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Walnut Shell Charcoal a Cost-effective Adsorbent for Removal of Methylene blue Dye from Aqueous Solution

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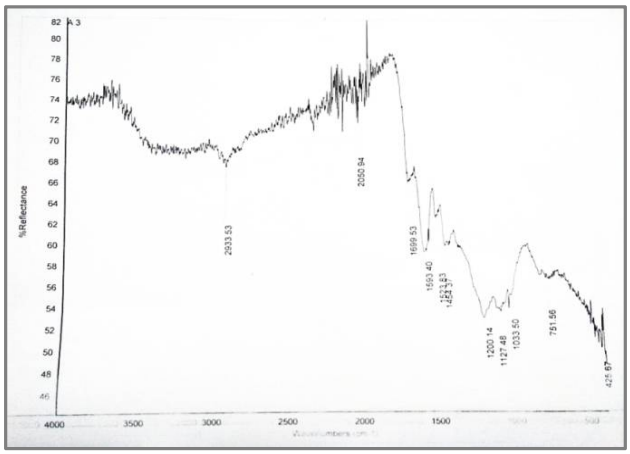
ABSTRACT

Walnut shell charcoal act as a good adsorbent for removal of methylene blue dye. A batch adsorption study was carried out with variable parameters like adsorbent amount, contact time, initial dye concentration, pH, and salt effect. The morphology and functional groups present in Activated carbon walnut shell charcoal were investigated by X-Ray Diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. Studies showed that the pH of aqueous solutions affected by dye removal as a result of removal efficiency increased with decreasing solution of pH, the results indicate that Walnut shell activated carbon could be employed as a low-cost alternative to commercial activated carbon in the removal of methylene blue from wastewater.

Graphical Abstract



FTIR spectrum of loaded methylene blue on ACWSC.

Keywords: Activated Carbon of Walnut Shell, Methylene Blue, Adsorption.

INTRODUCTION

Methylene blue (MB), a basic, cationic dye with the molecular formula $C_{16}H_{18}N_3SCl$, Molecular Weight =319.85. λ max = 660 nm. It has wide applications which includes,dyeing of silk, cottons, wools, silk, leather, colouring paper and plastics. The discharge of M.B from dying industries to the environment is worried for the ecosystem [1]. The MB dye cause harmful effects such as increased heart rate, vomiting, cyanosis, jaundice, quadriplegia, tissue necrosis, dermatitis, problems in respiratory tract, kidney, liver, brain, reproductive and central nervous system [2-4]. It is rather difficult to treat dye effluents because of their synthetic origins and mainly aromatic structures, which are biologically non-degradable [5-7]. The removal and recovery of MB dye from wastewater is important in the protection of environment and human health. The most commonly used methods for colour removal are Nano filtration [8], Reverse Osmosis [9], Adsorption [10], Electro dialysis, Sedimentation [11], Ozonisation [12], Coagulation [13], Oxidation [14-15], Biosorption and Biodegradation [16]. There are severe advantages and disadvantages of these methods for dye removal from wastewaters [17]. Among the various available water treatment techniques, "adsorption" is the most reliable and efficient technique for decolouration, in which the recovery and recycling of the adsorbent can be achieved along with distinct advantages of non-production of any toxic sludge and cost effectiveness [18]. This is attributed to its low cost, easy availability, simplicity of design, high efficiency, easy operation, biodegradability and ability to treat dyes in more concentrated forms [19, 20]. Activated carbon adsorption is one such method which has a great potential for the removal of dyes from wastewater [21-26]. Commercially available activated carbons are usually derived from natural materials such as wood or coal and still considered expensive [27]. This has led to the search for cheaper substitutes. Hence, low-cost activated carbons based on agricultural solid wastes have been investigated for a long time [28-29]. Agricultural by products and waste materials used for the production of activated carbons includes Aloe vera wastes [30], cashew nut shell [31], fly ash, clay, walnut shell [32], treated activated carbon [33], jack fruit leaf powder [34], dragon fruit skin [35], *Ficus caricabast* [36], mango seed kernel powder [37],wheat shells [38], neem leaf powder [39], rice husk [40], data pit [41], *Barleria cristata* Leaves [42], wool fiber and Cotton [43].The present investigation reports the results of removal of methylene blue dye from aqueous solution by adsorption onto activated carbon prepared from low cost walnut shell charcoal (WSC). The objective of the present work is to examine the effectiveness of the prepared WSC in removing MB from aqueous solution.

