Kinetics and Thermodynamics Studies on Removal of Methyl red dye by Green Synthesized Copper Oxide Nanoparticles (Colocasia esculenta)

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Abstract: *Nanoparticles are the spearheads of the rapidly expanding field of nanotechnology. Development of the green synthesis has gained environmental friendly protocol for synthesizing a wide range of metal and metal oxide nanoparticles. The present study is to undertake studies for Removal of Methyl red dye by Green Synthesized Copper Oxide Nanoparticles (Colocasia esculenta). The synthesized copper oxide nanoparticles were characterized by Ultraviolet Vis spectroscopy (UV-Vis), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Energy Dispersive X-ray (EDX), and Dynamic Light Scattering (DLS). Adsorption parameters such as Initial dye concentration, Adsorbent dosage, pH, contact time, and Temperature were studied. Adsorption isotherm has been used to test the adsorption data (Langmuir, Freundlich, Temkin), Kinetics and thermodynamic factors were also calculated.. The adsorption kinetics shows good agreement of pseudo second order kinetic model. Moreover, the negative value of ΔG^o reveals the spontaneous nature of the adsorption process and the negative value of ΔH^o indicates the adsorption process exothermic and the positive values of ΔS^o suggest increasing randomness of the adsorbent solution interface during the adsorption process of APT CuONPs. The green chemistry approach used in the present work for the synthesize of copper oxide nanoparticles is simple, cost effective, and good alternative method. The green synthesized copper oxide nanoparticles with high dye adsorption capacity might be a suitable option for dye removal from coloured aqueous solution. CuO nanoparticle prepared from above mentioned routes are expected to have more extensive applications such as Chemical sensor, Catalytic, Gas sensor, Semiconductor etc. This process is an economical method with respective to energy, time and its simplicity. Through this method a large scale of Green synthesized Copper Oxide Nanoparticles was produced.*

Keywords: Nanoparticles

I. INTRODUCTION

Nanotechnology can be defined as the manipulation of mater through certain chemical and physical process to create materials with specific properties which can be use particular application [1]. A nanoparticle can be defined as a microscopic particle that has at least one dimension less than 100 nm in size [2]. Nanotechnology generally involves the application of extremely small particles that are used across all field of science including chemistry, biology, medicine and material science [3-4]. Nanoparticles are the spearheads of the rapidly expanding field of nanotechnology. Different types of nanoparticles with desired shape and size have been fabricated using various approaches like physical, chemical and biological techniques [5].

II. EXPERIMENTAL SECTION

2.1 Materials

All chemicals used were of analytical reagent without any further purification in addition to deionised water, copper chloride dihydrate ($CuCl_2.2H_2O$), Sodium hydroxide (NaOH),hydrochloric acid (HCl), and ethanol (C_2H_5OH. Methyl

Red (MR) is an azo dye (Known as (2-{E)-[-4-(dimethylamenophenyl] diazinyl} benzoic acid) as well, it is a pH indicator, it is yellow in pH more than 6.2 red in pH values under 4.4 and orange in between.
It was selected as model system due to its intense colour in aqueous system and biodegradability because of benzene rings.

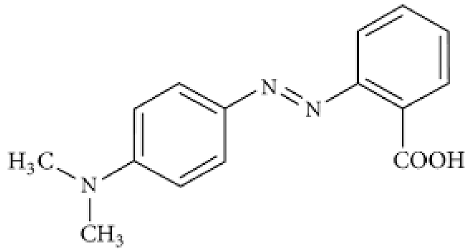

Fig. 1: Molecular structure of Methyl Red (MR)

The molecular structure of Methyl red is depicted in Fig.2 [37]. The chemical formula of methyl red is $C_{15}H_{15}N_3O_2$ with molecular weight (269.31 g/mol λ_{max} = 417nm) [38].

2.2 Methods

2.2.1 Preparation of Colocasia esculenta tuber Extract

The *Colocasia esculenta* tuber were collected from, cultivation land of nearby Tiruvannamalai Village. . The fresh tuberwas washed several times with tap water followed by distilled water to remove the dust particles. The clean and fresh sources are dried in a shaded place at room temperature for 10 to 15 days and then the leaves were pulverized using commercial blender. The fine powdered was stored at room temperature for further use. In a 250 ml of conical flask 10 gm of tuber powder were taken and to this 100 ml of double distilled water is added and it is heated at 80^{o}C for 30 minutes. Then the solution was filtered using Whatman filter paper and kept aside for further process. The obtained extract in pale brown colour and adjust the pH at 11 by adding 0.1M of sodium hydroxide solution.

