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Removal of Methyl Orange from Effluent Water by Silver/Copper Nanoparticles Deposited on Antigonon Leptopus Leaf Powder an Adsorbent

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Abstract:- This research includes the synthesis of silver/copper nanoparticles that were utilized to extract methyl orange (MO) from aqueous solutions using Antigonon Leptopus leaf extract. This method offers various benefits, including affordability, simplicity, the use of less harmful materials, and—most importantly—ecological friendliness. The synthesis of Silver/Copper nanoparticles using leaf extract has the requisite quality and is a simple, affordable process. The reduction reaction was examined by examining the color change after two to three hours after the leaf extract was combined with a solution of Silver Nitrate/Copper Sulphate and heated to a temperature of 60°C or 80°C. The variables (time, dosage, pH, concentration, and temperature) were correlated with the decolorization of Methyl Orange (MO) from aqueous solution using equilibrium experiments. The results obtained showed that the optimum conditions for the removal of Methyl Orange (MO) by using silver nanoparticles and leaf dust mixture were contact time of 105 min, dosage 1.75g, pH – 4, concentration – 40 ppm and temperature – 50°C which resulted in 84.62% dye removal from aqueous solution. And for Copper nanoparticles and leaf dust mixture were contact time of 90 min, dosage 2g, pH – 3, concentration – 40ppm and temperature –50°C which resulted in 89.24% dye removal from aqueous solution. Thus, the copper nanoparticles seem to be a good adsorbent than silver nanoparticles for the decolorization of Methyl Orange dye from effluent wastewater. The Van't Hoff equation is used to analyze the adsorption process thermodynamically and to estimate the thermodynamic equilibrium constant (Kc). Changes in enthalpy (ΔH°), Gibbs free energy (ΔG°), and entropy (ΔS°) are determined from the value of (Kc). If ΔG° is negative, the adsorption is spontaneous. Entropy changes that are positive (ΔS° > 0) imply that the processes are possible and irreversible.

I. INTRODUCTION

Nanoparticles have a size between 1 - 100 nanometers. A particle is a tiny item that functions as a single entity when it comes to its attributes and transport in nanotechnology. The diameter is used to further categorize particles. Fine particles range in size from 100 to 2,500 nanometers, whereas coarse particles fall between 2,500 - 10,000 nanometers. Ultrafine particles, often known as nanoparticles, are between 1 and 100 nanometers in size. As nanoparticles have so many potential uses in electronics, optics, and medicine, scientific research on them is very active [1], [2].

A dye is an organic material that gives colors to material like leather, food, plastic, hair, wax, and textile fibre. In the past, dyes were produced using natural plants. Nearly all dyes in use today, including those found naturally, are developed chemically [3].

When compared to other industries like the leather, paper, pulp, and food industries, the textile industries generally have great economic significance because of their contribution to overall industrial output, employment creation, increasing local income, and earning foreign exchange for the development of the country [4]. But most of them don't have wastewater treatment facilities. Instead, they dispense coloured and toxic effluent, which has not been treated, directly into the nearby canals, rivers, lakes, and streams. Due to their chemical makeup and persistent and recalcitrant nature, industrial wastewater discharge causes serious environmental issues [5].

Adsorption techniques for dye removal from wastewater are growing in popularity. It is the buildup of a substance at the boundary between two phases, such as solid and liquid or solid and gas. Adsorbate is the name for the substance that adheres to surfaces. Adsorbent refers to the substance that it adsorbs to. Adsorption is frequently a combination of both physical and chemical processes [6], [7]. Adsorption capacity is influenced by the physical and chemical properties of the adsorbent and adsorbate, as well as their concentration in a liquid solution, as well as the temperature and pH of the solution during the experiment and the amount of time the adsorbate is in contact with the adsorbent (residence time) [8].

Leptodon Antigonus leaves are the leaves are soft, narrowly heart-shaped, light green, heavily veined, and have wavy margins. Simple, alternately arranged leaves are borne on stalks that range in length from 1 to 5 cm and are borne along the stems. The slender stems attach to other plants using tendrils that are carried on the axils of the leaves [9].

