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SYNTHESIS OF COPPER NANOPARTICLES USING AMORPHOPHALLUS PAEONIIFOLIUS TUBER EXTRACT AND THEIR PHOTODEGRADATION ACTIVITIES ON METHYL ORANGE DYE

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ABSTRACT
The current study focuses on investigating the removal of methyl orange dye using green-synthesized copper oxide nanoparticles derived from Amorphophallus paeoniifolius tubers. The nanoparticles were characterized using various techniques, including UV-Vis spectroscopy, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX). Key parameters for adsorption, such as pH, contact time, adsorbent amount, and initial dye concentration, were examined. Additionally, the energy requirements for the pseudo-first and pseudo-second-order kinetic models were evaluated. This green synthesis method is efficient, cost-effective, and time-saving, leading to the production of copper oxide nanoparticles on a large scale.
Keywords: Amorphophallus Paeoniifolius TUBER, Methyl Orange, Cuo Np's, Photodegradation.
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INTRODUCTION

The release of effluents of azo colors into the water is wild on the grounds that the colors corrupt to cancer-causing and poisonous items. Among a wide cluster of techniques utilized for the treatment of wastewater, adsorption has gotten a large number since it is straightforward, savvy, and dependable. Subsequently, looking for successful adsorbents is progressively upgrading because most of the generally utilized adsorbent materials are extravagant, hard to recuperate and reuse, and furthermore need significant expense for actuation and reactivation.[1-4] The union course of nanomaterial's and the examination of their applications and properties are one of the rousing pieces of the high-level logical exploration. Different physical and compound techniques are utilized for the blend of metal oxide nanoparticles; be that as it may, the expectedly utilized strategies, for example, sol-gel, substance decrease, and aqueous are exorbitant techniques and non-eco-accommodating by delivering poisonous synthetics as finished results. Subsequently, eco-accommodating strategies for the combination of metal oxide nanoparticles are pulled into consideration, for example, the utilization of plant concentrate, microorganisms, and green growth. Among plant removes are engaged with redox responses, which diminish metal particles to shape nanoparticles. Metabolites like sugar, terpenoids, polyphenols, alkaloids, phenolic acids, and proteins assume fundamental parts in the decrease of metal particles to nanoparticles and support the security of nanoparticle.[5 -9] Previous studies have explored the synthesis of nanoparticles from various plant extracts, including Acalypha indica, Phyllanthus amarus, Terminalia arjuna, Calotropis gigantea, Malva sylvestris, Cassia alata, Gloriosa superba, and Carica papaya, and have reported on their antimicrobial activities. This study focuses on the use of Amorphophallus paeoniifolius tuber extracts for synthesizing nanoparticles, marking the first detailed report on the application of this plant for the green synthesis of copper oxide (CuO) nanoparticles. Amorphophallus paeoniifolius, commonly known as elephant foot yam or "Karunai Kizhangu" in local terms, is an herbaceous perennial in the Araceae family with yellow flesh and high

starch content. It is widely available in Bangladesh at a low cost. This plant contains various phytochemicals, including steroids, flavonoids, carbohydrates, tannins, saponins, and proteins, which contribute to its medicinal uses for conditions such as cough, vomiting, bronchitis, asthma, and anorexia. Additionally, these phytochemicals can facilitate the synthesis of metal nanoparticles through the reduction of metal ions. Recent research has reported the synthesis of silver nanoparticles (AgNPs) using Amorphophallus paeoniifolius tuber extracts and their potential antibacterial activity. In this study, we present a simple, cost-effective, and eco-friendly method for synthesizing copper oxide nanoparticles (CuO NPs) at room temperature, using the tuber extract of Amorphophallus paeoniifolius as a reducing and stabilizing agent, in adherence with the principles of green chemistry.[10-18]

EXPERIMENTAL

Preparation of Methyl Orange Solution

The Methyl Orange color has substance recipe $C_{23}H_{25}N_2Cl$ (sub-atomic weight = 364.90, λ max = 618nm).[19] Logical reagent was involved with no further sanitization notwithstanding deionized water, copper chloride di-hydrate ($CuC_{l2}.2H_2O$) Sodium hydroxide, hydrochloric corrosive, and ethanol.

