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## RESEARCH ARTICLE

### ADSORPTION OF DYES (METHYLENE BLUE, MALACHITE GREEN, METHYL VIOLET) ON ACTIVATED CARBON

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#### ABSTRACT

The objective of this work is the study of adsorption behaviours of three dye solution (methylene blue, methyl violet & malachite green) using commercial activated carbon prepared from copper pod. Removal of these three dyes from aqueous solution using commercial activated carbon has been investigated through batch experiment. Batch adsorption studies were carried out by observing the effect of contact time, adsorbent dosage, pH and temperature. The results obtained shows that copper pod could be employed as a low cost material for the removal of dyes and colour from aqueous solution.

## INTRODUCTION

In textile industry, various types of dyes are used to colour their products (Ranganathan, 2007). The dye containing wastewater is directly discharged into nearby water bodies. Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries (Mondal, 2008 and Shaobin Wang, 2007). Colour stuff discharged from these industries poses certain hazards and environmental problems. These coloured compounds in water system reduce sunlight penetration and affecting photosynthesis in aquatic ecosystem (Hameed, 2006 and Grag, 2003). It is difficult to remove dyes from wastewater because dyes are not easily degradable. The physical, chemical and biological processes are used for removing dyes from wastewater (Filipkowska, 2002; Mittal, 2013). These processes are very costly and cannot effectively be used to treat dyes from wastewater. The adsorption process is an effective and low-cost method for removing dyes from wastewater.

#### Experimental work

## MATERIALS AND METHODS

**Adsorbent:** Copper pod activated carbon, is used as adsorbent for dye removal.

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The copper pod fruit was first peeled off to obtain the outer skin of the fruit and then removal of the inner fleshy layer. The peel was washed with ordinary tap water to remove any dirt and sands. The washed material was sun dried for 2- 3 days to evaporate the moisture present in it. The dried materials were carbonized with 1:1 Sulphuric acid. The charred material was filtered and washed with excess of water to remove residual acid from pores of the carbon particles. The filtered material was kept in muffle furnace at 600 °C for 30 minutes. The carbonized material was ground to fine powder and then sieved with a particle size of 53  $\mu\text{m}$ . The sieved adsorbent was kept in an airtight container for further adsorption studies.

#### Preparation of adsorbate

In the present study three dyes (methylene blue, methyl violet & malachite green) are used for the adsorption. A stock solution of 1000mg/L of methylene blue, methyl violet & malachite green was prepared by dissolving an appropriate amount of each dye which was diluted to required concentration. The working solutions were prepared by diluting the stock solution with distilled water to get the appropriate concentration of the working solutions. The concentration of the residual dye solution was measured using UV/Visible spectrometer at a  $\lambda_{\text{max}}$  value of 663nm for methylene blue, 617nm for malachite green and 590nm for methyl violet.

## Adsorption Studies

**Effect of contact time:** 50 ml of dye solution with different dye concentration (10, 20, 30, 40 & 50mg/L) is to be prepared in a different 250 ml conical flask with adsorbent concentration (0.1g/50ml). The conical flasks were well corked and agitated in a shaker. Dye concentration to be estimated at the wavelength corresponding to maximum absorbance,  $\lambda_{max}$ , using a spectrophotometer. The samples to be withdrawn from the orbital shaker at predetermined time intervals and then the absorbance of the solution is measured. The final dye concentration is to be measured after different time intervals (10 - 100mins) until equilibrium reaches.

**Effect of initial pH:** 50ml of dye solution was prepared in a different conical flask with different dye concentration (10, 20, 30, 40 & 50mg/L) and adsorbent concentration (0.1g/50ml) and initial pH of the conical flask solution is to be measured. The pH of the dye solution was controlled using 0.1M HCl or 0.1M NaOH by using a pH meter. The pH of dye solution was changed from 2 to 12. The final dye concentration was measured using UV spectrophotometer.

