for testing of impact of pH, adsorbent dose, adsorption time and initial dye concentration.

## 2. MATERIAL AND METHODS

### *2.1 Adsorbent*

Walnut shell was collected from local market area in Nagpur, Maharashtra, India. Shells were separated out from the fruits. These Walnuts shells are washed several times with double distilled water, after that this shell was washed with 40% HCl so that the impurity of the surface of the walnut's shells are removed properly and again then wash with double distilled water several time. The shells are dried in sunlight for 6 hrs and then 105ºC for 6 hrs in hot air oven. These dried shells are crushed into several small pieces. After that these walnuts shells piece was carbonized by using muffle furnace at the range of 250ºC for during 2 to 3 hrs. Removed carbonized shell from muffle furnace and cooled at room temperature known as carbon. After cooling, these newly prepared carbon was poured in 95% $H_2SO_4$ with the ratio of 1:2 for the activation process. This solution was kept at least 12 hrs. This activated sample was filtrated through whatman filter paper and washed with distilled water several time. The resulting activated carbon prepared from walnuts shell are name as ACWS. ACWS was characterized by using FTIR and SEM.

### 2.2 Preparation of Methylene Blue solution

Methylene blue ($C_{16}H_{18}N_3SCl.3H_2O$) was procured in AR grade from Market, India, and utilised without additional purification. The solution was made by dissolving the appropriate amount of dye in distilled water and prepared artificial synthetic methylene blue dye.

### 2.3 Experimental work for removal of dye in different parameters

Batch adsorption studies were performed with a sentence of 250 mL conical piston containing ACWS-Adsorbent and 100 mL MB solution at different initial concentrations. The flasks were shaken in a rotator shaker at 120 rpm and 30 ± 1 °C until equilibrium was achieved. Following decantation and filtration, the equilibrium concentrations of dye in the solution were determined at 665 nm using a UV-visible spectrophotometer. The pH of the solution was mentioned using 1N HCl and 1N NaOH solutions. The amount of dye adsorbed and percent clearance of MB were determined using Eq.

$$Qe = \frac{Co-ce}{co}\, x\, 100$$

Where Qe = Adsorption efficiency in percentage

Co = Initial concentration of dye

Ce= Equilibrium constant of dye

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of ACWS adsorbent

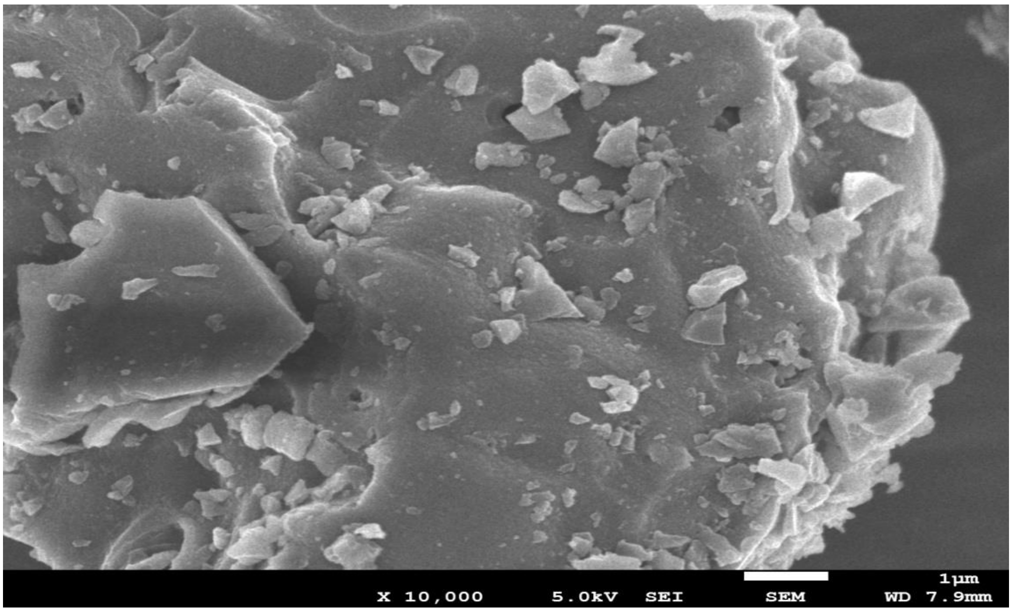


Fig 1: - SEM image of Activated Carbon of Walnut Shell (ACWS)

