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Removal of dyes (methylene blue, malachite green, methyl violet) from aqueous solution by waste materials of copper pod flower

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Abstract : In the present study adsorption capacity of copper pod flower was explored for the removal of methylene blue, malachite green and methyl violet dye from aqueous solution. The experiments were carried out in a batch system to optimize various parameters such as initial dye concentration, contact time, adsorbent dosages, pH and temperature. The obtained results confirmed the applicability of this copper pod flower as an efficient and low cost biosorbent for cationic dyes from aqueous solution.
Key words : Copper pod flower, Methylene blue, Malachite green & Methyl violet, Adsorption.

1. Introduction

Many dyes are used extensively in industrial products such as paper, plastics, textile, rubber and cosmetics [1]. Dyes are considered as hazardous pollutant because of their toxicity even at low concentration. Removal of these toxic dyes from wastewater is important for environmental pollution control [2]. Industrial wastes are the major sources of various kinds of dye pollution for the natural water bodies. These dyes enter into the natural water bodies through the wastewater discharge from tanning and dye manufacturing [3, 4]. Industrial waste water are mostly loaded with dyes that are not biodegradable and leads to accumulate into aquatic organism. Most commercial dyes are chemically stable and are difficult to be removed from wastewater [5, 6]. In order to decrease the content of dyes in the environment, it is necessary to treat wastewater before its discharge. Various treatment methods used to remove the dyes from the industrial wastewater include reverse osmosis, chemical precipitation, electrodialysis, membrane filtration and ion exchange etc., Various researchers used plant material as adsorbents includes tea waste, cotton waste, coconut husk, rice hull and plant biomass [7, 8]. The effluents from textile industries are important sources of dye pollution. Among these methods, adsorption is a widely used for dye removal from wastewater. Activated carbon is the most common adsorbent for the removal of dyes from wastewater. This study was performed to utilize the copper pod flower as a low cost adsorbent with respect to various parameters such as different adsorbent dosages, contact time and pH.

2. Experimental work

2.1 Materials and methods

2.1.1 Adsorbent

The present studies Copper Pod flowers were used as adsorbent for the removal malachite green dye from aqueous solution. They were collected from in around PSG College of Arts and Science, Coimbatore District, Tamilnadu, India which were available in abundant.

The copper pod flowers were washed thoroughly with ordinary tap water to remove any dust and twice with distilled water. The washed materials were dried in sun light to evaporate the moisture present in it. The dried material was ground to fine powder and then sieved with a particle size of 53μm. The sieved adsorbent sample prepared was kept in an airtight container and used for further adsorption studies.

2.1.2 Preparation of adsorbate

Three dyes (methylene blue, methyl violet & malachite green) were used in this study for the adsorption. 1000mg/L stock solution of methylene blue, methyl violet & malachite green was prepared by dissolving the required amount of dye in double distilled water. The working solutions of the desired concentrations were obtained by successive dilutions. The concentration of the residual dye solution was measured using UV/Visible spectrometer at a λ_{max} value of 663nm for methylene blue, 617nm for malaghite green and 590nm for methyl violet.

2.2 Adsorption Studies

2.2.1 Effect of contact time

The effect of contact time on adsorption was studied at concentration ranging from 10 to 50 $mg.L^{-1}$ in case of methylene blue, methyl violet & malachite green at different time intervals of 10 to 100 miniutes. The conical flasks were well corked and the mixture was constantly shaken in a rotary shaker. Dye concentration to be estimated at the wavelength corresponding to maximum absorbance, λ_{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.

2.2.2 Effect of initial pH

The effect of pH on the adsorption was investigated at a pH ranging from 2 to 10 in the presence of different initial dye concentrations of 10 to 50 $mg.L^{-1}$. The pH of the dye solution was controlled by the addition of 0.1M HCl or 0.1M NaOH by using a pH meter. The final dye concentration was measured using UV spectrophotometer.

2.2.3 Effect of adsorbent dose

The effect of adsorbent dosage on adsorption was investigated at different dye concentration ranging from 10 to 50 $mg.L^{-1}$ and different adsorbent dosage of 0.1 – 1g. The conical flasks were well corked and the mixture was constantly shaken in a shaker for 60 minutes. The final dye concentration readings were measured after agitation.

2.2.4 Effect of temperature

The effect of temperature was investigated with dye concentration of 40 $mg.L^{-1}$in case of methylene blue, malachite green and methyl violet and adsorbent dose (0.1g/50ml) and at different temperatures of 30, 40, 45,50,55,60 ^{0}C for 60 minutes at a constant stirring speed.

3. Results and discussion

3.1 Adsorption studies

3.1.2 Effect of contact time

Three dyes were taken in separate conical flasks and treated with 1.0g adsorbent dosage. The percentage removal of dyes with time has been shown in figure 1 to 3. It was observed that the removal of methylene blue are 44 to 96% in 10ppm, 58 to 97% in 20ppm, 48 to 93% in 30ppm, 61 to 91% in 40ppm, 63 to 87% in 50ppm. It also shows that the percentage removal of malachite green and methyl violet are 68 to 84% in 10ppm, 75 to 89% in 20ppm, 76 to 90% in 30ppm, 76 to 90% in 40ppm, 73 to 87% in 50ppm and 81 to 97% in 10ppm, 83 to 98% in 20ppm, 78 to 97% in 30ppm, 76 to 95% in 40ppm, 60 to 92% in 50ppm respectively. The optimum time is 100min for both the dyes at which equilibrium is obtained [9, 10]. The increase in the extent of removal of dyes with increasing time because adsorbate generally formed monolayer on the biosorbent surface.