MATERIALS AND METHODS

Materials: The Walnut shells were collected from local area of Baramulla in Kashmir region. The walnut shells were extensively washed with tap water to remove dust, sprayed with distilled water and then dried in an oven at 130ºC. Then the adsorbent materials were burnt in the absence of free access of air to get its charcoal.These dried walnut shell charcoals were crushed in a mechanical crusher to a constant powder size, the charcoal of walnut shells (WSC) was sieved to different particles sizes. Then for further chemical modification with separate acid (0.1M H_2SO_4) and base (0.1M KOH)treatment and kept overnight at different intervals. The charcoal material obtained was washed thoroughly with distilled water to remove residual acid or base and the pH of carbon checked. The wet carbon materials were dried at 140°C for 10 h. The obtained activated carbon was preserved in a desiccator as adsorbent for further use.

A stock solution of 1000 mg L^{-1} of MB in figure 1 ((NICE Chemical) was prepared by dissolving an appropriate amount of a dye which was diluted to required concentration. Batch adsorption experiments were carried out to investigate the effect of pH, ionic strength, adsorbent dose, initial dye concentration and contact time on the adsorption of MB on WSC. The experiments were carried out in 150 mL conical flasks by mixing a pre-weighed amount of adsorbent with 40 mL of dye solution and the solution was agitated at 200 rpm on a stirrer at constant temperature and centrifuged (Remi

Research centrifuge). The dye concentration in supernatant solution was determined at characteristic wavelength (MB λ_{max}= 660 nm) by single beam UV–Visible Spectrophotometer (Systronics 2202).

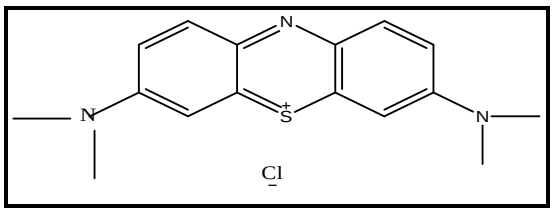


Figure 1. Structure of Methylene Blue.

Experimental solutions were prepared by pipetting a known amount of MB dye into a 1litre Erlenmeyer flask and diluting it with a known amount of distilled water. Batch experiments for decolorization were conducted in 500 mL conical flask containing 300 mL of dye solution at room temperature, to evaluate dye removal efficiency and capacity of the media. The media (waste residue) was placed in the flask and then stirred continuously at a constant slow mixing rate with magnetic stirrer during the experiment. The effect of dose of the media, contact time, system pH, Ionic strength and initial concentration of the dye were investigated by varying any one of the process parameters and keeping the other parameters constant. All the experiments were performed and the results were reported [**44**].

Fourier Transform Infrared Spectroscopy (FTIR) of the adsorbent (WSC) was done by using an FTIR spectrophotometer (Perkin Elmer FTIR Spectrophotometer, Model RZX). The spectra of FTIR in the range of 500-4000 cm^{-1} and with a resolution of 4 cm^{-1}. The resulting spectra data were explained in the discussion. The sample were also characterized through X-ray diffraction (XRD) and used to investigate the morphology structure of the sample. The XRD intensity ranges from 250-2700 cm^{-1} and 2 theta ranges.

The percentage removal of dye and amount of dye adsorbed on adsorbents (qe) was calculated by Eq.(1) and (2) respectively

$$\% \text{ removal}=100(Co-Ce/Co- \quad --1$$

$$qe =(Co-Ce)\ V\backslash M \quad --2$$

Where qe is the amount of dye adsorbed on adsorbent at equilibrium (mg g^{-1}), Co and Ce are the initial and equilibrium concentration (mg L^{-1}) of dye in solution, respectively, V is the volume of solution (L) and M is the mass of adsorbent (g).