2.2.2 Preparation of Copper Oxide Nanoparticles

In a 250 ml conical flask, 50 ml of *Colocasia esculenta* tuber extract was taken and to this 100 ml of 0.1 M $CuCl_2.2H_2O$ solution is added slowly at room temperature under static conditions. The colour change of the reaction was observed and the time taken for the changes was noted. The solution colour changes immediately from pale brownish to yellowish grey colour indicating the formation of copper oxide nanoparticles (CuONP). Further the solution is centrifuged and precipitated is extracted and dried in electrical oven for 24 hours at 100^{o}C. the dried sample kept in muffle furnace for 4 hours at 500^{o}C. the green synthesised CuONPs is formed at uniform particle size and stored for further characterisation and uses.

2.3 Preparation of Adsorbate

The synthetic dye such as Methyl Red (MR) were purchased from kevin laboratories in Chennai. A stock solution of (1000mg/L) was prepared by dissolving 1.0 g of dye distilled water. Distilled water was used for preparing all the solution and reagents.

III. RESULTS AND DISCUSSION

3.1. Characterizationstudy of Copper Oxide Nanoparticles.

3.1.1. UV- VIS Absorption Spectroscopy for copper oxide Nanoparticles.

The Green approach for the formation of copper oxide nanoparticles using tuber extract was reported. Formation of copper oxide nanoparticle were confirmed by UV-vis spectrophotometry. Fig 3. shows the UV-Vis absorption spectrum of copper oxide nanoparticle. The adsorption spectrum was recorded for the sample in the range of 200 – 800 nm. The spectrum showed the absorbance peak at 240 nm corresponding to the characteristic band of copper oxide nanoparticle [39].

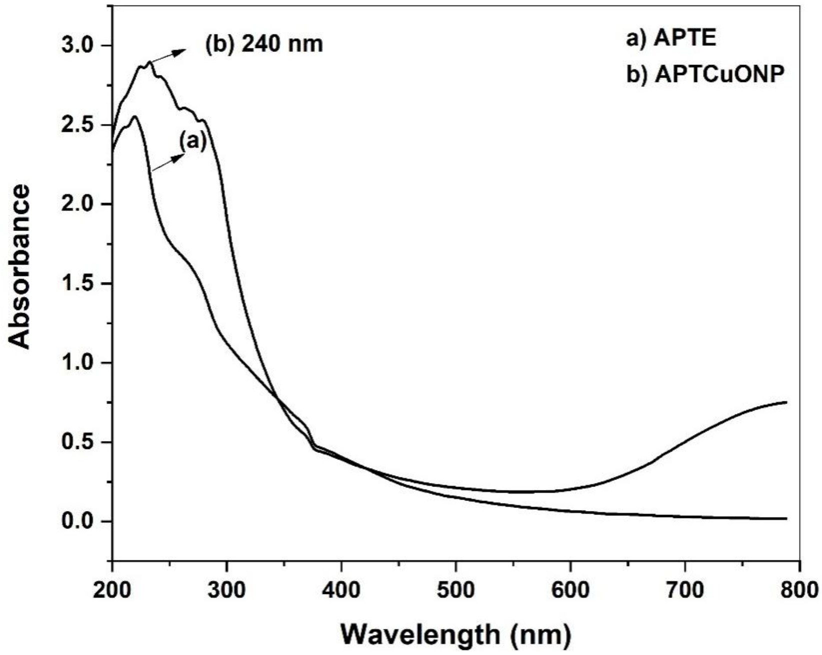

Fig 2 UV-visible adsorption spectrum of APT extract and APT CuONPs

3.1.2. X-ray Diffraction

The x-ray diffraction (XRD) study was undertaken to Determine and confirm the crystalline structure of synthesized CuONPs. Fig (4) Shows the appearance of diffraction pattern at 2θ= 33.3, 35.4, 38.8, 48.7, 58.3, 61.8, 66.28 and 68.0 which are assigned to the planes (110), (022), (111), (200), (202), (020), (202), (022) respectively of monoclinic phase CuONPs. No characteristic peak due to any impurity was observed in the diffraction grams Suggesting the formation of pure crystalline CuO.