Preparation of Amorphophallus Paeoniifoliusis Tuber Extract

Amorphophallus paeoniifolius tuber were gathered from close to a Vegetable market in Chennai (Tamilnadu), cleaned from suspended soil, and Mud washed a few times whipped into little species, and dried in Daylight for 4 days. In this manner, the dried tuber is ground with an electric processor and put away from wet. 10g of this powder was added to (200 ml) of refined water and bubbled for 15 minutes. The shade of arrangement changes into brown. The acquired arrangement was cooled at room temperature and sifted. Centrifuged the filtrate at 1200rpm for 10 minutes. And afterward sifted earthy colored arrangements change at pH = 12 and put away the concentrate at room temperature until use.

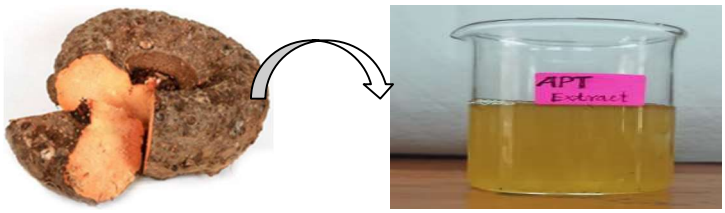

Fig.-1: Amorphophallus Paeoniifoliusis Tuber Extract

Preparation of Copper Oxide Nanoparticles

Take 50ml of Amorphophallus paeoniifolius tuber concentrate and afterward 0.1M of copper chloride di-hydrate ($CuCl_2.\ 2H_2O$) arrangement added at Room temperature where the variety changed from light blue to yellowish dim Variety was framed. It was then separated and dried in the electrical stove for 24 hrs. at 100ºC. The dried example was saved in a mute heater for 4 hours at 500ºC. The Green integrated CuO NPs are shaped at uniform molecule size and put away for additional portrayal and utilizations.

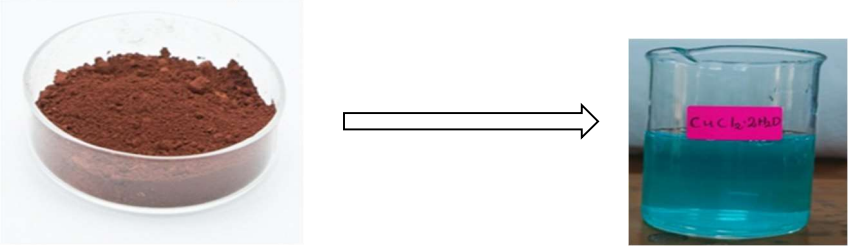

Fig.-2: Green synthesized APT CuO Nanoparticle

Preparation of Adsorbate

The designed variety, for instance, Methyl Orange was purchased from Kevin's study emphases in Chennai. A stock design of (1000mg/L) was prepared by dissolving 1.0 g of a variety of refined water. Refined water was used for setting up all the courses of action and chemical reagents. The level of the expulsion of variety from the color arrangement is decided by the accompanying recipe,

$$\% \text{ removal of colour } = \frac{(Co - Ce)}{Co} X\ 100 \quad (1)$$

The most extreme MG take-up qe (in mg g-1) was determined as shown below:

$$q_e = [(Co\text{-}Ce)V]/M \quad (2)$$

Where, Co and Ce are the beginning and last MO grouping in mg/L, separately W is how much CuO NP (in g), and V is the volume of dye solution (MO)

RESULTS AND DISCUSSION

Characterization Study of Copper Oxide Nanoparticles

UV- Visible Adsorption Spectroscopy for Copper Nanoparticles

The Green methodology for the arrangement of copper oxide nanoparticles utilizing Amorphophallus Paeoniifolius tuber remove was accounted for. UV-Vis spectroscopy was utilized to screen the course of the bio decrease of $CuCl_2$. $2H_2O$ to CuO nanoparticles and to screen the arrangement and enhancement of CuO Np's. Variety change was the direct data for the development of CuO NP's which was additionally affirmed by the presence of trademark Surface Plasmon Reverberation (SPR) top between 206 to 212 nm Fig.-3. Shows the UV-noticeable assimilation range of copper oxide nanoparticles. The range showed the absorbance top at 242 nm relating to the trademark band of copper oxide nanoparticle.[20]