**Effect of adsorbent dose:** 50ml of dye solution was prepared in a different conical flasks with different dye concentration (10, 20, 30, 40 & 50mg/L) and different adsorbent dosage of 0.1 – 1g. The conical flasks were well corked and agitated in a shaker for 60 minutes. The final dye concentration readings were measured after agitation.

**Effect of temperature:** 50 ml of dye solution was prepared in conical flask with dye concentration (40mg/L) and adsorbent dose (0.1g/50ml) and different temperatures of 30, 40, 45,50,55,60 °C for 60 minutes.

### Scanning Electron micrograph study

The Scanning Electron Microscopic (SEM) image is used to investigate the nature and surface characteristics of the prepared activated carbon. The Scanning electron micrograph of the adsorbent was obtained using JOEL/EO 1.1 Model: JSM 5610 Scanning Electron Microscope. The image was measured before the adsorption of dye on the adsorbent.

### X-Ray diffraction (XRD) Measurement

X-ray diffraction patterns were recorded using Panalytical X'Pert Powder X'Celerator diffractometer. This instrument was equipped at a voltage of 30 kV and a current of 30 mA with a Cu K $\alpha$  radiation and scanning range of  $2\theta$  configuration. This XRD pattern was analysed to investigate the crystallographic structural changes during adsorption processes.

## RESULTS AND DISCUSSION

### Adsorption studies

**Effect of contact time:** The effect of contact time on dye removal can be seen from Figure 1 to 3 for the dyes. The result indicates that the extent of dye removal was rapid in the initial stages of contact time and becomes slow in later stages of contact time till the equilibrium was attained. After that there is no significant change in the extent of adsorption

(Namasivayam, 2002). This shows that adsorption of dyes reaching the equilibrium within 60 minutes.

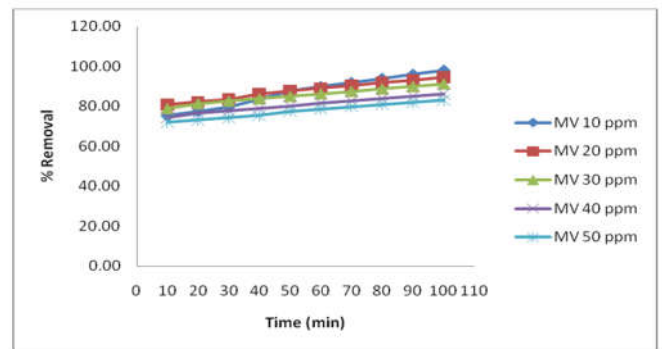


Fig 1. Effect of contact Time on Methyl Violet adsorption on Activated carbon (initial dye concentration – (10 – 50) mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

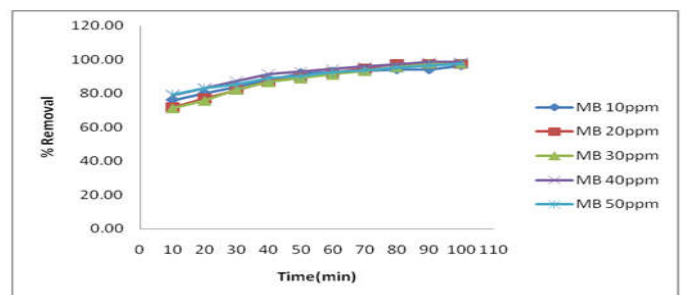


Fig. 2. Effect of contact Time on Methylene Blue adsorption on Activated carbon (initial dye concentration – (10 – 50) mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