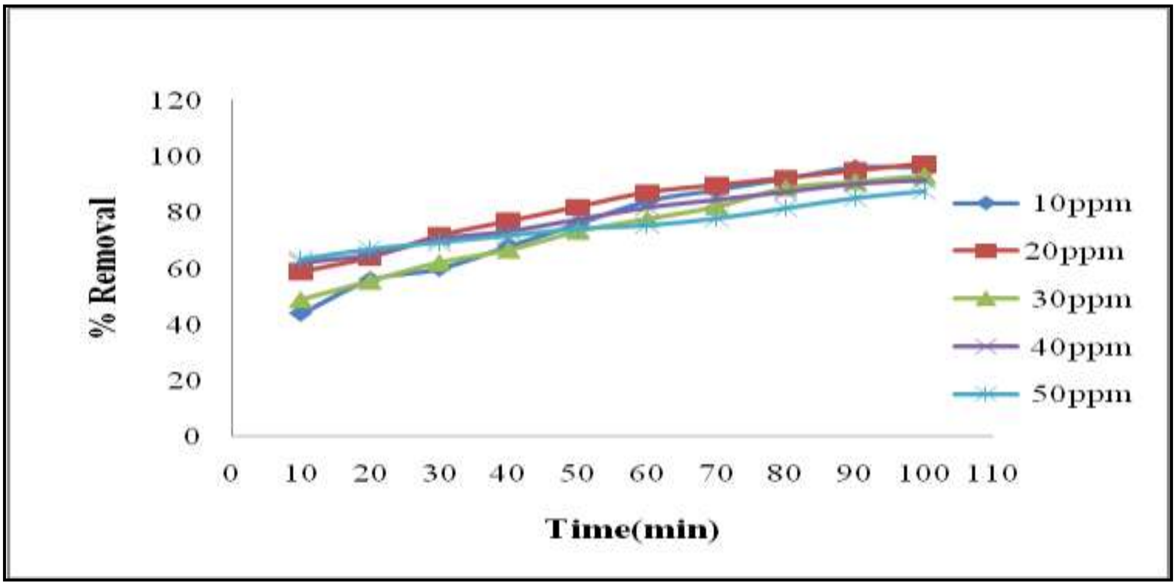

Figure 1. Effect of contact Time on Methylene Blue onto Copper pod flower (initial dye concentration – (10 – 50) mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

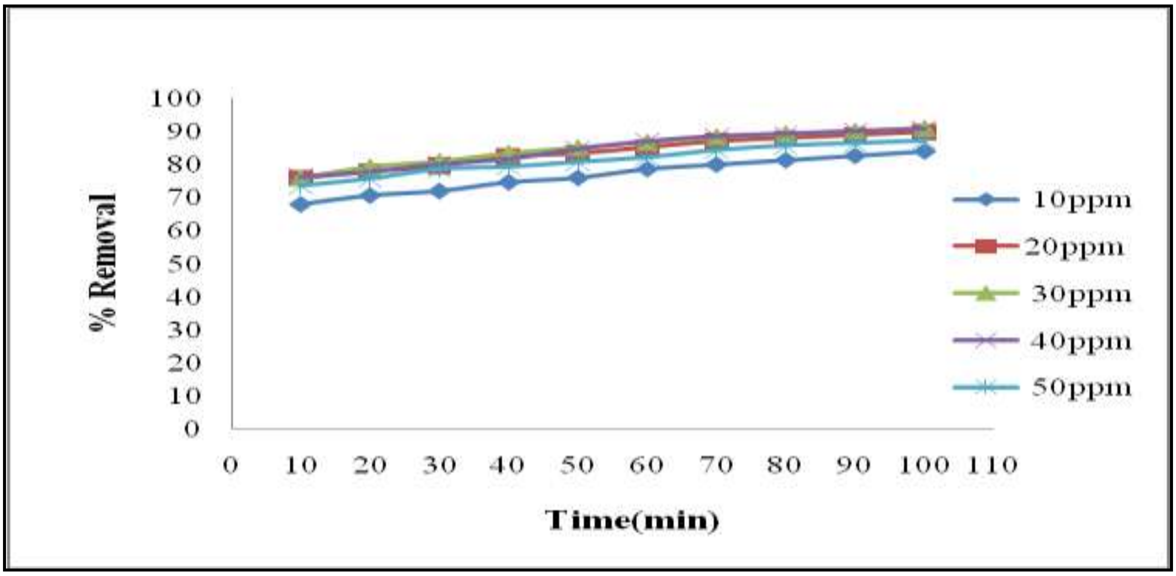

Figure 2. Effect of contact Time on Malachite Green onto Copper pod flower (initial dye concentration – (10 – 50) mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