Fig1 show the SEM image of Activated Carbon of Walnut Shell (ACWS) having the magnification at x10000. This micrograph images show that the surface of activated carbon is porous which is suitable to adsorbed methylene blue dye. It is also seen that there are small cavity and cave type opening on the ACWS surface which proves for better surface area for adsorption process. Also, that the surface is solid structure.

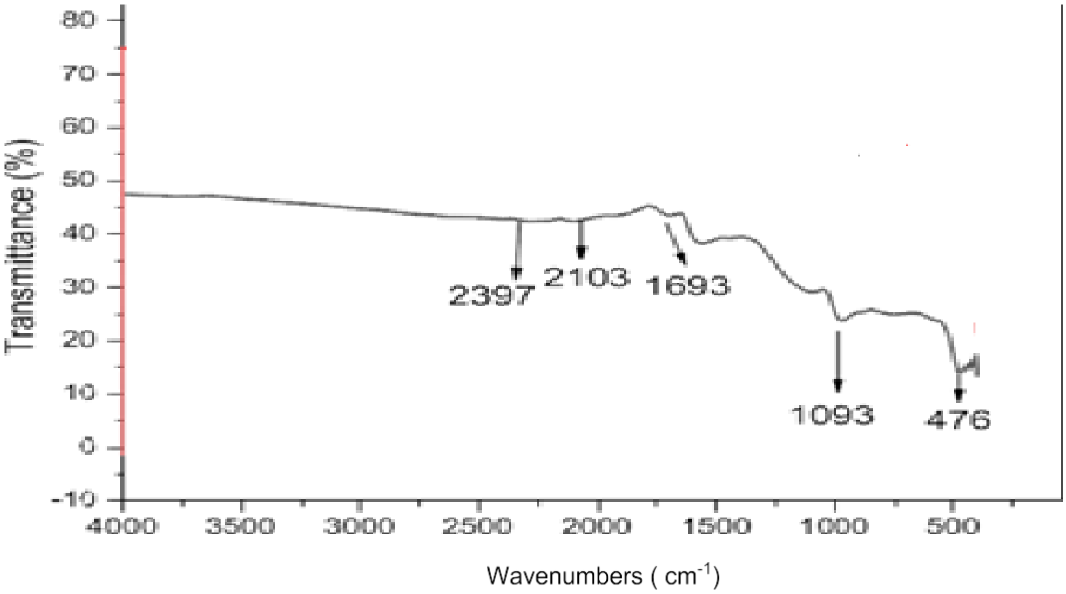


Fig 2: - FTIR Graph of Activated Carbon of Walnut Shell (ACWS)

In the figure 2, the Adsorption FTIR spectrum shows a broad 2103 $cm^{-1}$indicating the presence of C-H bonds in the alkane group. The presence of (C-C) function groups is indicated by adsorption talk at a wavelength of 2397 $cm^{-1}$. Peaks associated with C=C were generated at 1693 $cm^{-1}$. A strong stretch of C-OH (alcohol) is shown with a top tape of 1093 $cm^{-1}$. Peak 476 $cm^{-1}$indicates the presence of O-H vibrational bands.

## 3.2 Removal of methylene blue dye from solution

### *3.2.1 Effect of Adsorbent Dose*

The doses of adsorbent ranged from 0.5 to 7 gm. Figure 4 makes it clear that when the adsorbent concentration increased from 0.5 to 5 gm, the MB removal increased significantly. This will be due to the fact there are greater adsorbent voids sites available, and certain adsorbent surfaces are greater effortlessly available (Fig.3). However, after an adsorbent dose of 5 to 7 gm, no discernible changes in removal efficiency were seen (Fig. 3).