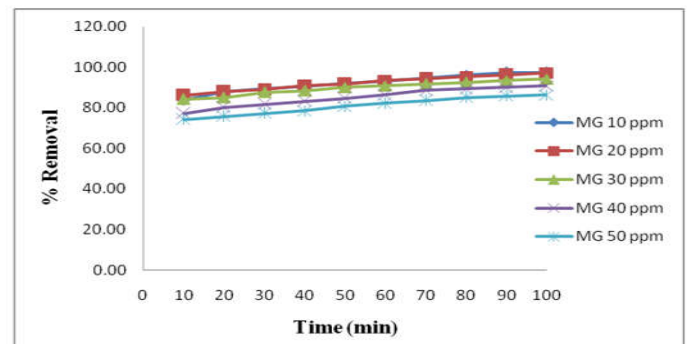


Fig. 3. Effect of contact Time on Malachite Green adsorption on Activated carbon (initial dye concentration – (10 – 50) mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

### Effect of initial pH of the solution

The effects of initial pH on dye solution of three dyes removal was illustrated in figure 4 to 6. When the pH of dye solution increased from 2 to 12, the adsorption of dye also increased. It was seen that adsorption found to increase with increase in pH of dye solution upto 7 and decreased with further increasing in pH of dye solution. The dye molecules are positively charged at low pH. There was attraction between dye molecules and activated carbon decreased, resulting in the formation of decreasing of dye removal. The low dye removal (at high pH) was due to the strong repulsion interaction between the negatively charged adsorbent and deprotonated dye molecules. The result showed that availability of negatively charged groups at the activated carbon surface are necessary for the

adsorption of basic dyes to proceed (Mittal, 2013; Emad, 2006).

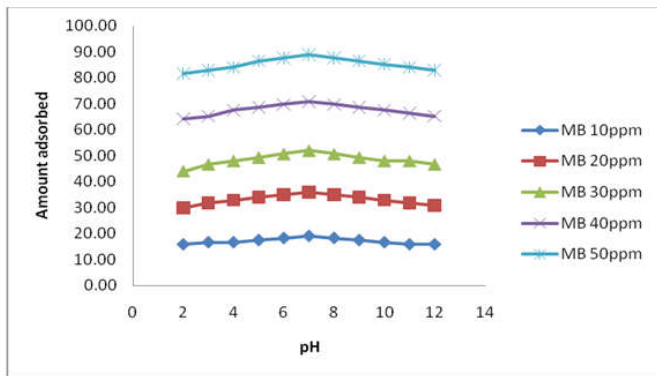


Fig. 4. Effect of Initial pH on Methylene Blue adsorption on Activated carbon (Temperature – room temperature, speed-120 rpm) and adsorbent dosage-100mg/50ml)

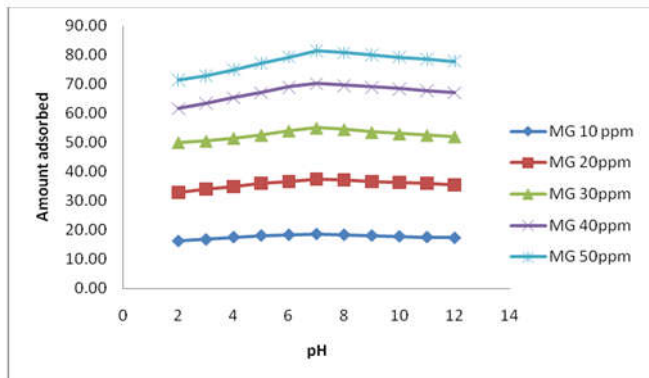


Fig. 5. Effect of Initial pH on Malaghte Green adsorption on Activated carbon (Temperature – room temperature, speed-120 rpm) and adsorbent dosage-100mg/50ml)