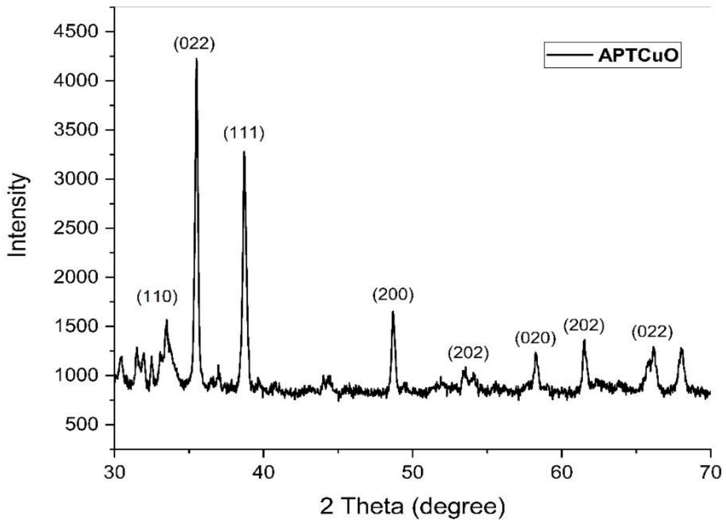

Fig 3: X-ray diffraction pattern of *Colocasia esculenta* tuber extract- mediated synthesized CuONPs

The average size of the CuO was calculated by using the Debye-Scherer Equation (3) [40]. A sharp peak at 2θ=35.4 and 38.8 with the diffraction of the (022) and (111) plane indicates that confirmation of CuONPs. The average crystallite size in the samples of CuONPs is below 21nm.

$D = 0.9\lambda / \beta \cos \theta$ Eq. (3)

Where λ is the wavelength of the x-ray radiation (0.154nm), θ is the Diffraction angle and β is the full width at half maximum.

3.1.3 Fourier Transform Infrared (FT-IR) Spectroscopy

FTIR spectroscopy analysis also revealed the possible biomolecules and functional group responsible for capping or stabilizing of the synthesized CuONPs were expressed in fig (5). Taking the spectrum of tuber Extract as control the involvement of different functional groups of *Colocasia esculenta* tuber extract in reducing and stabilizing process of nanoparticles synthesis was evaluated. Absorbance bands at 3248, 2127, 1362, and 752 cm^{-1} were observed in the spectrum of *Colocasia esculenta* tuber extract. A broad band at 3248 cm^{-1} was due to the O-H stretching of alcohol compounds. The peaks at 1827 and 1363 $cm^{-1}$are Containing $-NH_2$ group and C=O groups of flavonoids [41-42]. 775 cm^{-1} is containing C-H bonds. FTIR spectrum of CuONP for the peak appeared at 3393, 1632, 1015, 709, and 562 cm^{-1}. The peaks at 3393, 1632 and 1015 cm^{-1} corresponding to hydroxyl group (-OH) Stretching, hydroxyl (-OH) bending and C-O stretching respectively. The Narrow bands at 562 confirm the formation of CuONPs.

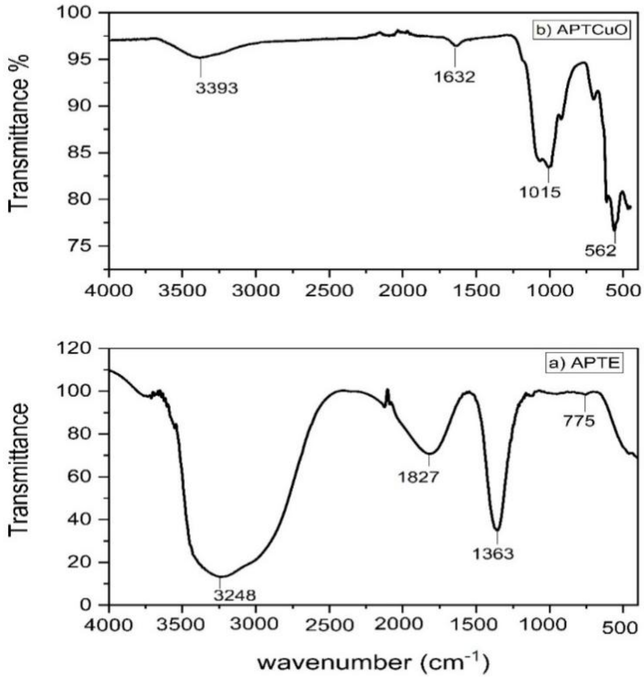

Fig 4. FTIR spectrum of *Colocasia esculenta* extract and *Colocasia esculenta* green synthesized CuO NPs

3.1.4. Scanning Electron Microscope (SEM)

The morphology of CuO nanoparticles studied by SEM analysis. Fig (6) showa the surface morphology of the copper oxide nanoparticles was observed in the SEM image. It seems that the diameter of CuO nanoparticles range between 60-80 nm as calculated by image J programme [43].