II. PROCEDURE

The present experimentation is carried out in batch process, on biosorption of dye (Methyl Orange MO) from aqueous solutions by using Antigonon Leptopus leaves extract and silver/copper nano particles mixture as adsorbent.

- *Preparation of Antigonon Leptopus Leaves Extract Solution:*

In this process 10 gm of fresh and cleaned leaves of Antigonon Leptopus are taken in a beaker & add 100 ml of distilled water to this leaves and kept on magnetic stirrer at 80ºC and 900 to 1000 rpm of speed for 2 hours. After 2 hours the solution is filtered in 250 ml conical flask using normal filter paper and it is kept aside for further process. The obtained solution is in pale yellow color.

- *Preparation of Stock Solution for Nano Particles:*

Prepare stock solutions of 0.1mM of silver nitrate solution AgNO3 and copper sulphate CuSO4.5H2O solution. These solutions are used for the preparation of nano particles which are used as adsorbent for the dye removal.

- *Preparation of Nano Particles and Leaf Extract Mixture Adsorbent:*

In order to produce nanoparticles, a 500 ml conical flask containing 100/70 ml of leaf extract solution and 250/200 ml of 0.1 mM $AgNO_3$/0.1 mM $CuSO_4.5H_2O$ is heated for about 2/3 hours at 600/800 degrees Celsius. When the light – yellow color is changed to a dark brown color, the nanoparticle formation is apparent. This solution obtained is further centrifuged at 1500 rpm so that the leaf extract along with silver/copper nanoparticles gets suspended at the bottom of the glass tubes. It is slowly removed from the tube and dried to make it as leaf extract and silver/copper nanoparticles mixture which obtain is used for various dyes degradation process of different concentrations with different dosages.

- *Preparation of 1000 Mg/L Dye Stock Solutions:*

To make a stock solution of 1000 ppm of methyl orange (MO) In one litre of distilled water, 1000 mg of Methyl Orange analytical reagent (AR) grade are dissolved. Synthetic samples with various dye concentrations were created from this stock solution using the proper dilutions. By adding distilled water to 10 ml of a 1000 ppm dye stock solution in a 100 ml volumetric flask, up to the mark, 100 ppm dye solution was created. Similar, to that, preparations for the experimental procedure included solutions with various dye concentrations, including 40, 60, 80, 100, 120, 150, and 180 ppm solutions.

- *Removal of Dye from Aqueous Solutions:*

The dye removal process is done in batch operation by using bio sorbent of silver/copper nanoparticles and leaf extract powder. Different parameters are studied during dye removal process. At first equilibrium time is obtained then we can vary with other parameters by keeping one parameter as constant. All these experiments are carried out in orbital shaker by adding optimal quantity of adsorbent dosage to the studying concentration of dye solution and kept for optimal time on shaker by maintaining desired pH measured with pH meter and after optimal time is completed. The sample solution is tested in UV spectroscopy for the absorbance to be noted from that the percentage of dye removal is calculated at that operating conditions.

III. RESULTS AND DISCUSSIONS

- *SEM Analysis*:

Images of Scanning Electron Microscope (SEM) conforming the presence of the nano particles on the ground leaf powder particles are shown below.