RESULTS AND DISCUSSION

Characterization of ACWSC

FTIR (Perkin Elmer FTIR Spectrophotometer, Model RZX) spectroscopy: It is an important analytical technique that detects the vibration characteristics of chemical functional groups present on adsorbent surfaces. Besides porosity, adsorption behavior of WSC is also influenced by the chemical reactivity of the surface especially in the form of chemisorbed oxygen in various forms of functional groups. The ACWSC spectrum in figure 2 shows the surface functional group with the following peaks: a peak at 1703 cm^{-1}: C=O group (carbonyl group); 1503 cm^{-1}: C=C stretching group; 1446 cm^{-1}: C-H Bending.

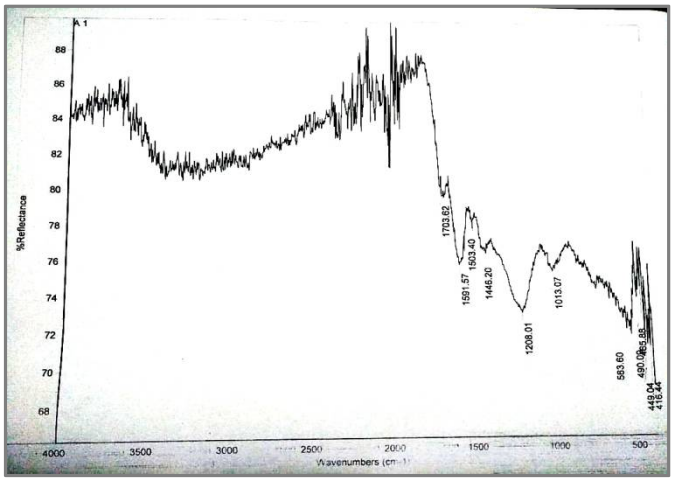


Figure 2. FTIR spectrum of ACWSC.

However, after the MB dye adsorption onto ACWSC in figure 3, the observation peaks are: a peak at 2933 cm^{-1}: could be assigned to stretching of C-H bond of methyl and methylene group; 2050 cm^{-1}:C-H Bending Aromatic compound overtone; 1699 cm^{-1}: C=O Stretching; 1593 cm^{-1}: N-H Bending amine; 1523 cm^{-1}: C=C Stretching Cyclic alkene; 1454 cm^{-1}: C-H Bending; 1200 cm^{-1}: C-N Stretching.

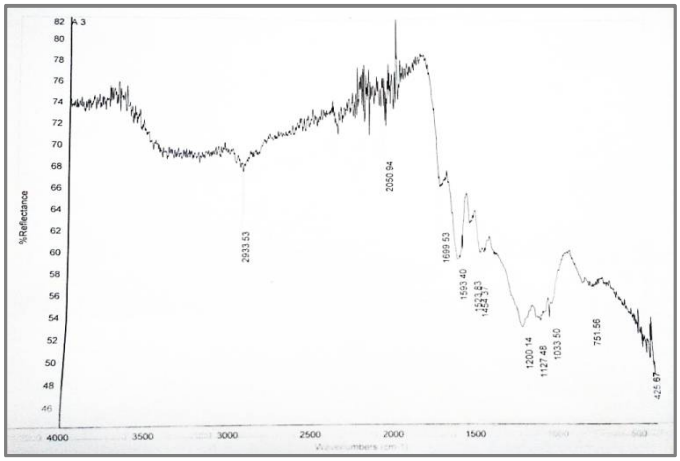


Figure 3. FTIR spectrum of loaded methylene blue on ACWSC.

XRD Analysis: The X-ray diffraction profiles shown in figure 4 exhibit sharp peaks and absence of broad peak revealed predominantly crystalline structure, which is an advantageous property for well-defined adsorbents. However, the occurrence of sharp peaks around 7˚, 13˚, 18˚, 21˚, 23˚ and 26˚ showed signs of formation of a crystalline carbonaceous structure, resulting in better layer alignment [**45, 46**]. The size of the crystallite Sharrer formula

$$D= K \lambda/\beta \cos\theta$$

Where the K is Sharpe factor, λ is the X-ray wavelength, β is the line broadening at the half maximum intensity (FMWH) in the radian, and θ is Bragg angle.