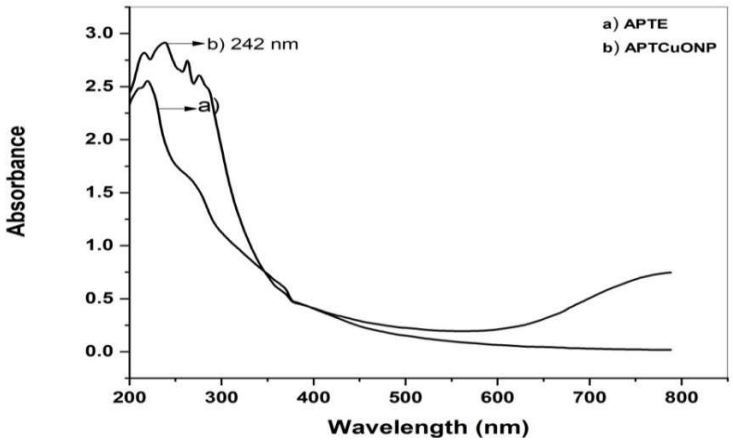

Fig.-3: UV-Visible Adsorption Spectrum of a) APT Extract and b) APT CuO NP's

Fourier Transform-Infrared (FT-IR) Spectroscopy

FT-IR examination was utilized to research the presence of a few utilitarian gatherings in both the APTE and the orchestrated CuO NPs which are liable for diminishing as well as covering specialists. Figure-4 shows the FT-IR assimilation spectra of green orchestrated CuO NPs and APTE in the scope of 400 cm-1 to 4000 cm^{-1}.

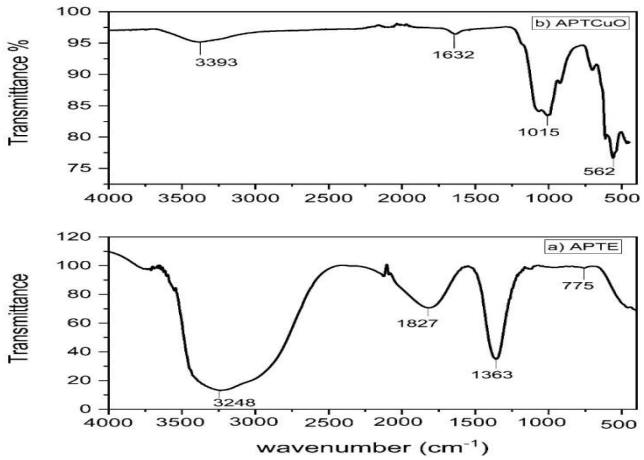

Fig.-4: FTIR Spectrum of a) Amorphophallus Paeoniifolius Tuber b) CuO NP's

Absorbance groups at 3248, 2127, 1362, and 752 cm-1 were seen in the range of Amorphophallus Paeoniifolius tuber remove. A wide band at 3248 cm^{-1} was because of the O-H extending of liquor compounds. The tops at 1827 and 1363 cm^{-1} contain - NH_2 bunch and C=O gatherings of flavonoids [21]. 775 cm-1 is because of C-H bonds. FTIR range of CuO NPs for the pinnacle showed up at 3393, 1632, 1015, 709, and 562 cm^{-1}. The tops at 3393, 1632, and 1015 cm^{-1} relate to hydroxyl bunch (- Goodness) Extending, hydroxyl (- Gracious) twisting, and C-O extending separately. The Tight groups at 562 affirm the arrangement of CuO Np's.

XRD Pattern Analysis

The copper oxide nanoparticles integrated by utilizing the green strategy from the plant Amorphophallus Paeoniifolius tuber separate. To assess the glasslike design, size, and virtue of the pre-arranged CuO Np's, the XRD investigation was performed [22] Figure-5 shows diffraction tops for green integrated CuO NP's were seen at 2θ upsides of Gloats plot for 33.4O ¬(110), 35.4O (002), 38.8O (111), 48.2 O (200), 55.23 O (202), 59.3 O (020) and 62.2 O (202), separately, was utilized to portray the monoclinic construction of CuO NP's.