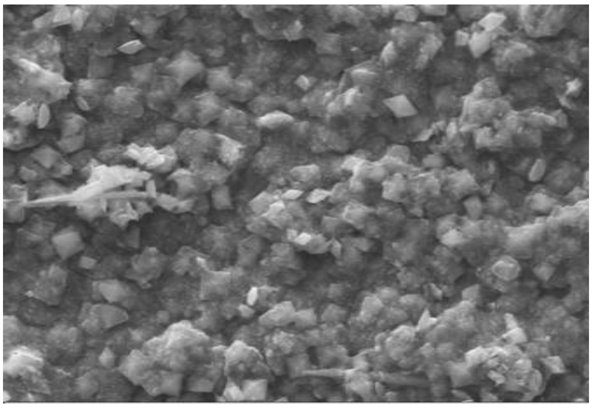

Fig 1 Silver Nanoparticles on Antigonon Leptopus Leaf Powder

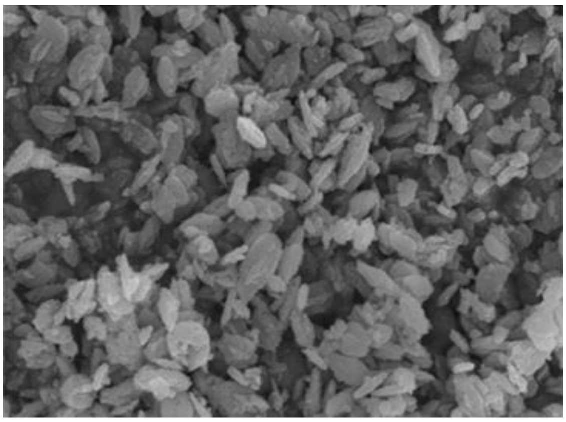

Fig 2 Copper Nanoparticles on Antigonon Leptopus Leaf Powder

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- *Silver Nanoparticles and Leaf Powder as Adsorbents:*

- *Time Course of Adsorption:*

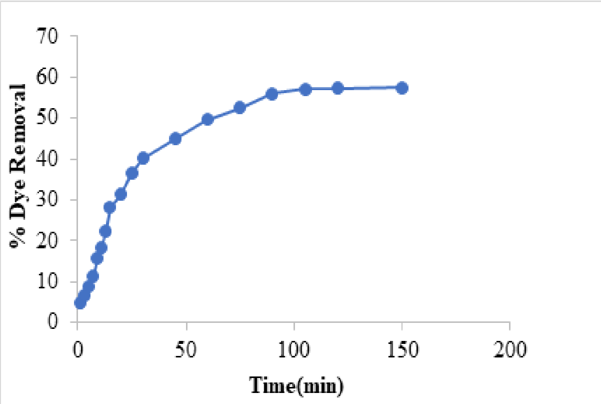

Fig 3 Time Course of Adsorption

As can be seen that the color removal started at a brisk phase, gradually slowing down to become study at 57 % after 105 minutes. Thus, a treatment time of 105 minutes is good enough for the dye removal and this is continued for the rest of experimentation.

- *Effect of Adsorbent Dosage:*

A 50 ppm of 100 ml of methyl orange (MO) dye solution was treated for an optimum time of 105 min with different dosages ranging from 0.25g to 2g of (silver nanoparticle + leaf dust/powder) at room temperature is studied and the percentage removal variations were obtained at different dosages. Data obtained is represented as figure 4.

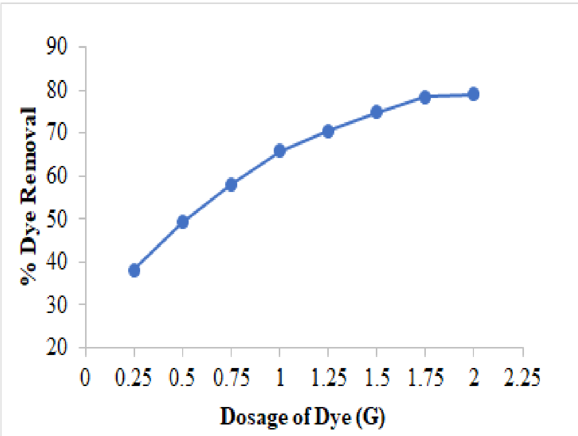

Fig 4 Effect of Adsorbent Dosage

From the figure it is observed that the percentage removal of MO dye is increasing when the dosage quantity of adsorbent (silver nanoparticles + leaf dust/powder) is gradually increasing. Increase in dosage levelfrom1.75g to 2g of (silver nanoparticles + leaf dust/powder) adsorbent the removal of dye is minimal and becoming constant slowly and attained a dye removal of 78.96 % at 2g of adsorbent dosage. Thus, a dosage of1.75g of (silver nanoparticles + leaf dust/powder) adsorbent is taken as optimal quantity for the further experimental study.