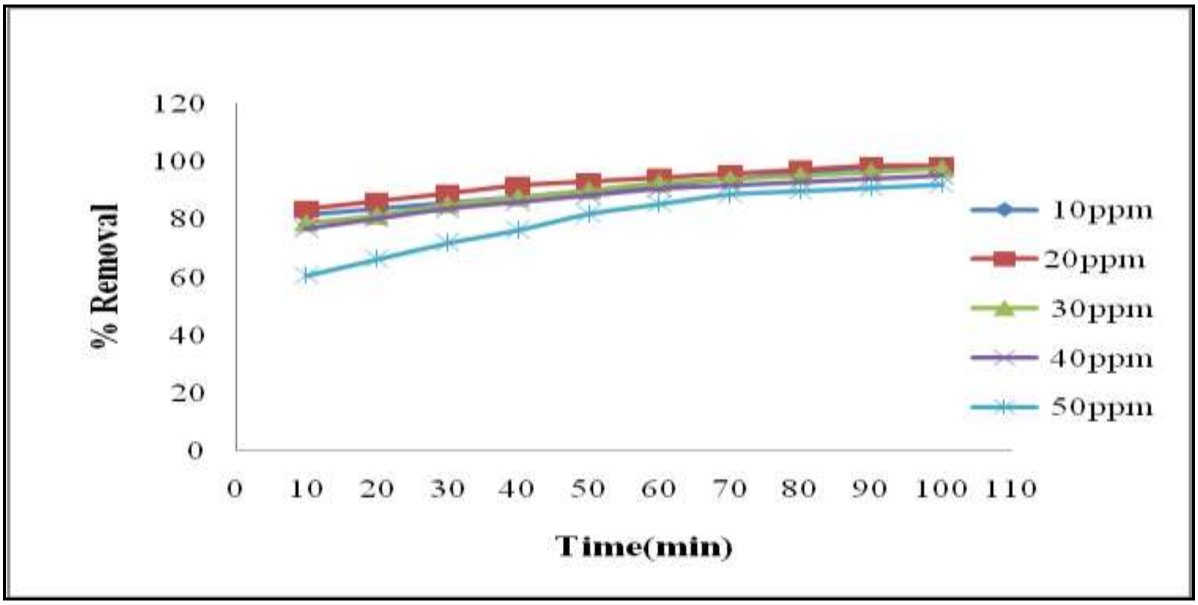

Figure 3. Effect of contact Time on Methyl Violet onto Copper pod flower (initial dye concentration – (10 – 50) mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

3.1.3 Effect of initial pH of the solution

The pH of the solution is an important parameter for controlling the adsorption process. 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 dye uptake was found to increase. From the figure, it is evident that adsorption found to increase with increase in pH of dye solution upto 7 and decreased gradually until pH 12. From this study, it is observed that maximum dye adsorption takes place at pH 7. The increase in percentage of dye removal due to increase in pH may be explained on the basis of a decrease in competition between proton(H^+) and positively charged dye at the surface sites [11, 12]. When the pH value increased from 8 – 12, there was a further decrease in the rate of adsorption by the adsorbent [13]. At high pH, the adsorbent surface becomes positively charged and high concentration of H^+ ions which compete with cationic dye causing decrease in dye uptake.

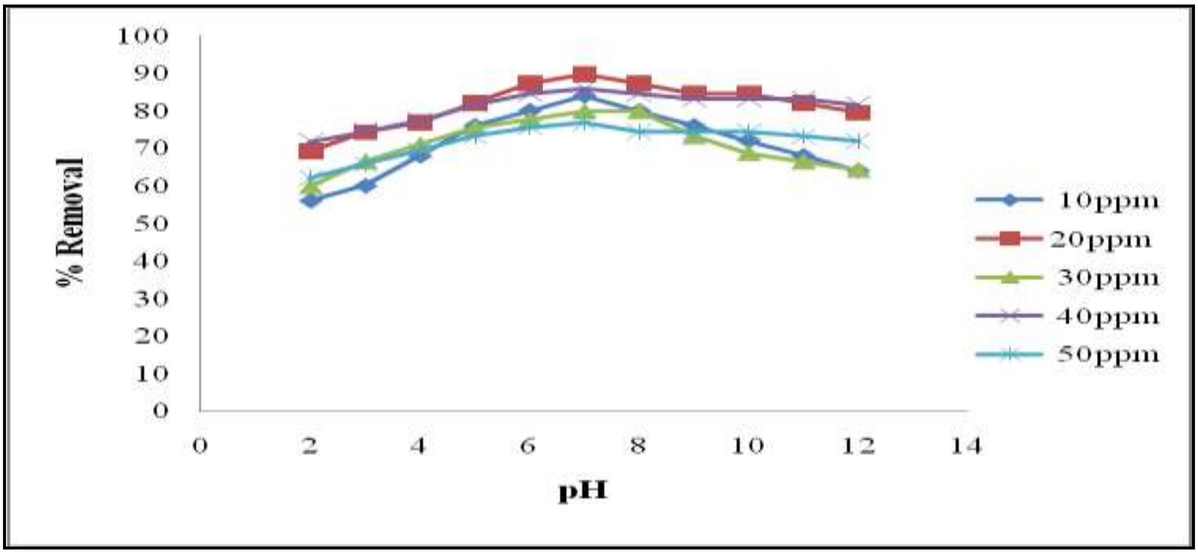

Figure 4. Effect of Initial pH on Methylene Blue onto Copper pod flower (Temperature – room temperature, speed-120 rpm) and adsorbent dosage-100mg/50ml)