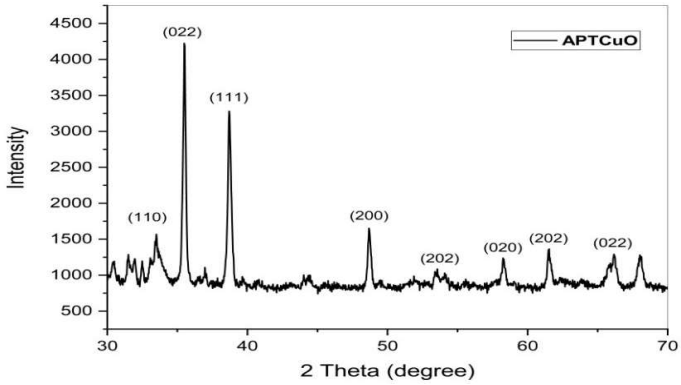

Fig.-5: X-ray Diffraction Pattern of APT Extract- Mediated Synthesized CuO NP's

The typical molecule size of blended copper oxide nanoparticles was determined utilizing Debye-Scherrer's recipe.

$$D = 0.9\lambda/\beta \text{ Cos } \theta$$

A sharp top at 2θ =35.4 and 38.8 with the diffraction of the (022) and (111) plane demonstrates that affirmation of CuO Np's. The typical crystallite size in the examples of CuO NPs is below 38.91nm.

Scanning Electron Microscope (SEM) Analysis

The morphology and surface characteristics of the synthesized CuO nanoparticles (NPs) were analyzed using scanning electron microscopy (SEM), with the resulting micrograph shown in Fig.-6. The nanoparticles were predominantly spherical and exhibited minimal agglomeration. Previous studies have similarly reported the circular shape of CuO NPs. Particle size analysis using Image software indicated an average particle size of 59.99 nm. The particle size distribution of CuO NPs observed in this study is consistent with findings from previous research.[23-26]

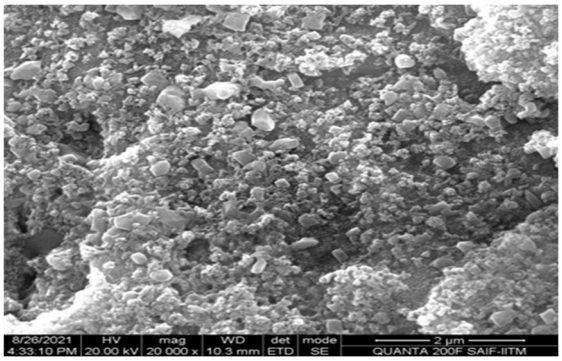

Fig.-6: SEM Image of Green Synthesized Copper Oxide Nanoparticles

Energy Dispersive X-Ray Diffractive (EDAX) Analysis

To acquire further knowledge into the highlights of the green blended CuO NPs, the compound structure of the NPs was investigated utilizing EDAX Fig.-7. The energy-dispersive spectra of the examples obtained from the SEM-EDS uncovered that the example arranged by utilizing Amorphophallus paeoniifolius tuber remove has unadulterated CuO stages. The outcomes demonstrate that the response item is made out of high virtue CuO NP's which concurs with the outcome acquired from XRD. The weighting structure obtained from the EDAX investigation of the standardized range was Cu (78.07%) and oxygen (21.93%). EDAX additionally uncovered the development of nonstoichiometric CuO NPs with oxygen opening which could prompt better antibacterial movement.[27]

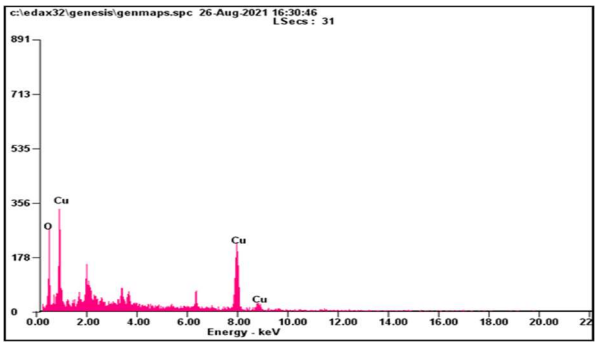

Fig.-7. EDAX Spectrum of Copper Oxide Nanoparticles

Transmission Electron Microscope (Tem)

The point-by-point morphological and size examinations of green combined copper oxide nanoparticles were concentrated on utilizing an electron magnifying lens and the results displayed in Fig.-8. The TEM picture uncovers that the biosynthesis CuO NP's we agglomerated which are interconnected to one another and circular in shape which is likewise in concurrence with the result acquired from SEM. The gauge of the molecule is viewed as between 10-60 nm. The molecule size is determined by a histogram. The molecule size decided TEM near XRD.[28]