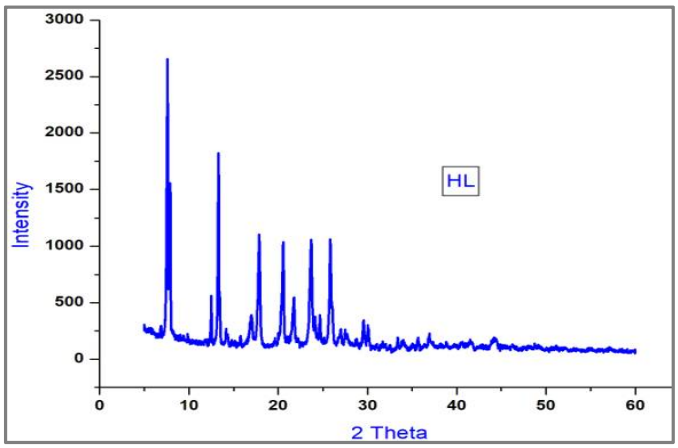


Figure 4. XRD spectrum of activated carbon walnut shell charcoal.

Effect of pH: The effect of pH on the removal of Methylene blue dye by walnut shell carbon was studied with the samples having adsorbate concentration 10 mg L^{-1}, temperature of the medium 37°C and adsorbent at the different pH values 2.0. 4.0, 6.0, 8.0 ,10.0 and 12.0. Dye adsorption was determined by fixing the other parameters constant. The hydrogen ion concentration primarily affects the degree of ionization of the dyes and the surface properties of the adsorbents. Figure 5 shows that the adsorption of the dye decreases with pH. It is apparent from the figure that the percentage removal of MB increases with increase in acidity and there is no significant increase in the dye removal while increasing the alkalinity. The removal of dyes from aqueous solution by adsorption is dependent on pH of the solution, which affects the surface charge of the adsorbent, degree of ionization, and speciation of the adsorbate. The initial pH of the aqueous solution plays an important role in the whole adsorption process and, particularly, on the adsorption capacity of adsorbent. The acidity of solution, influencing not only the surface charge of the adsorbent and the degree of ionization of the material present in the solution, but also the solution chemistry of adsorbent. Therefore, it is important to indicate the effect of pH on adsorption capacity of prepared charcoal adsorbent. The decrease in MB dyes adsorption on walnut shell carbon with increasing pH.

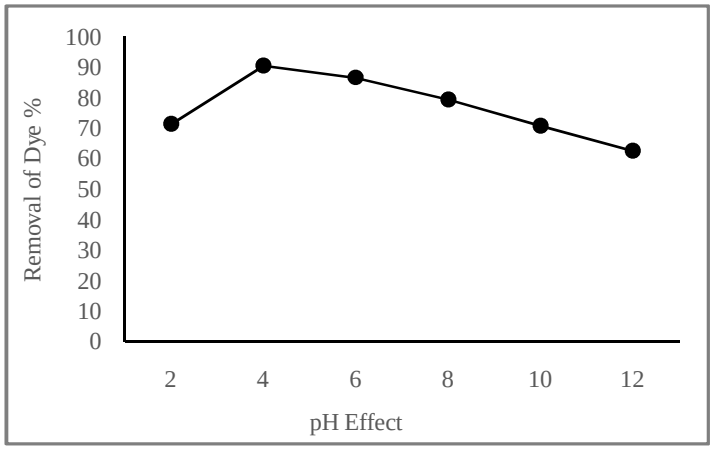


Figure 5. Effect of pH on adsorption of methylene blue.