- *pH Effect In Dye Removal:*

At room temperature and an optimal time of 105 min, 50 ppm of 100 ml methyl orange (MO) dye solution was treated with a dosage of 1.75g (silver nanoparticle + leaf dust/powder) at different pH values ranging from 2 to 8 is studied and the dye removal percentage were obtained at different pH values. Data obtained is shown as figure 5.

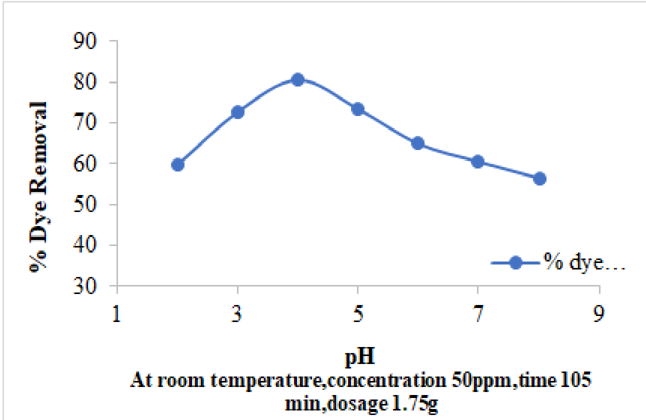

Fig 5 pH Effect in Dye Removal

From the figure it is observed that the dye removal is increasing gradually with variation in pH ranges from 2 to 4 and attains a maximum percentage dye removal of 80.5% at pH value of 4, when optimal conditions are maintained. Thereafter increasing in pH from 4 to 8 the percentage of dye removal is decreasing. Thus, an optimum pH value of 4 is considered for further experiments.

- *Dye Removal with Concentration Variations:*

At room temperature and an optimal time of 105min, a dosage of 1.75gm (silver nanoparticle + leaf dust/powder) and with a pH of 4, adsorbent is treated with different concentrations ranges from 40 ppm to 180 ppm of 100 ml of methyl orange (MO) dye solution is studied and the dye removal percentage were obtained at different concentration values of the dye solution. From the figure it is concluded that the dye removal is eventually decreasing with the increase in concentration of the treating methyl orange (MO) dye solution.

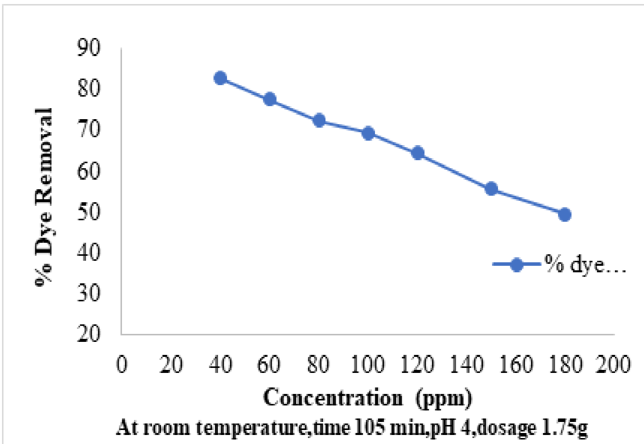

Fig 6 Dye Removal with Concentration Variations

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When maintained the optimal conditions, 82.65% of dye removal is achieved when 40ppm concentration of 100ml dye solution treated with 1.75g dosage of (silver nanoparticle + leaf dust/powder) adsorbent.

- *Temperature Effects in Dye Removal:*

A 50ppm concentration of 100 ml of methyl orange (MO) dye solution was treated for an optimum time of 105 min with a dosage of 1.75g (silver nanoparticle + leaf dust/powder) adsorbent at room temperature and maintaining a pH of 4 is studied and the percentage removal were obtained at different temperatures.