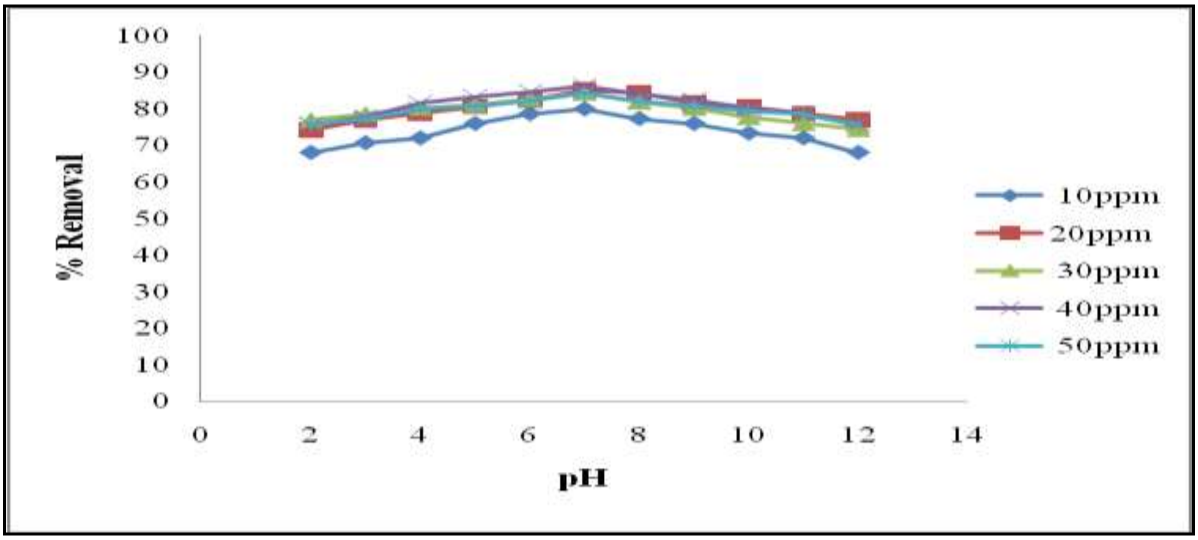

Figure 5. Effect of Initial pH on Malaghite Green onto Copper pod flower (Temperature – room temperature, speed-120 rpm) and adsorbent dosage-100mg/50ml)

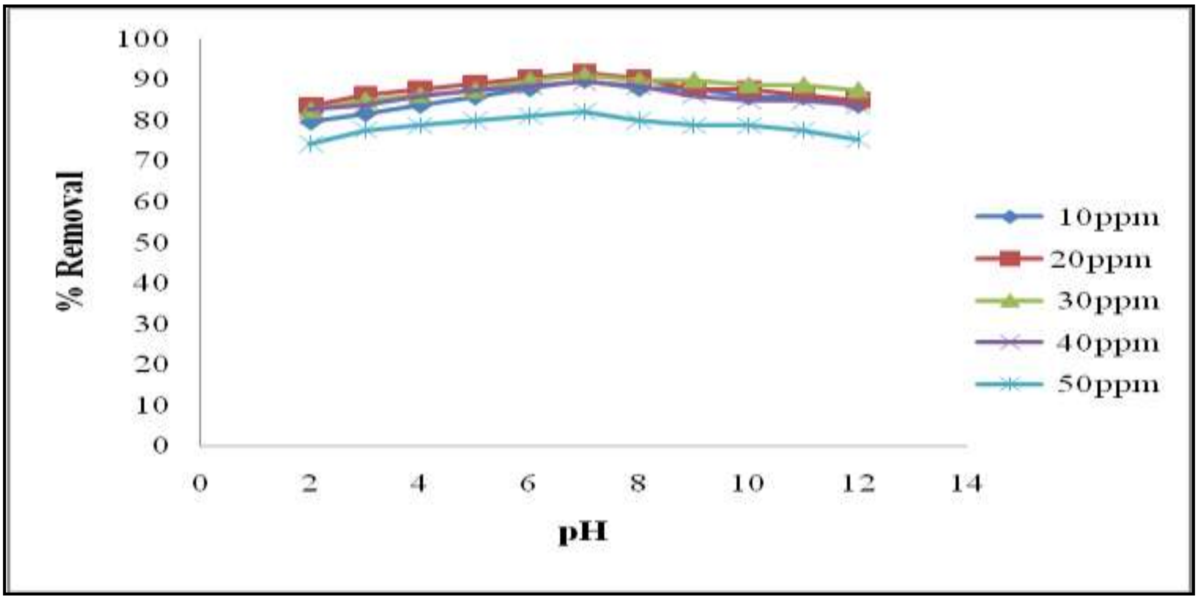

Figure 6. Effect of Initial pH on Methyl violet onto Copper pod flower (Temperature – room temperature, speed-120 rpm) and adsorbent dosage-100mg/50ml)

3.1.4 Effect of adsorbent dosage

The effect of adsorbent dosage was also investigated for the removal of dyes from aqueous solution. The experiment were carried out with adsorbent dosage varied from 0.1g to 1.0g with keeping other parameters are constant. The effects of adsorbent dosage on dye solution of three dyes removal was shown in figure 7 to 9. The removal of dyes were found to be 52 to 90% for 10ppm,64 to 94% for 20ppm, 53 to 95% for 30ppm, 63 to 95% for 40ppm, 64 to 89% for 50ppm and 70 to 93% for 10ppm,76 to 94% for 20ppm, 77 to 94% for 30ppm, 77 to 93% for 40ppm, 75 to 88% for 50ppm and 75 to 97% for 10ppm 82 to 98% for 20ppm, 81 to 98% for 30ppm, 79 to 93% for 40ppm, 75 to 94% for 50ppm in case of methylene blue, malachite green and methyl violet respectively. Initially the percentage of dye removal was found to be rapid which slowed down as the adsorbent dose increased [14]. The initial increase in adsorption with increase in amount of adsorbent dose is due to larger driving force and lesser surface area. The increase in the percentage removal of dyes with adsorbent dose due to the introduction of more binding sites for adsorption. The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose [15, 16].