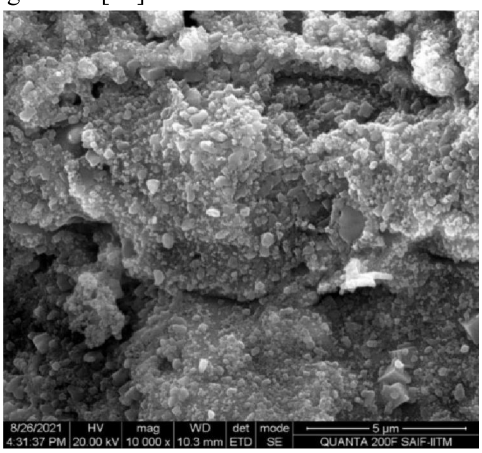

Fig 5. SEM image of Green synthesized copper oxide nanoparticles**.**

3.1.5. Energy dispersive X-ray Diffractive (EDX) analysis

The Energy Dispersive X-ray (EDX) study was carried out for the green synthesized CuO nanoparticles to know about the elemental composition. EDX confirm the presence of Cu and O signals of CuO nanoparticles as shown in table 1. The elemental analysis of nanoparticles yields Cu 78.07% and 21.93% of oxygen which process that the produce nanoparticles is in its highest purified form [44].

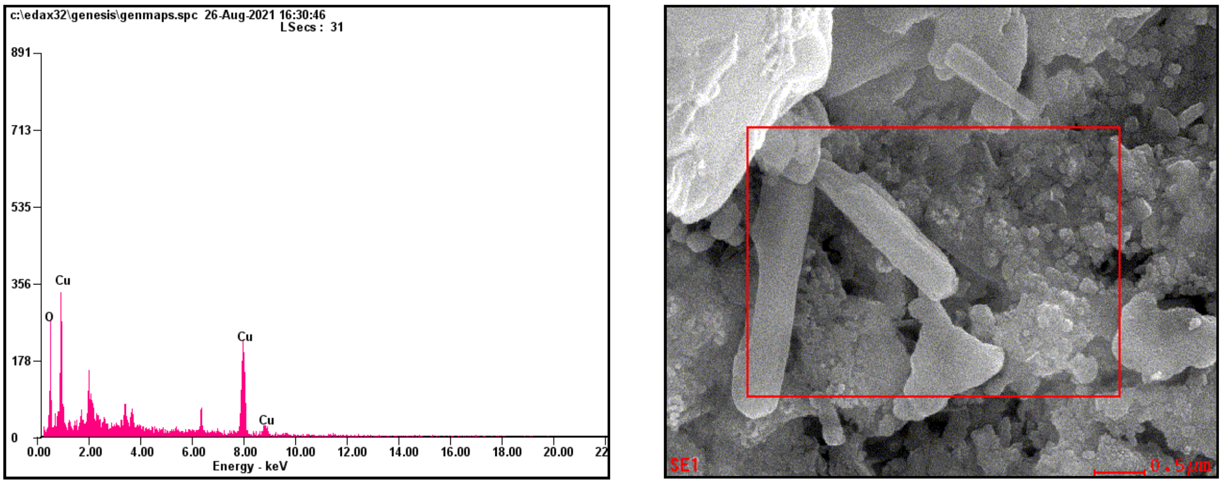

Fig 6. EDX spectrum of copper oxide nanoparticles

Table 1: EDX analysis for synthesized copper oxide nanoparticles.

S.NO	Element	Weight (%)
1.	Cu	78.07
2.	O	21.93

3.1.6 Transmission Electron Microscope (TEM) : The detailed morphological and size analyses of green synthesized copper oxide nanoparticles were studied using electron microscope and results shown in fig 7