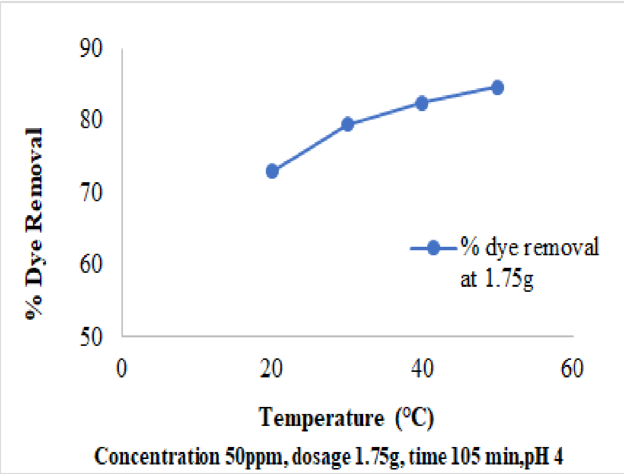

Fig 7 Temperature Effects in Dye Removal

From the experimental study it is clearly observed that the removal of color is increasing with proportional to temperature. While maintaining the optimal conditions of 105 min time and a pH value of 4 with an adsorbent dosage of 1.75g (silver nanoparticle + leaf dust/powder) 84.62 % of methyl orange (MO) dye removal is attained from 50ppm of 100ml color solution at 50°C temperature.

- *Thermodynamic Analysis:*

By employing Van't Hoff's plot, the adsorption process is subjected to a thermodynamic analysis, and the thermodynamic equilibrium constant (Kc) is obtained. Equations are used to calculate the changes in enthalpy ($\Delta H°$), Gibbs free energy ($\Delta G°$), and entropy ($\Delta S°$) based on the value of (Kc). Using the equation for the linear trend line from Van't Hoff's plot, we can solve for (1) and (2).

$$\Delta G = -RT \ln Kc \text{.. (1)}$$

$$\ln\left(\frac{qe}{Ce}\right) = Kc = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \text{........................ (2)}$$

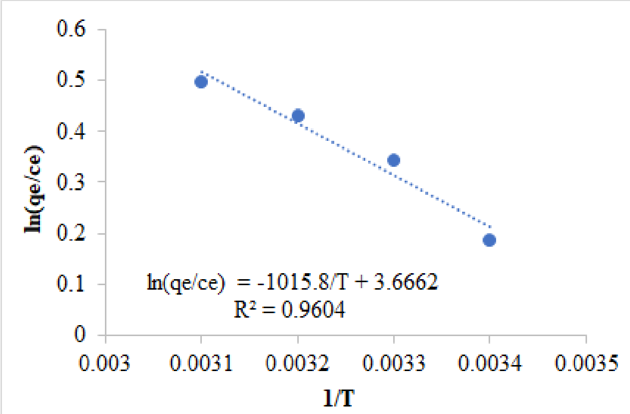

Fig 8 Van't Hoff's Plot for Adsorption of MO using Silver Nanoparticles + Antigonon Liptopus Leaf Powder Mixture

From the figure changes in enthalpy, Gibb's free energy, and entropy are calculated to explore the nature of adsorption from the linear equation by using slope and intercept, and the values are shown below.

$\Delta H° = 8.44$ KJ mole^{-1}
$\Delta S° = 30.48$ J mole^{-1}K^{-1}
$\Delta G° = -1.4$ KJ mole^{-1}

Enthalpy change is endothermic process (+ 8.44 KJmole^{-1}) as it is positive. The adsorption is spontaneous because G° = is negative (-)1.4 KJ mole^{-1}.

Entropy change of 30.48 Jmole^{-1}K^{-1} (>0) points to the possibility and irreversibility of the process.

➢ *Copper Nanoparticles and Leaf Powder as Adsorbents:*

- *Time Course of Adsorption:*

A 100 ppm of 100 ml of methyl orange (MO) dye solution was treated with 1g of (copper nano particles + leaf dust/powder) at room temperature and the percentage of dye removal were obtained at different time intervals.