### *3.2.2 Effect of Initial concentration*

The effect of dye concentration on the adsorption of methylene blue onto ACWS was carried out in the concentration range of 10, 15,20 ....70 mg/ 100 ml (Fig. 4). Equilibrium adsorption capacity decreases with an increase in methylene blue concentration from 10 to 70 mg/L. This is due to the fact that at low concentrations there will be occupied active sites on the adsorbent surface so that at low concentration removal % is high. The active region required for dye adsorption is missing above the optimum methylene blue concentrations mentioned above [15][16]. By employing walnut shells, this slows down the overall methylene blue adsorption by activated carbon.

### *3.2.3 Effect of Contact Time*

The effect of contact time on the removal of methylene blue is shown in Fig. 5. The highest 86.76% dye removal takes place at 70 min for ACWS and then the equilibrium was reached after 70 min. The fact that all of the adsorbent sites are initially empty and the solute concentration gradient is quite high could be the cause of the shift in the adsorption rate. Later, fewer adsorbent and dye concentrations have available sites, which results in a reduced adsorption rate. The potential monolayer development of Methylene blue on the adsorbent surface is indicated by the decreased adsorption rate, especially towards the conclusion of trials [17][18]. This could be because there aren't enough active sites available for further absorption once the equilibrium is reached [19].

### *3.2.4 Effect of pH*

The adsorption of methylene blue onto ACWS is significantly influenced by the pH of a dye solution. The effect of pH values on adsorption on ACW is shown in Figure 6. At pH 5, the greatest amount of methylene blue was removed (79.36%). When the basic (cationic) dye is dissolved in water, positively charged of ions are dissociated. As a result, the positively charged surface of the adsorbent tends to prevent the cationic adsorbate from adhering in an acidic solution. Methylene Blue-dye adsorption increases with increasing pH values of the dye solution, increasing the electrostatic attraction between the negatively charged adsorbent and the positively charged dye [20].