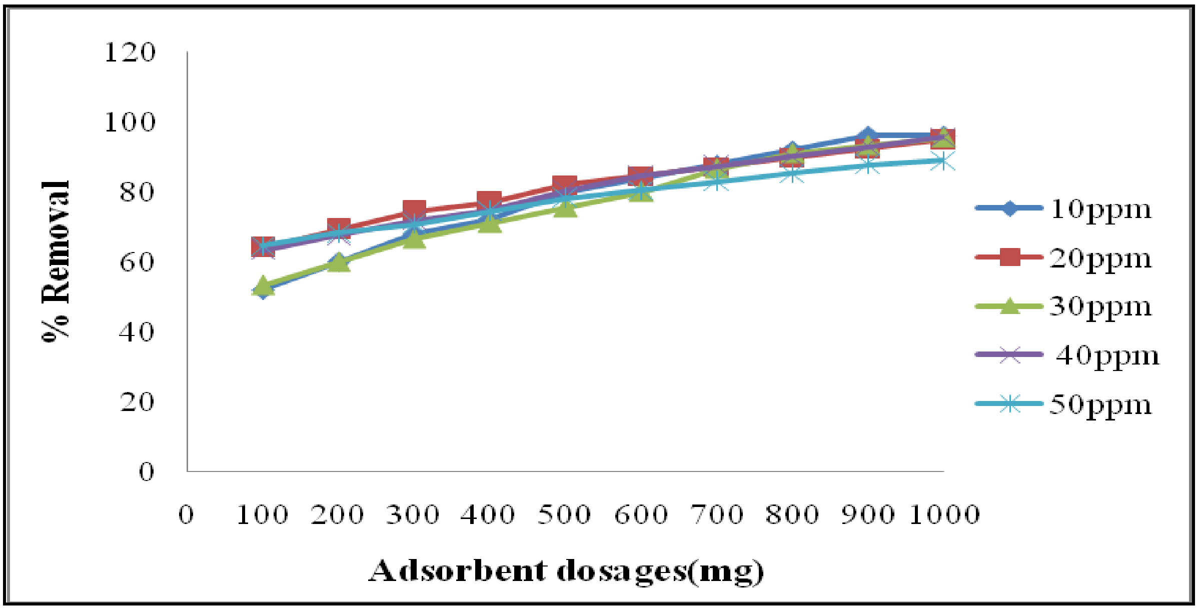

Figure 7. Effect of adsorbent dosage on Methylene Blue onto Copper pod flower (Temperature – room temperature, pH-solution pH, speed-120 rpm).

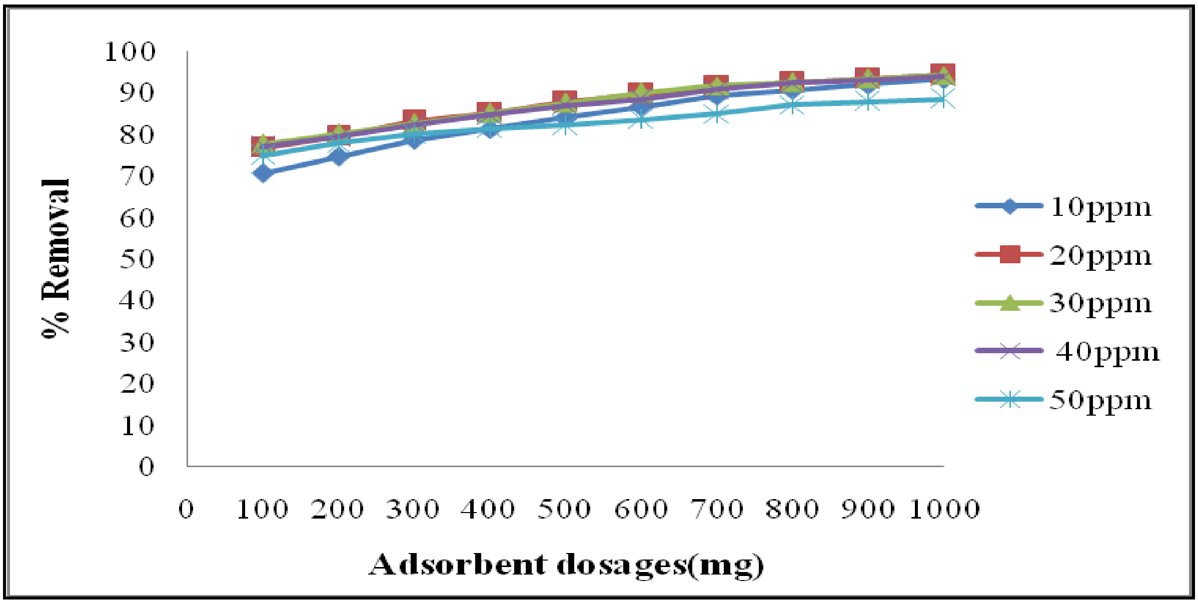

Figure 8. Effect of adsorbent dosage on Malaghite Green onto Copper pod flower (Temperature – room temperature, pH-solution pH, speed-120 rpm).