The data obtained is shown as figure 9

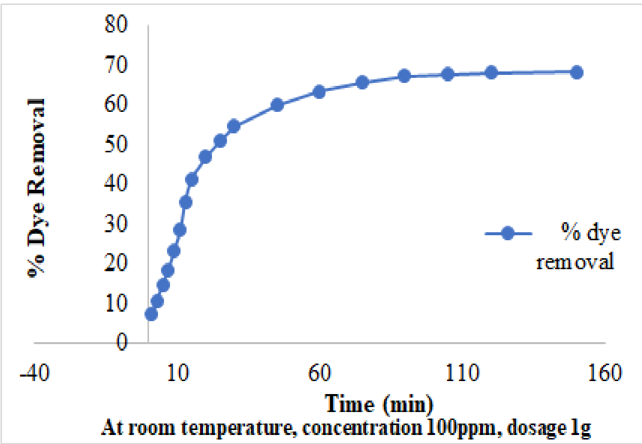

Fig 9 Time Course of Adsorption

From the figure the Methyl Orange (MO) dye removal started at a brisk phase, gradually slowing down to become study at 67.3% after 90 minutes. Thus, an experiment operational time of 90 minutes is good enough for the dye removal and this is continued for the rest of experimentation.

- *Effect of Adsorbent Dosage:*

Prepare 50 ppm of 100 ml of methyl orange (MO) dye solution and was treated for an optimum time of 90 min with different dosages of (copper nanoparticle + leaf dust/powder) adsorbent ranging from 0.25g to 2.25g at room temperature is studied and the percentage removal of color were obtained at different dosages.

From the figure 10, it is observed that the percentage removal of MO dye is increasing when the dosage quantity of adsorbent (copper nanoparticles + leaf dust/powder) is gradually increasing. Increase in dosage level from 2g to 2.25g of (copper nanoparticles + leaf dust/powder) adsorbent the removal of dye is minimal and slowly becoming constant and attained a dye removal of 82.95 % at 2.25g of adsorbent dosage.

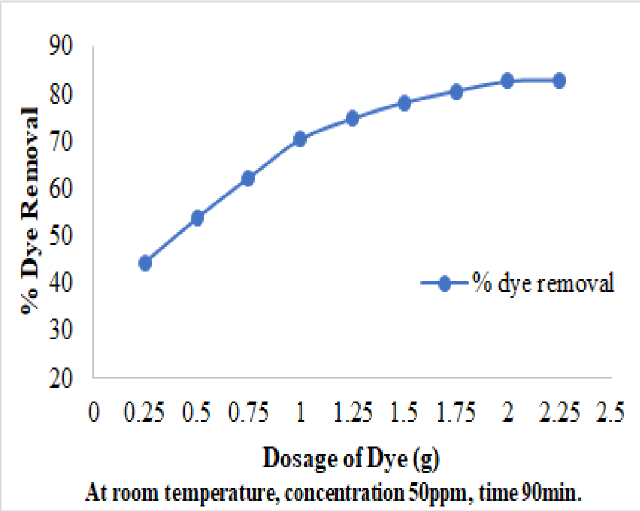

Fig 10 Effect of Adsorbent Dosage

Thus, a dosage of 2g of (copper nanoparticles + leaf dust/powder) adsorbent is taken as optimal quantity for the further experimental study.

- *pH Effect in Dye Removal:*

At room temperature and an optimal time of 90 min, 50 ppm of 100 ml methyl orange (MO) dye solution was treated with a dosage of 2g (copper nanoparticle + leaf dust/powder) at different pH values ranging from 1 to 7 is observed and the dye removal percentage were obtained at different pH values. Data obtained is shown as figure 11.

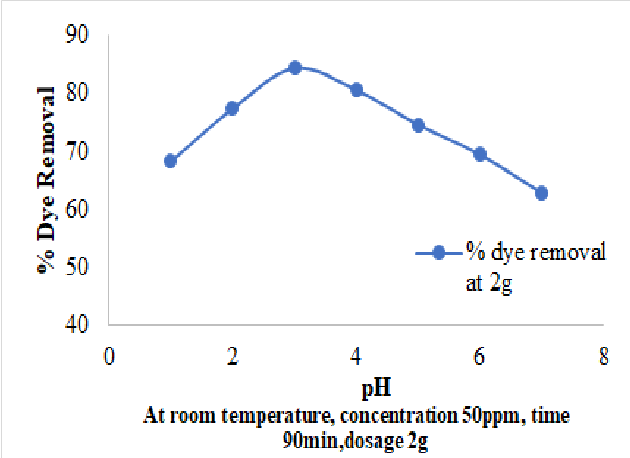

Fig 11 pH Effect In Dye Removal

From the experiments and the figure, it is observed that the dye removal is increasing gradually with increase in pH from 2 to 3 and attains a percentage color removal of 84.35% as highest. Thereafter increasing in pH from 3 to 7 the percentage of color removal is decreasing. Thus, an optimal pH value of 3 is taken for further experimental studies.