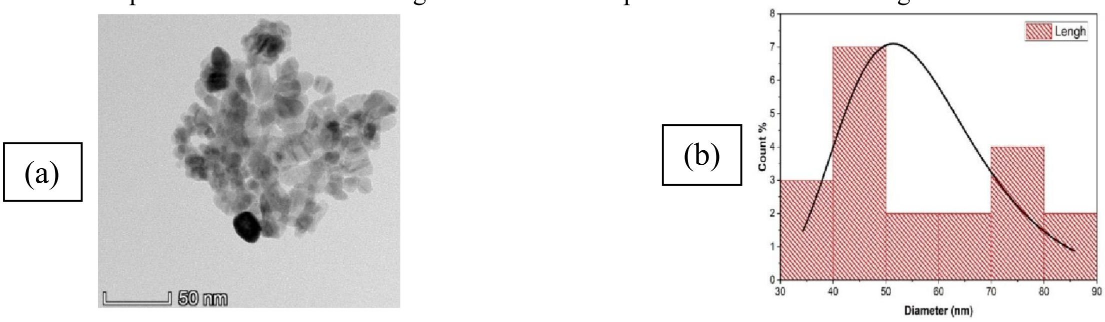

Fig 7. a) HR-TEM image b) Histogram of APT copper oxide nanoparticles

3.2 Thermodynamics

Thermodynamic parameters are important in adsorption studies they provide a better understanding of the effect of temperature on the adsorption process. The standard changes in Gibb's energy (ΔG^O) enthalpy (ΔH^O) and entropy (ΔS^O) were calculated using the following

$\Delta G^O = -RT \ln K$ Eq. (10)

$\log K = \Delta S^o/2.303\ R - \Delta H^o/2.303\ RT$ Eq. (11)

Where R is the universal gas constant (8.314 J) T is the absolute temperature (k) and K is the equilibrium constant. Plots of ln K vs 1/T should be a straight line as shown in fig (19).

All thermodynamic parameters were tabulated in table (4). ΔG^ovalues were negative at all temperature studies. During the adsorption process the negative values of ΔG^o for the experimental temperature indicate spontaneous and favourable MR adsorption onto the surface of GS-CuONPs.

The negative enthalpy (ΔH^o) values obtained indicate the adsorption process was exothermic in nature. The positive entropy change (ΔS^o) values of corresponds to an increase in randomness occurred at solid-solution interface during the adsorption process. This is indirectly showing the affinity of adsorbent towards dye molecules [55].

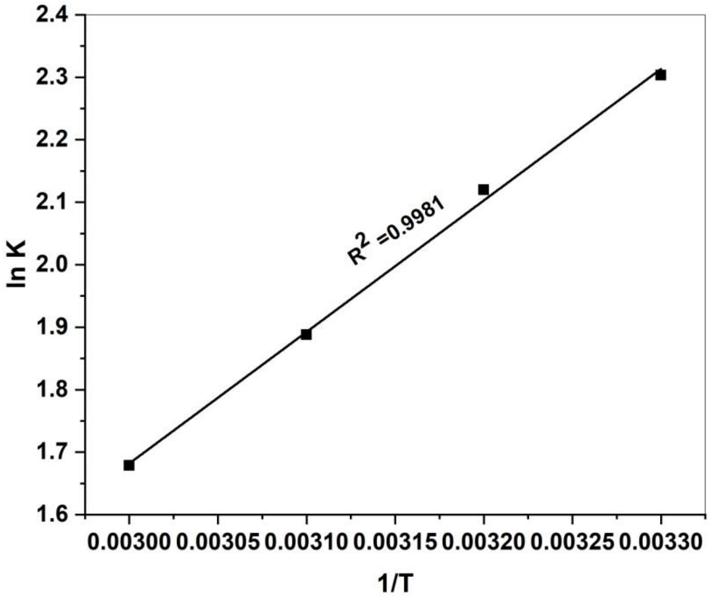

Fig 8. Thermodynamic parameter plot for the adsorption of MR onto GS-CuONPs

Table (2). Thermodynamic parameters values for adsorption of MR onto GS-APTCuONPs

Temperature (K)	ΔG^o ($J.mol^{-1}$)	ΔH^o ($KJ.mol^{-1}$)	ΔS^o ($J.mol^{-}K^{-1}$)	R^2
298	-5.7063	-40.2875	88.6589	0.9981
308	-5.4281			
318	-4.9915			
328	-4.5788			

IV. CONCLUSION

In this study, an eco-friendly and convenient green method from copper chloride dihydrate solution using *Colocasia esculenta* Tuber extract was developed. The green synthesized copper oxide nanoparticles were confirmed by UV-vis, XRD, FT-IR, SEM-EDX, TEM . The synthesized copper oxide nanoparticles can be used as a promising catalyst for the removal of methyl red dye. The adsorption parameters such as initial dye concentration, Adsorbent dosage, pH, contact time, and Temperature also studied. The adsorption showed that the adsorption was best fitted to the Langmuir isotherm model as compared to the Freundlich and Temkin isotherm model. The rates of sorption were best fitted the pseudo second order kinetics. Thermodynamic study showed the spontaneous and exothermic in nature of biosorption process due to negative values of free energy change and negative values of enthalpy change. It was concluding this research found that the copper oxide nanoparticles with high dye adsorption capacity and good alternative for the removal of methyl red dye from aqueous solution very effectively.