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Adsorptive Removal of Lanaset Green Dye onto Activated Carbon Prepared from Walnut (*Jaglans regia*) Shell

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ABSTRACT: Activated carbon prepared from Walnut (*Jaglans regia*) shell by chemical activation with zinc chloride was investigated for the adsorption of Lanaset Green Dye from aqueous solutions. The activated carbon sample prepared at carbonization temperature 400ºC was analyzed by Chemical methods such as Iodine number and Methylene blue number to identify micropore and mesopore content. The activated carbon was further analyzed by instrumental techniques like XRD and SEM. The SEM of the activated carbon indicates the pores of different diameters whereas XRD profile exhibited two broad diffraction peaks indicating the amorphous nature of the activated carbon. The adsorption of the dye has been investigated by batch adsorption studies. The effect of parameters like pH, contact time and adsorbent dose for the adsorption process have been evaluated and found to be 2, 180 minutes and 2g/L respectively. The obtained results revealed that the activated carbon prepared from Walnut Shell can be considered as a potential adsorbent for removal of the dye from aqueous solutions.

KEYWORDS: Lanaset Green Dye, Activated carbon, Walnut Shell, Chemical activation

I. INTRODUCTION

Rapid industrialization and urbanization have caused global increase in water pollution. Dyes are one of the water pollutants of greatest environmental concern [1]. The wide use of dyes in industries such as textiles, rubber, plastics, printing, leather, cosmetics, etc., to color their products, generate a considerable amount of colored wastewater. Severe problems to the aquatic life, food web and causes damage to the aesthetic nature of the environment have been caused by the discharge of dye-containing wastewater into natural streams and rivers. Dyes in very small amounts in water even less than 1ppm for some dyes is highly visible and undesirable. The remediation of color from waste water is a major environmental problem and they are the first contaminant to be recognized in water [2]. The removal of dyes from industrial effluents on a continuous industrial scale has been given much attention in the last few years, not only because of its potential toxicity, but also mainly due to the problem of visibility. Many treatment technologies have been applied for remediation of dye from wastewater such as adsorption, oxidation, nano-filtration, chemical precipitation, ion-exchange, reverse osmosis, electrochemical degradation, ultra-filtration etc. Except adsorption most of these methods have some drawbacks such as high operation cost, capital and the disposal of the residual metal sludge which are not suitable for small-scale industries. Amongthe treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent.Some of the advantages of adsorption process are possible regeneration at low cost, availability of known process equipment, sludge-free operation and recovery of the adsorbate.

Because of extended surface area, micro-pore structures, high adsorption capacity and high degree of surface reactivity, activated carbon is the most widely used adsorbent for dye removal. However, commercially available activated carbon is very expensive and has high regeneration cost while being exhausted. Furthermore, generation using solution produces a small additional effluent while regeneration by refractory technique results in a 10–15 % loss of adsorbent and its uptake capacity. This has led to search for cheaper substances for the preparation of adsorbents. Many agricultural waste materials such as peach stone [3], date stone [4], water hyacinth [5], corn stalk [6], coconut shell [7], Miswak leaves [8], Elaeagnus stone [9] etc. have been utilized for the preparation of activated carbon for remediation of different dyes from aqueous solutions. The Lanaset Green dye has been applied for dyeing wool, polyamide and silk. The molecular formula of the dye is **$C_{38}H_{24}N_2Na_2O_{10}S_2$**. Due to the presence of anionic solubilizing group in dye molecule, it is soluble in aqueous liquor. The molecular structure of the dye is shown in Fig. 1.The present study deals with the activated carbon prepared from Walnut shell as shown in Fig.2 for the removal of Lanaset Green dye. Walnut shells have been left as waste materials after using walnuts as shown in Fig.3

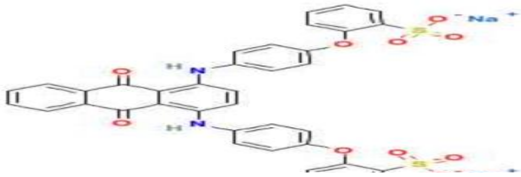


Figure 1 Structure of Lanaset Green Dye

Figure 2 Walnut shells

Figure 3 Walnuts

II. EXPERIMENTAL

Materials: The precursor used in this study is Walnut shell. The precursor was washed with tap water and then with distilled water. The precursor was crushed and sieved to a size range of 300 μm and was mixed with zinc chloride in the ratio of 1:1. The mixture was dried in an oven at 110 º C. The dried Walnut shell particles were carbonized under high purity nitrogen flow of 75 ml min^{-1}at 400 º C in tubular furnace and kept at this temperature for three hours. The prepared activated carbon was then cooled at room temperature and washed with dil. HCl and then with warm distilled water until the pH of the washing reached 7.