Effect of Contact Time: The time dependent nature of the dye adsorption was examined by varying the contact time between methylene blue and low-cost activated carbons of the walnut shell carbon (ACWSC) in a duration of 10 to 60 min. The Dye concentration was kept as 10 mg L^{-1} while the amount of adsorbent added was 0.2g at room temperature. From experiment point of view indicated that the adsorption of the dye reached equilibrium in approximately 50 min. In figure 6 the removal of MB by adsorption increased with time and attained maximum value in 60 min and thereafter it

remained slightly constant for the studied. The maximum percentage removal of MB observed in 60 min was 92.7 by WSC. The Increase in removal efficiency with an increase in time of contact is due to the fact that more time becomes available for the adsorbate to coordinate with the adsorbent. Initial removal occurs immediately, as soon as the dye and charcoal come into contact. However, after that, when some of the easily available active sites become unavailable, the dye needs time to find more active sites for binding. It is concluded that MB and charcoal should be in contact for at least 30-60 min for good adsorption. Our results are conformity with the results of several authors [**47-49**]

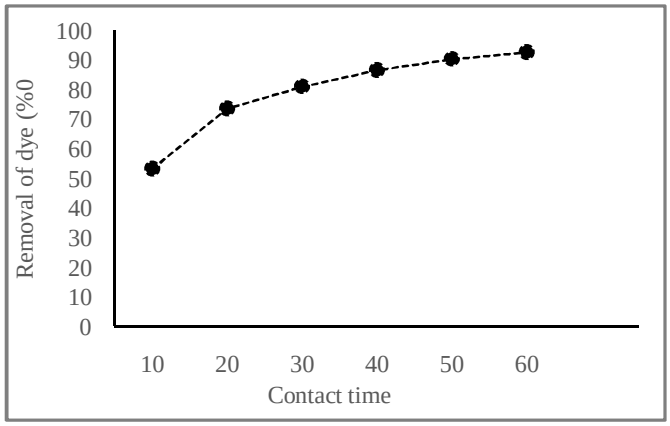


Figure 6. Effect of contact time on adsorption of methylene blue.

Effect of Adsorbent Dose: The dye removal capacity plotted as a function of adsorbent dosage is shown in figure 7. The percentage removal of dye increased with the increase in adsorbent dose of all the selected low-cost materials of Walnut shell carbon (WSC) and reached a constant value after a particular dosage for the dyes studied. The maximum percentage removal of 92.8 is obtained for adsorbent, by keeping all other parameters constant. The increase in adsorption of dyes with adsorbent WSC dosage is due to the availability of more surface area or sites of the adsorbent, WSC for adsorption. When adsorbent dose is low, surface active sites are readily accessible by dye molecules leading to higher adsorption capacity. On the other hand, an increase in adsorbent dose increases the number of active sites. Hence more number of dye molecules can be adsorbed into available surface-active sites of the adsorbent. Therefore, a higher adsorbent dosage increases adsorption capacity.

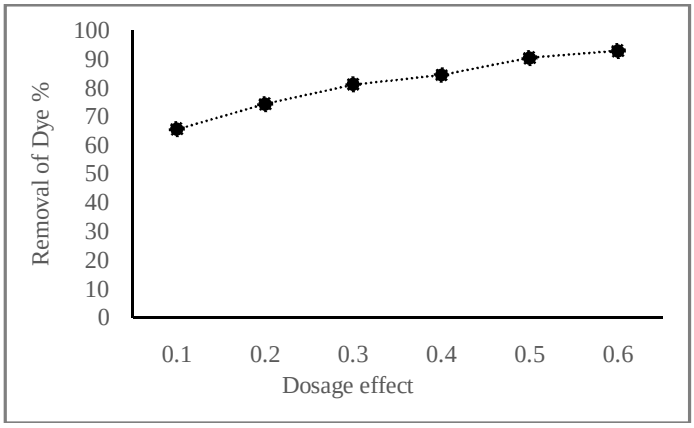


Figure 7. Effect of dosage on adsorption of methylene blue.