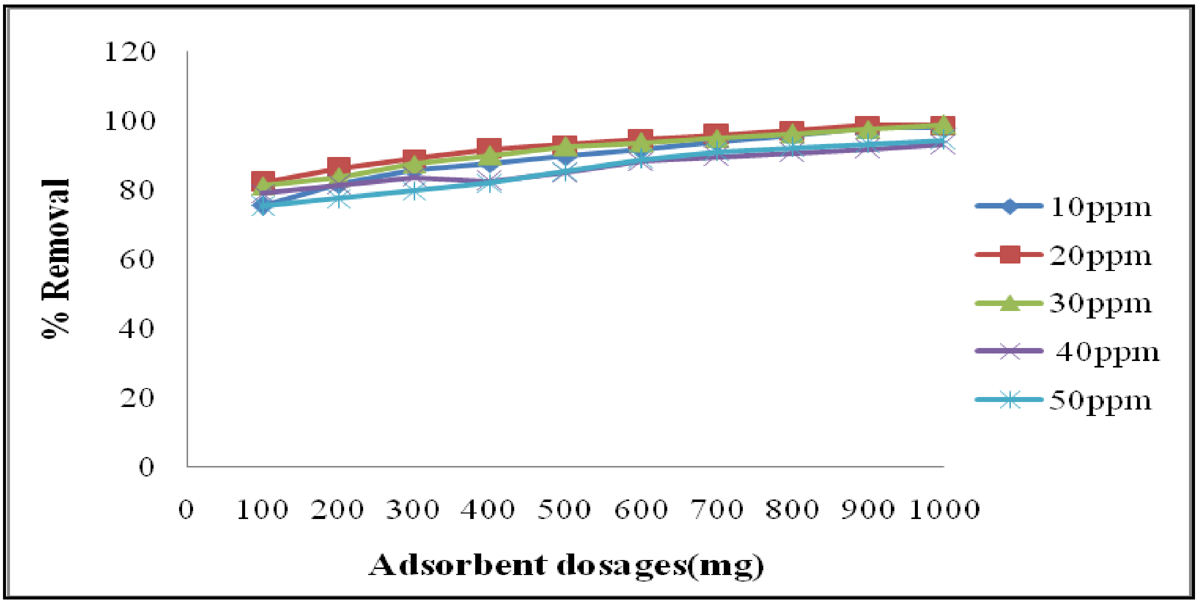

Figure 9. Effect of adsorbent dosage on Methyl violet onto Copper pod flower (Temperature – room temperature, pH-solution pH, speed-120 rpm).

3.1.5 Effect of Temperature

The percentage of three dyes (methylene blue, malachite green and methyl violet) removed at different temperature has been shown in figure 10 to 12.The percentage removal of methylene blue, malachite green and methyl violet has been studied at a temperature of 30°, 40°, 45°, 50°, 55° and 60°C with initial concentration of 40ppm. The removal of dyes were found to be 61 to 91% at 30⁰C,50 to 73% at 40⁰C, 46 to 71% at 45⁰C, 42 to 66% at 50⁰C, 36 to 66% at 55⁰C, 33 to 63% at 60⁰C and 77 to 91% at 30⁰C ,75 to 90% at 40⁰C, 74 to 90% at 45⁰C, 69 to 87% at 50⁰C, 61 to 80% at 55⁰C, 65 to 90% at 60⁰C and 59 to 82% at 30⁰C ,41 to 79% at 40⁰C, 30 to 68% at 45⁰C, 18 to 58% at 50⁰C, 6 to 53% at 55⁰C, 1 to 34% at 60⁰C in case of methylene blue, malachite green and methyl violet respectively.