- *Dye Removal with Concentration Variations:*

With an operational time of 90 min, a dosage of 2g (copper nanoparticle + leaf dust/powder) adsorbent is treated with different concentrations of 100ml methyl orange (MO) dye solution ranges from 40 ppm to 180 ppm at room temperature and maintaining pH value of 3 is studied and the dye removal percentage were obtained at different concentrations of the dye solution.

The data found is expressed as figure 12

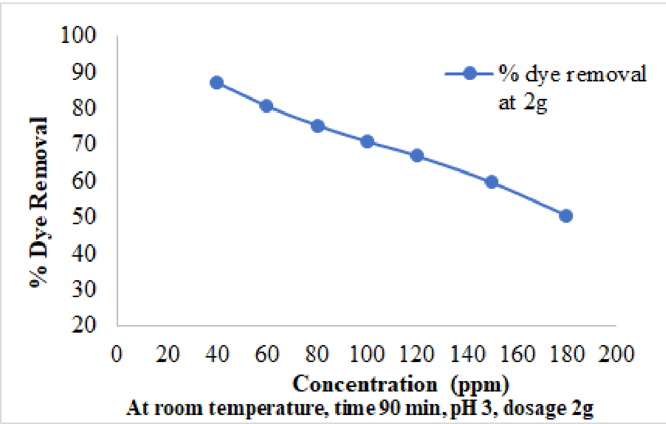

Fig 12 Dye Removal with Concentrations

From the figure it is observed that the dye removal is decreasing gradually with the increase in concentration of the operating methyl orange (MO) dye solution.

When maintained the optimum conditions of time 90 min pH value 3, 87.2% of dye removal is obtained when 40ppm concentration of 100ml (MO) dye solution is treated with 2g dosage of (copper nanoparticle + leaf dust/powder) adsorbent.

- *Temperature Effects tn Dye Removal:*

A 50ppm concentration of 100 ml of methyl orange (MO) dye solution was treated for an optimum time of 90 min with a dosage of 2g (copper nanoparticle + leaf dust/powder) adsorbent at room temperature and maintaining a pH of 3 is studied and the percentage removal were obtained at different temperatures.

The data obtained is represented as figure 13.

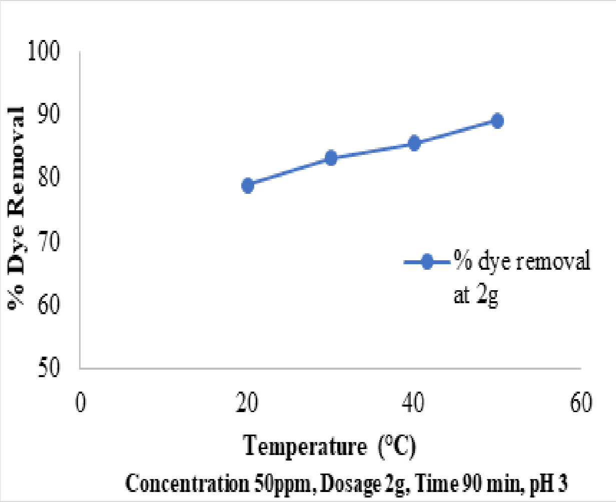

Fig 13 Temperature Effects in Dye Removal

From the experimental data it is clearly observed that the removal of color is increasing with increasing in temperature up to certain range after that the removal percentage becomes slower.

While maintaining the optimal conditions of 90 min time and a pH value of 3 with an adsorbent dosage of 2g (copper nanoparticle + leaf dust/powder)89.24 % of methyl orange (MO) dye removal is attained from 50ppm of 100ml color solution at 50°C temperature.