Chemicals and Equipment: The chemicals and reagents used are of analytical grade (Merck and Qualigens Company). Stock solutions of Lanaset Green dye were prepared from the dye in distilled water. To adjust pH of solutions Digital pH meter was used. The adsorption experiments were carried out by using Shaker (Digital VDRL Rotator RPM-S). The concentration of Lanaset Green Dye after adsorption onto activated carbon was determined byUV –Visible Spectrophotometer.

Adsorption Experiments: To investigate the adsorption experiments Batch mode of adsorption has been used. The adsorption studies were carried out by using adsorbents in 50 mL stopper conical flask at optimum pH value, contact time and adsorbent dosage level. The flasks were then stirred well on Digital VDRL Rotator-RPM-S at 225 rpm. The experiment was carried by using 0.05 g of adsorbent in 25 ml adsorbate solution taken in the conical flasks under optimum conditions set out for the experiment. The amount of the adsorbed was determined by UV-Visible Spectrophotometer.

The amount of the dye (II) adsorbed can determined by the following equation [10].

$$q_e = \frac{(C_o - C_e)}{W} \times V \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where $q_e$is the amount of the dye adsorbed
C_O and C_e are the initial and equilibrium concentrations of the dye in mg L^{-1} respectively,
V is the volume of the solution in Liter; W is the mass of adsorbent in gram
The removal of the dye in percentage (Rem %) can be calculated by the following formula [11].

$$(\text{Rem } \%) = \frac{(C_o - C_e) \times 100}{C_o} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Methylene blue number and Iodine number: Methylene blue number and Iodine number have been determined to find amount of micropore and mesopore content in activated carbon. Methylene blue number is the amount of the dye adsorbed by one gram of the adsorbent while the iodine number indicates the amount of iodine adsorbed per gram of activated carbon at an equilibrium concentration. Methylene blue number can be calculated by the following formula [12].

$$MB_N \left(\frac{mg}{g}\right) = \frac{(C_o - C_e) \times 100}{M} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where C_o and C_e are initial and equilibrium concentration of MB (mg / L) respectively,
M is the mass of adsorbent in gram and V is the volume of the solution in liter.
Iodine number can be calculated by the equation as follows [13].

Figure 2Walnut shells

$$\text{Iodine number}\left(\frac{mg}{g}\right)=\frac{\text{Amount of iodine adsorbed in mg by the carbon}}{\text{Weight of the carbon in gram}}\ \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

III. RESULTS AND DISCUSSION

Effect of pH: Fig. 4 demonstrates the effect of solution pH on adsorption of the dye onto activated carbon. The adsorption of the dye was studied from pH 2 to 9. The percentage of removal of the dye was observed highest at pH 2 and then decreased with the rise in pH value. When the pH of solution is increased, the amount of negatively charged sites tends to increase while the amount of positively charged sites tends to decrease. A negatively charged surface site on the adsorbent does not favor the adsorption of the dye due to electrostatic repulsion.

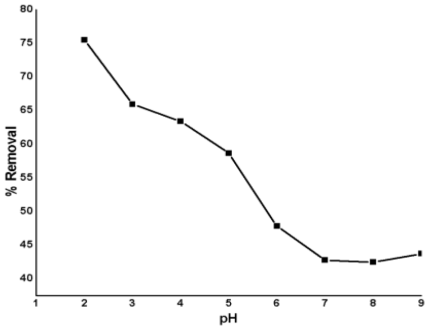


Figure 4 Effect of pH

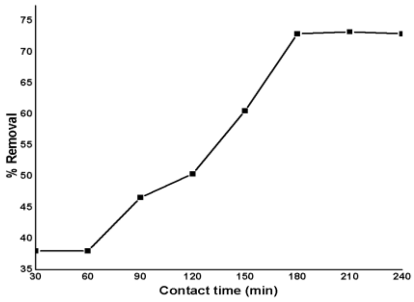
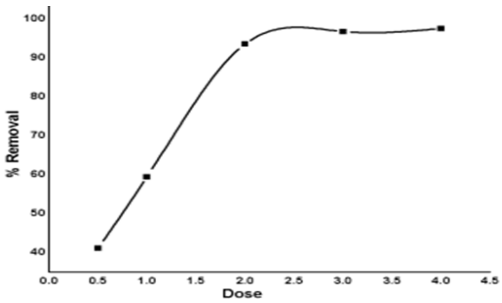
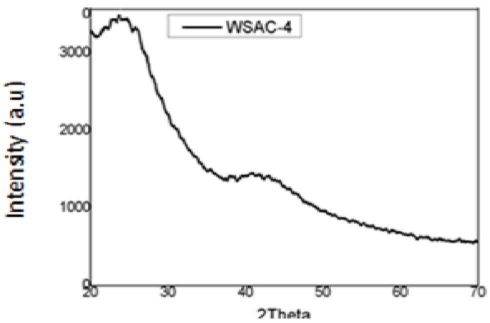