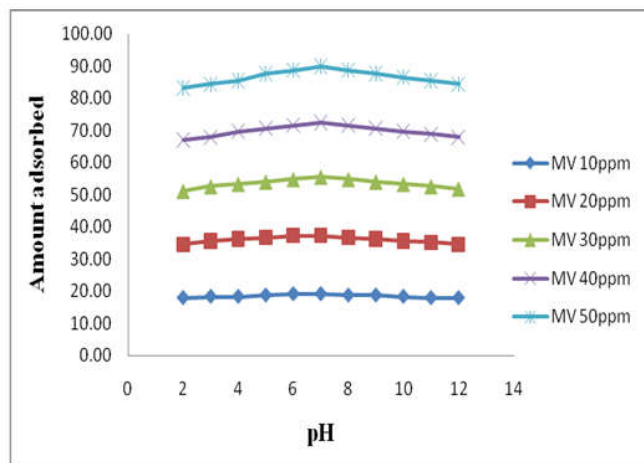


Fig 6. Effect of Initial pH on Methyl violet adsorption on Activated carbon (Temperature – room temperature, speed-120 rpm) and adsorbent dosage-100mg/50ml)

**Effect of adsorbent dosage**

The effects of adsorbent dosage on dye solution of three dyes removal was shown in figure 7 to 9. The result shows that the percentage of dye removal increased with increase in adsorbent dosage. This is due to the increase in surface area and availability of more binding sites of the adsorbent (Hema, 2009 and Indra Deo Mall, 2005).

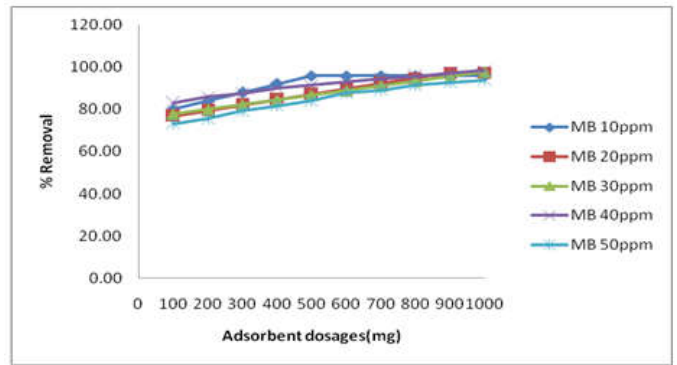


Fig. 7. Effect of adsorbent dosage on Methylene Blue adsorption on Activated carbon (Temperature – room temperature, pH-solution pH, speed-120 rpm)

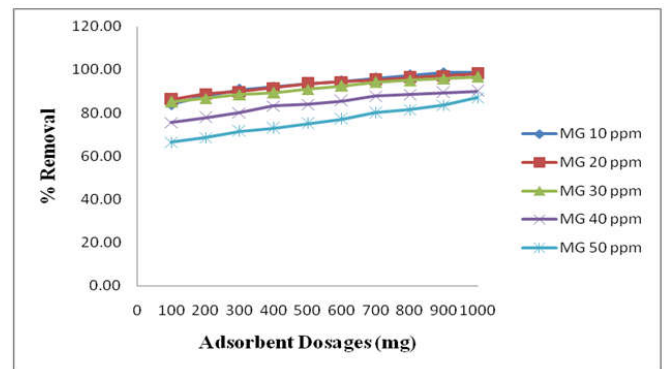


Fig. 8. Effect of adsorbent dosage on Malaghte Green adsorption on Activated carbon (Temperature – room temperature, pH-solution pH, speed-120 rpm)