- *Thermodynamic Analysis*

By employing Van't Hoff's plot, the adsorption process is subjected to a thermodynamic analysis, and the thermodynamic equilibrium constant (Kc) is obtained. Equations are used to calculate the changes in enthalpy ($\Delta H°$), Gibbs free energy ($\Delta G°$), and entropy ($\Delta S°$) based on the value of (Kc). Using the equation for the linear trend line from Van't Hoff's plot, we can solve for (1) and (2).

$$\Delta G = -RT\ lnKc \ldots\ldots \quad (1)$$

$$\ln\left(\frac{qe}{Ce}\right) = Kc = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \ldots\ldots \quad (2)$$

From the figure, changes in enthalpy, Gibb's free energy, and entropy are calculated to explore the nature of adsorption from the linear equation by using slope and intercept, and the values are shown below.

$$\Delta H° = 9.25 \text{ KJ mole}^{-1}$$

$$\Delta S° = 33.69 \text{ J mole}^{-1}\text{K}^{-1}$$

$$\Delta G° = -\ 1.6 \text{ KJ mole}^{-1}$$

Enthalpy change is endothermic process (+ 9.25 $KJmole^{-1}$) as it is positive. The adsorption is spontaneous because G° = is negative (-)1.6 KJ $mole^{-1}$.

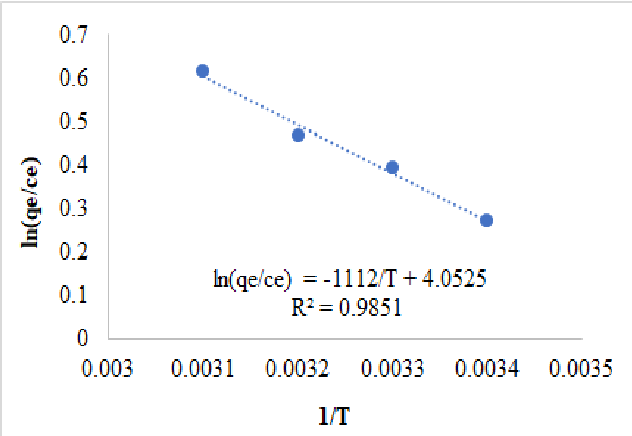

Fig 14 Van't Hoff's Plot for Adsorption of Methyl Orange (MO) using Copper Nanoparticles + Antigonon Liptopus Leaf Powder Mixture

Entropy change of 33.69 $Jmole^{-1}K^{-1}$ (>0) points to the possibility and irreversibility of the process.

IV. CONCLUSION

Investigations are carried out to find out the equilibrium conditions and the optimal removal of Methyl Orange (MO) from an aqueous solution using Silver nanoparticles and Antigonon Leptopus leaf dust mixture as adsorbent show that The maximum adsorption of Methyl Orange (MO) dye is (84.62%) with Antigonon Leptopus leaf dust and Silver nanoparticle mixture is observed when the processing parameters are set to be as: time 105min, pH = 4, dosage = 1.75g, Concentration = 40ppm and temperature = 50°C Also, the thermodynamic properties are indicated with a positive change of enthalpy (+ 8.44 $KJmole^{-1}$) which tells us that the process is endothermic. $\Delta G°$ = is negative (-) 1.4 KJ $mole^{-1}$ and hence the adsorption is spontaneous. A change in entropy of 30.48 J $mole^{-1}K^{-1}$ (>0) suggests that the process is feasible and irreversible. Similarly, the conditions of experiments with copper nanoparticles and Antigonon Leptopus leaf dust mixture are concluded as the maximum adsorption of Methyl Orange (MO) dye is (89.24%) with Antigonon Leptopus leaf dust and Copper nanoparticle mixture is observed when the processing parameters are set as: time 90min, pH = 3, dosage = 2g, Concentration = 40ppm and temperature =50°C. the thermodynamic properties are indicated as a positive change of enthalpy $\Delta H°$ = (+ 9.25 KJ $mole^{-1}$) indicates that the process is endothermic. $\Delta G°$ = is negative (-) 1.6 KJ $mole^{-1}$ and hence the adsorption is spontaneous. A change in entropy of 33.69 J $mole^{-1}K^{-1}$ (>0) suggests that the process is feasible and irreversible.

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