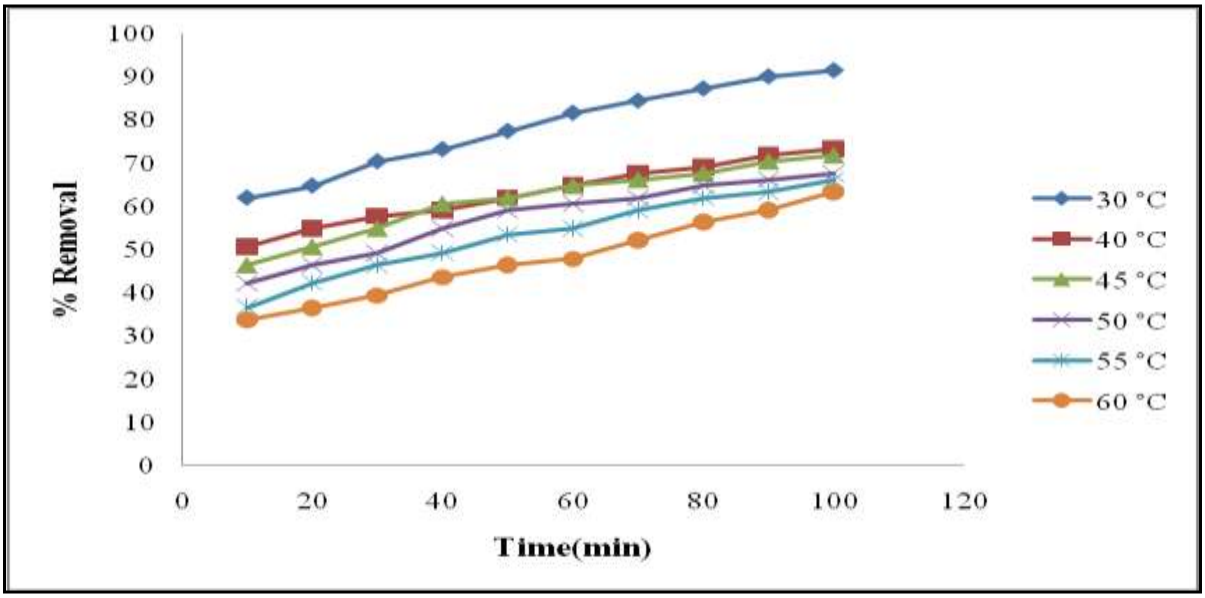

Figure 10. Effect of Temperature on Methylene Blue onto Copper pod flower (initial dye concentration - 40 mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

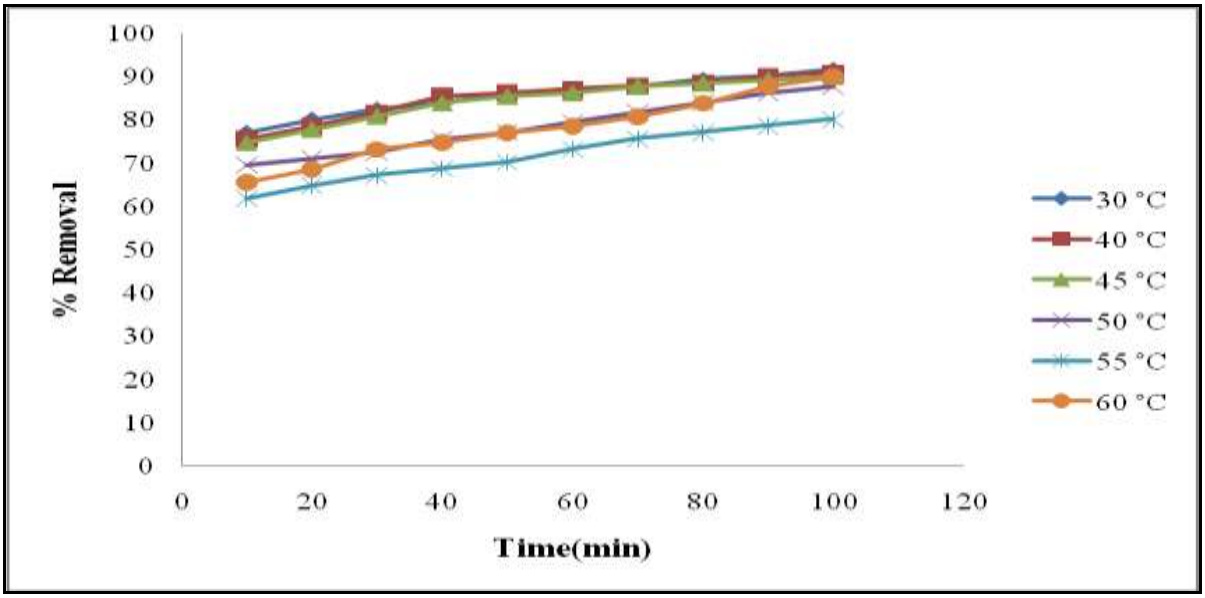

Figure 11. Effect of Temperature on Malaghite green onto Copper pod flower (initial dye concentration - 40 mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

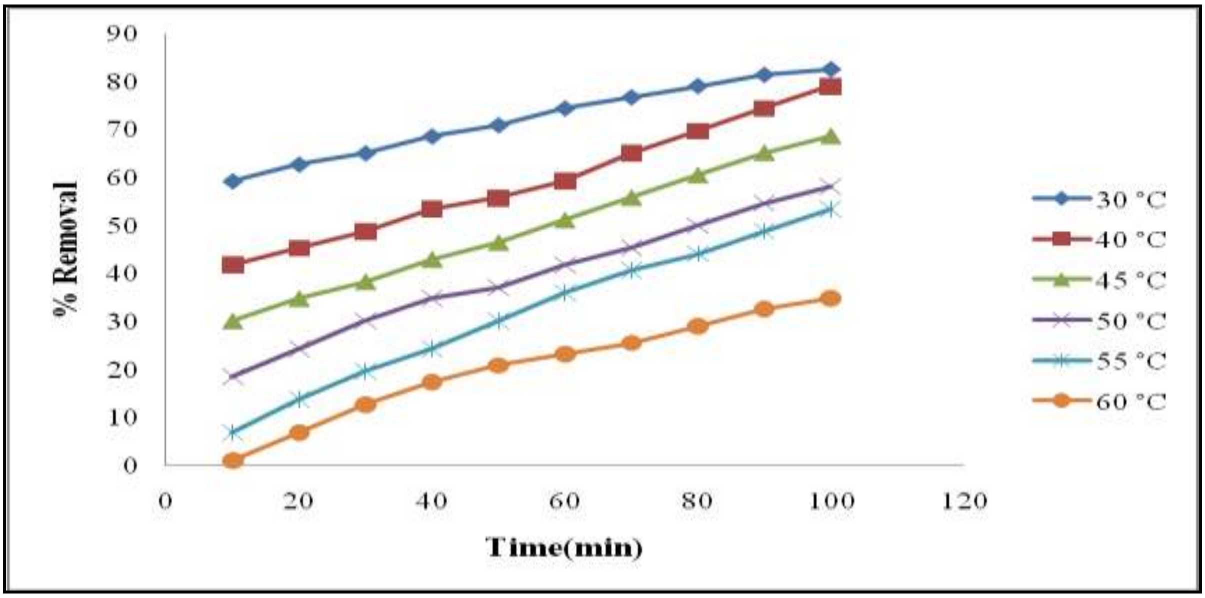

Figure 12. Effect of Temperature on Methyl violet onto Copper pod flower (initial dye concentration - 40 mg/L, pH-solution pH, speed-120 rpm) and adsorbent dosage-100mg/50ml)