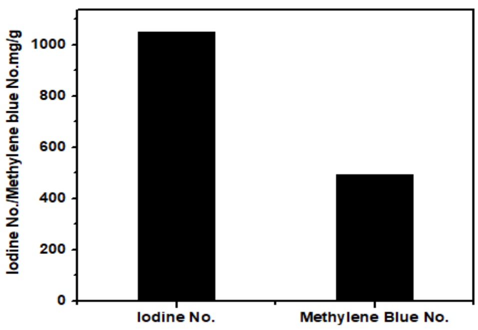
Figure 5 Effect of contact time

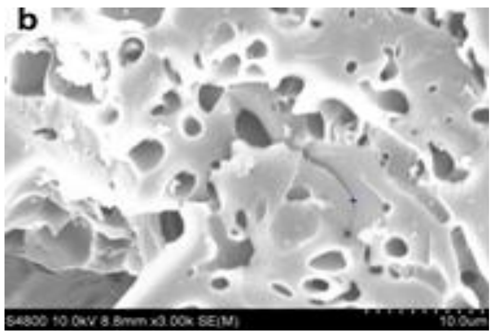
Effect of Contact time: The percentage removal of the dye onto the activated carbon against time is presented in Fig.5. The removal the dye in percentage increases with time and attains a maximum value at 180 minutes. The fast adsorption at initial stage may be due to the higher driving force owing to the availability of the large concentration of active sites for adsorption. At equilibrium all the active sites will be covered by the dye and no further adsorption takes place.





Effect of Adsorbent dosage: The percentage removal of the dye is affected by adsorbent dose. The effect of adsorbent dosage on the percentage removal of the dye is presented in Fig 6. The percentage removal of the dye increased from 0.5 to 2g/L and then remained almost constant. This may be due to the availability of more adsorption sites because of increase in adsorbent dosage. Adsorbent dosage of 2 g/ L has been observed as optimum contact time for effective adsorption of the dye from the aqueous solutions.





XRD (X-ray diffraction): Two broad diffraction peaks located near at 2θ = 25.5 º and 43º reflected from 002 and 001 planes have been revealed by XRD analysis of the activated as shown in Fig.7. The two broad diffraction peaks indicate the amorphous nature of the activated. The amorphous nature of the activated carbon increases surface area which is the important part for the adsorption process.

Methylene blue number (MB_N) and Iodine number (I_N): The chemical methods like Methylene blue number and Iodine blue number have been determined to find the mesopores and micropore content in the Activated carbon and are presented in Fig. 8. Methylene blue and iodine numbers are found to be 499.54 mg/g and 1053.44 mg/g respectively.The measurement of iodine number can be used to roughly estimate the surface area of activated carbon

SEM (Scanning Electron Microscope):SEM image of activated carbon as shown in Fig.9 exhibits the pores with different diameters. The formation of pores in the activated carbon may be caused by the dehydrating action of zinc chloride. Owing to the dehydrating action it removes oxygen and hydrogen from the precursor as water and pores are formed.

IV. CONCLUSION

This study demonstrates that activated carbon prepared from Walnut shells by chemical activation with zinc chloride can be potentially used as an adsorbent for the removal of Lanaset Green dye from aqueous solutions. The various parameters affecting adsorption like pH, contact time and adsorbent dose were examined to evaluate the adsorption of the dye onto the adsorbent. The results exhibited that the optimum pH, contact time and adsorbent dosage for the adsorption of the dye have been found to be 2, 180 minutes and 2 g / L respectively. SEM of activated carbon exhibits the pores of different diameters. XRD analysis indicates two broad diffraction peaks located near at $2\theta = 25.5^{o}$ and 43^{o} reflected from 002 and 100 planes. Methylene blue number and Iodine number are found to be 499.54 mg/g and 1053.44 mg/g respectively.

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