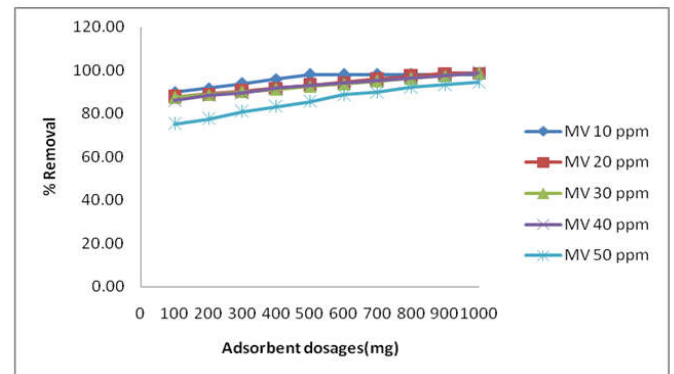
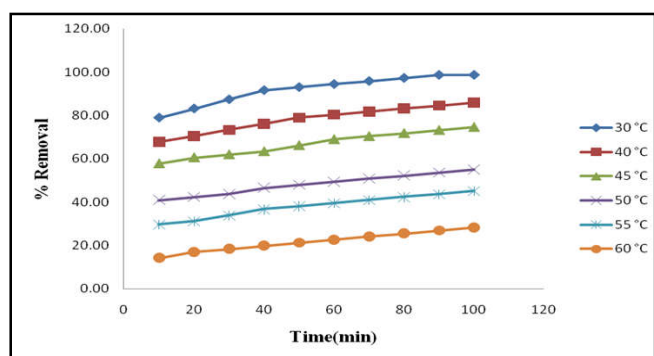


Fig. 9. Effect of adsorbent dosage on Methyl violet adsorption on Activated carbon (Temperature – room temperature, pH-solution pH, speed-120 rpm)

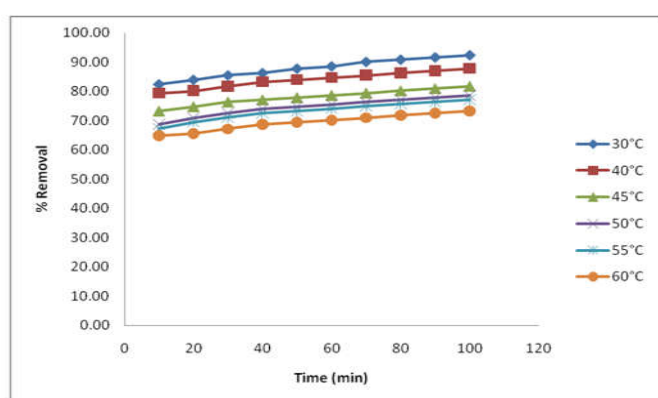
**Effect of Temperature**

The effect of temperature on adsorption of dye solution with initial concentration of 40mg/ L at different temperatures of 40°, 45°, 50°, 55° and 60°C has been determined. The percentage of three dyes (methylene blue, malachite green and methyl violet) removed at different temperature has been shown in Figure 10 to 12. In the present investigations it was observed that the adsorption capacity of activated carbon for the three dyes (methylene blue, malachite green and methyl violet) decreased with temperature. This is due to higher temperature may decrease the adsorptive forces between the dye molecules and the active sites of the adsorbent surface [13, 14, 15]. The optimum temperature at which maximum dye removal was 30° C. The result also indicates that the

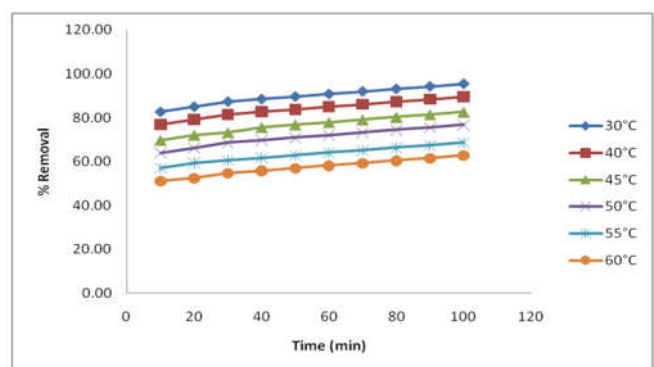
adsorption process is an exothermic in nature when temperature was increased from 30°C to 60°C and initial dye concentration of 40mg/lit.