The obtained results confirmed that the adsorption capacity of biosorbent for the three dyes (methylene blue, malachite green and methyl violet) decreased with increasing temperature. It is because of higher temperature may decrease the adsorptive forces between the dye molecules and active sites on the biosorbent [17, 18]. The maximum percentage removal of dye was obtained at 30^{o}C. The uptake of dye decrease with the increase in temperature, indicating the exothermic nature.

3.5. Scanning Electron Microscope analysis

The SEM photograph of the adsorbent is shown in figure.5. From the figure, it was observed that porous structure, cavities and rough surface morphology on the carbon. Pores developed on the surface of carbon increases active sites [19, 20]. This active sites increased more number of dye adsorbed molecule on the surface of the carbon.

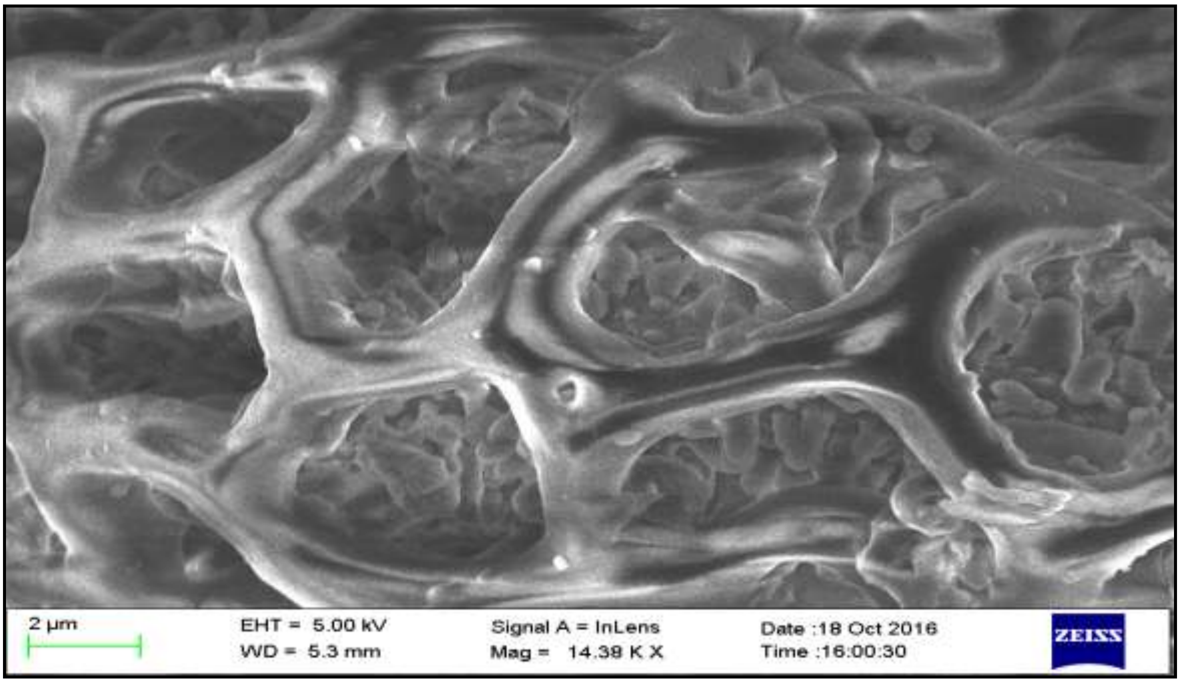

Figure13. SEM image of activated carbon

4. Conclusion

The removal of dyes (methylene blue, malachite green and methyl violet) from aqueous solutions by waste materials of copper pod flower has been experimentally determined. The percentage of colour removed increase with increasing contact time, adsorbent dosage, temperature and varied with dye solution pH. From the experimental results it was observed that the Optimum adsorbent dose for the dye is 1g. The percentage of colour removal increased with increasing adsorbent dosage. This is due to increase in surface area and the number of more binding sites of the biosorbent. The adsorption studies revealed that the optimum contact time required for equilibrium to be achieved was found to be nearly 100 minutes. The effect of temperature on percentage dye removal by copper pod flower decreases with increase in temperature from 30 to 60^oC and initial dye concentration of 40mg/L which indicates that exothermic nature of the process. Optimum temperature was found to be 30^oC for the removal of MB, MG and MV by copper pod flower. 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 SEM study also made support to it by observing difference in surface morphology of adsorbent. From the present study it is concluded that, copper pod flower which are easily available, have a potential to be used as a low cost and eco-friendly biosorbent and can be used as an alternative to the current expensive methods of removing dyes (methylene blue, malachite green and methyl violet) from aqueous solution. The scope of the further study is to try these biosorbents for designing and fabricating an economically cheap process for the treatment of wastewater.

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