Effect of Initial Dye Concentration: The effect of concentration of MB on the adsorbent WSC was studied at constant contact time, adsorbent dosage, and pH. The initial MB concentrations were taken as 2, 4, 6, 8, 10 and 12 mg L^{-1} with adsorbent dosage of 0.2 g for contact time of 20 min. The percentage removal of MB gets increased gradually with the increase in dye concentration. This is due

to increase in the driving force of the concentration gradient with an increase in the initial dye concentration. At lower MB concentration, fractional adsorption (the ratio between the numbers of dye molecules to the number of available actives sites) is low and adsorption is independent of initial dye concentration. On the other hand, the number of dye molecules is higher when concentration is increased. This results to a higher fractional adsorption ratio, hence an increase in adsorption. Generally, the initial MB concentration provides an important initial driving force to overcome all the mass transfer resistance between the aqueous and solid surfaces. Hence, a higher initial MB dye concentration enhances the sorption process.

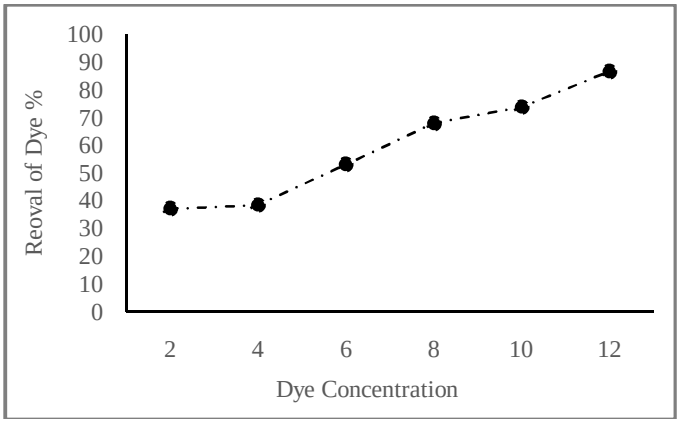


Figure 8. Effect of dye concentration on adsorption of methylene blue.

Effect of ionic strength: The Various salt and ions exist in the dye containing waste water. The presence of ions leads to high ionic strength, which may significantly affect the performance of the adsorption process. In figure 9 showed that the salt (KCl) existing in the solution affected the MB adsorption onto WSC. It was seen that the adsorption amount of dye decreased respectively, as the salt concentrations increased from 0.1 to 0.6 mol L^{-1}. This could be attributed to the competitive effect between dye cations and K^+ ions for the available adsorption sites. As the ionic strength increased, the activity of MB with the active sites for adsorption decreased, therefore, the adsorption amount of MB shows continuously decreased with higher concentration of salt [**51**].

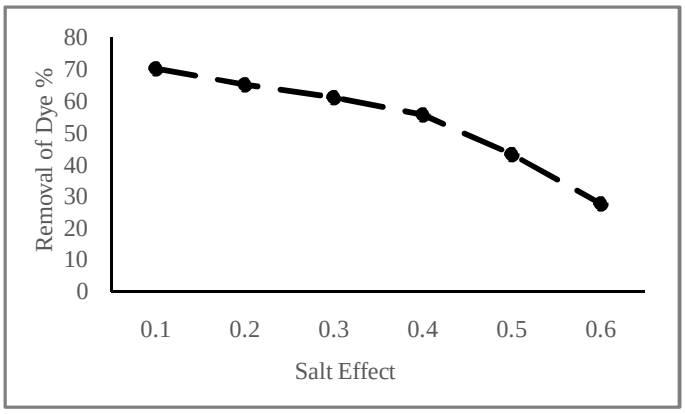


Figure 9. Effect of salt concentration on adsorption of methylene blue.

APPLICATION

This is an efficient and eco-friendly method for the removal of methylene blue dye from test samples. Adsorbent used in this method is easily available and economically efficient. This method can be applied for waste water alleviation technologies for removal of heavy metal ions and toxic effluents.

CONCLUSION

From the results of the study it can be concluded that ACWSC could be effectively used for the removal of MB from aqueous solutions. The amount of MB adsorbed per unit mass of ACWSC was found to increase with increase in Dye concentration, contact time and adsorbent dosages. Removal of MB dye is pH dependent and the maximum removal was attained at pH 2.

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