**Fig. 10.** Effect of Temperature on Methylene Blue adsorption on Activated carbon (initial dye concentration - 40 mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)



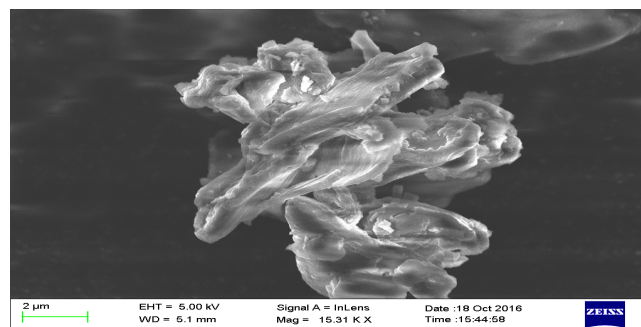
**Fig. 11.** Effect of Temperature on Malachite green adsorption on Activated carbon (initial dye concentration - 40 mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)



**Fig.12.** Effect of Temperature on Methyl violet adsorption on Activated carbon (initial dye concentration - 40 mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

### Scanning electron micrograph study

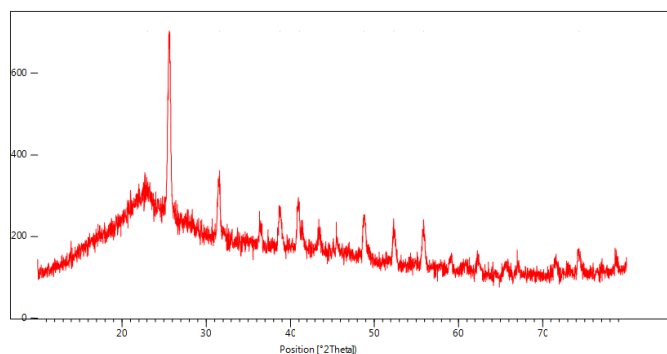
The surface morphology of the adsorbents sample was analysed using Scanning Electron Microscopy. Figure.13. shows SEM image of the adsorbents. This image observed that pores of different size and shape of the adsorbents. The number of pores developed on the adsorbent is used for adsorption (Yamin Yasin and Grabowska Ewa Lorenc, 2007). This image also shows a clear view of the grains of the materials used as an adsorbent in this study.



**Fig. 13.** SEM image of the activated carbon

### X-Ray Diffraction (XRD) Measurement

The powder X-ray diffraction analysis of sample AC-H<sub>2</sub>SO<sub>4</sub> investigated and displayed in Figure.14. In activated carbons, a broad peak due to reflections from the planes can be clearly seen. The broadness of the peak indicates the amorphous nature of the carbon sample (Bulut, 2006; Nagarethinam Kannan, 2001 and Rahman, 2005).



**Fig. 14.** XRD pattern for prepared activated carbon

### Conclusion

The removal of dyes (methylene blue, malachite green and methyl violet) from aqueous solutions by adsorption with activated carbon prepared from copper pod has been experimentally determined and the following observations are made:

- The percentage of colour removed increase with increasing adsorbent dosage, contact time, temperature and varied with dye solution pH.
- The adsorption studies revealed that the Optimum contact time required for equilibrium to be achieved was found to be nearly 100 minutes.
- From the experimental results it was observed that the Optimum adsorbent dose for the dye is 1g/100ml. The percentage of colour removal increased with increasing adsorbent dose. This is due to increase in surface area and the number of free active sites of the adsorbent.
- The percentage of colour removal of dyes (methylene blue, malachite green and methyl violet) increased with increasing pH from 2 to 7. Maximum adsorption was found to be pH = 7.
- The adsorption capacity of activated carbon for the three dyes (methylene blue, malachite green and methyl violet) increased with decreasing temperature from 30 to 60°C and initial dye concentration of 40mg/L which indicates that the adsorption process is exothermic in

nature. Optimum temperature was found to be 30°C for the removal of MB, MG and MV by copper pod. Finally it is concluded that, the present adsorbent could be a good alternative for the removal MB, MG and MV from aqueous solution and is inexpensive material.

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