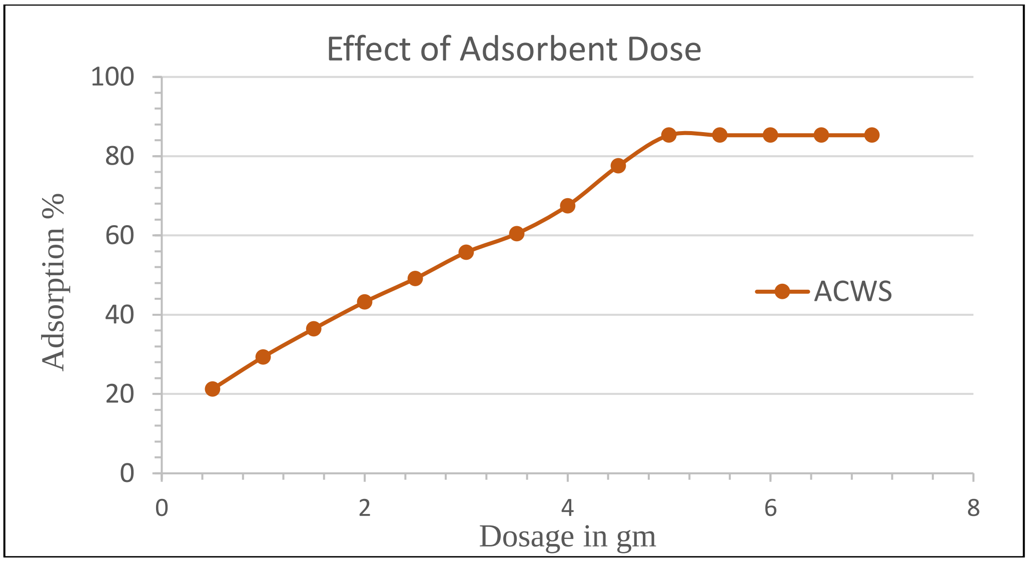


Fig 3: - Effect of Adsorbent Dose

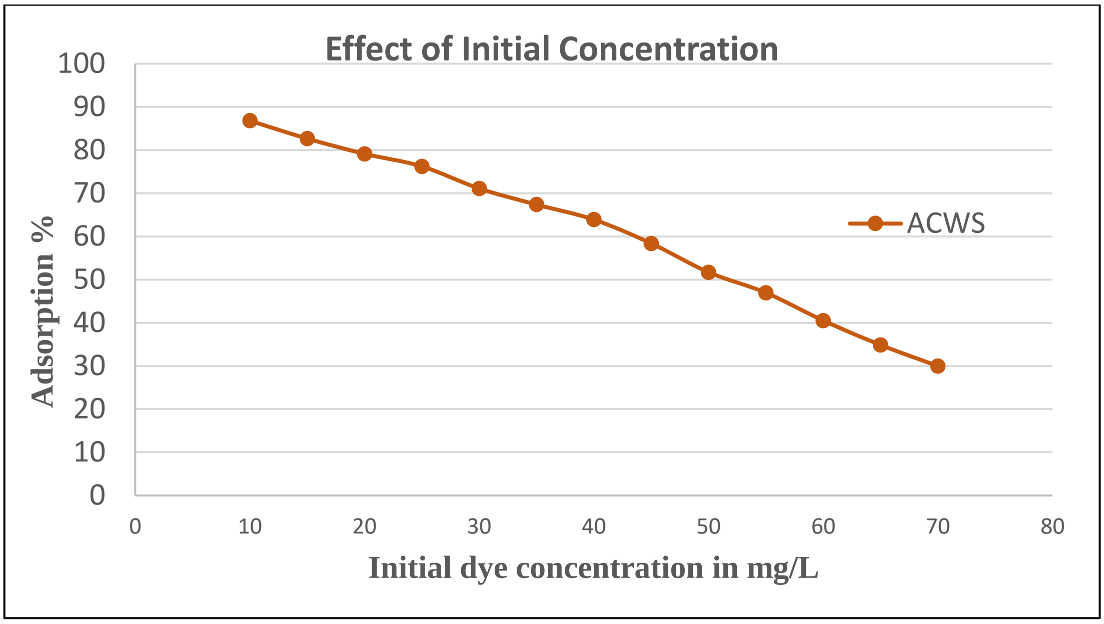


Fig 4: - Effect of Initial Concentration

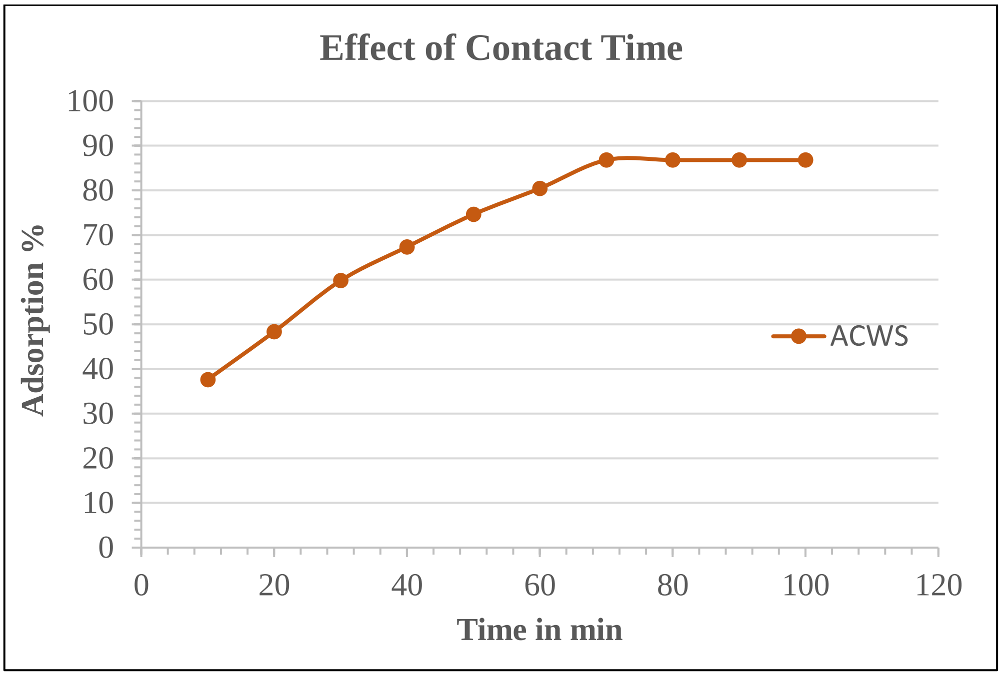


Fig 5: - Effect of Contact Time

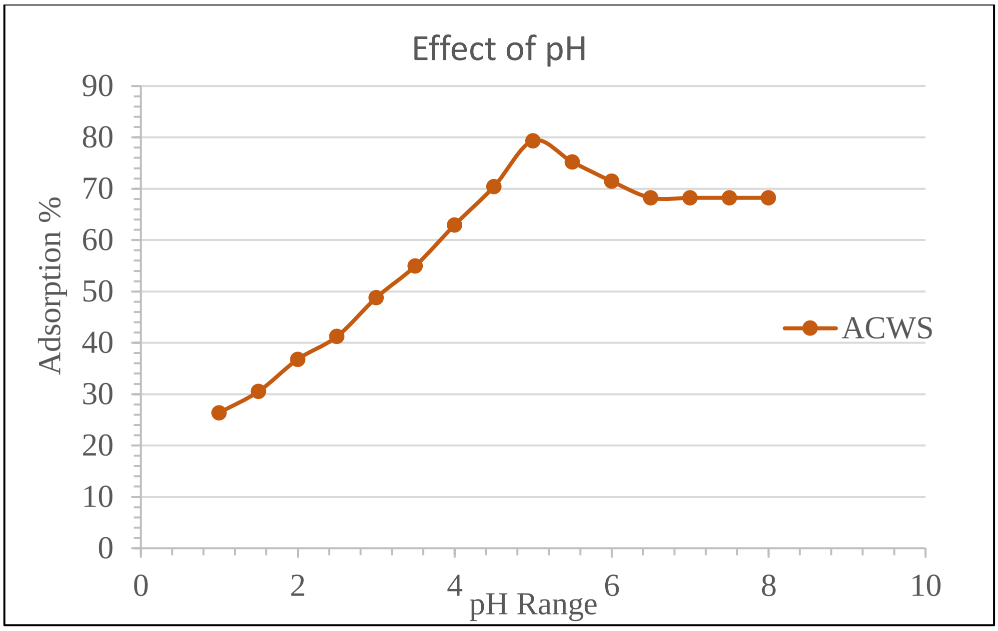


Fig 6.: - Effect of pH

## 4. CONCLUSION

In this study, carbon is successfully prepared from Walnuts shells and successfully activated by using activating agent. This prepared activated carbon of walnut shell name as ACWS. The Characterization of newly prepared activated carbon successfully done and result show that various number of function group attached with the activated carbon and there are number of hole, cavity and small opening are found on the surface of activated carbon. On other hand methylene blue dye is dissolved in water and polluted it. this water is harmful for humans, plant and animal so that it is necessary to remove methylene blue dyes from water. ACWS shows good adsorption capacity for methylene blue removal. The operating parameters for the maximum adsorption were dye solution remove in concentration (10 mg/L100 ml), Adsorbent dosage (5 gm), contact time (70 min). Removal of methylene blue dye is pH dependent and the maximum removal was attained at pH 5.

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