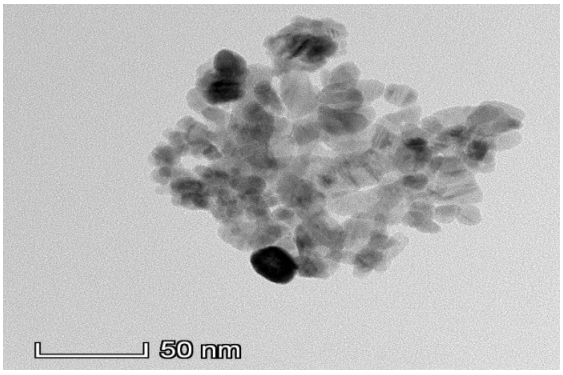

Fig.-8: HR-TEM image of Copper Oxide Nanoparticles

Effect of Adsorption Process Parameters on Methyl Orange

Effect of pH Solution

The underlying pH of the functioning arrangement was changed between 3-10 by expansion of weakening HCl and NaOH arrangement. Fig (9) shows the impact of pH on the adsorption of MG by GS-APTCuONP. The rate evacuation expanded with expanding pH = 3 to pH = 7 and from there on somewhat diminished from 8 to 10 because of achieved harmony. GS-APTCuO NP's had the greatest color adsorption close to 100% at pH 7. It very well may be seen that color adsorption was troublesome in pH <4. The lessening in the adsorption with a decline in pH might be ascribed to two reasons. As the pH of the framework diminished the quantity of negatively charged adsorbent locales diminished and the quantity of positively charged surface destinations expanded, which didn't incline toward the adsorption of +ve charged color cations because of electrostatic shock.[29] While expanding pH protonation is adversely charged adsorption destinations the electrostatic fascination between surfaces of GS-APTCuO NP's and decidedly charged cationic color become predominant.

Effect of Adsorbent Dosage

The dosage of adsorbent is moreover expected a critical part of the adsorption cycle. Since it chooses the restriction of an adsorbent for a given starting gathering of the adsorbate. The effect of adsorbent estimation was focused on a variety are removal. Different Boundaries were fixed; the measurement used was changed from 0.2 to 1.0 g against an answer volume of 50 mg/L MG color.

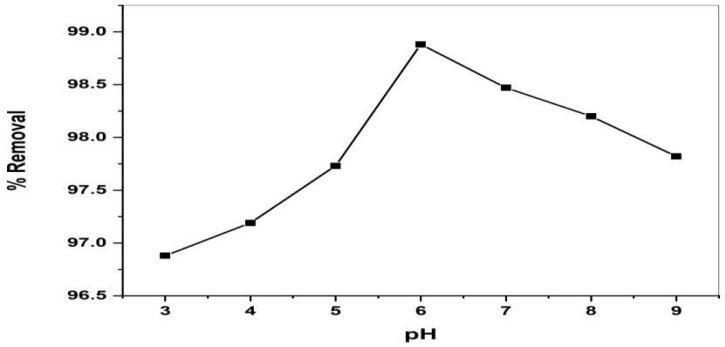

Fig.-9: Effect pH on the Adsorption of Methyl Orange onto GS-APTCuO NP's

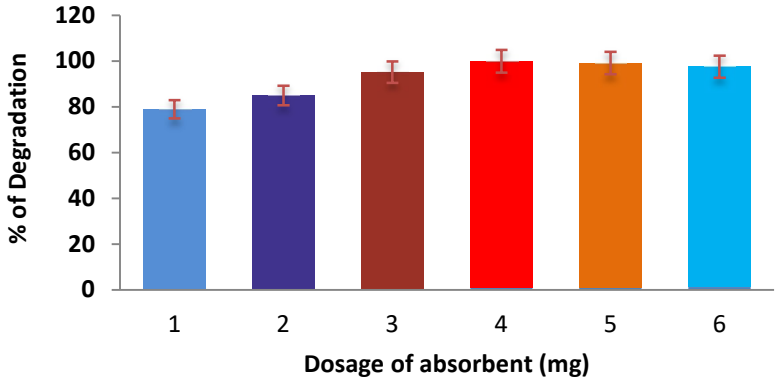

Fig.-10: Effect of Adsorbent Dose on Removal of Methyl Orange

The negligible part of the adsorbed colorant strengthened with the combined adsorbent amount inferable from expanded accessibility of sorption destinations and surface region.[30,31] The outcomes displayed in fig. (10), how much MG color evacuation expanded with expansion in adsorbent measurement from 0.2 g to 0.8. From that point, the level of color evacuation is diminished. The most extreme sorption was acquired at 0.8g. Since, the % of porosity increases with extending in adsorbent assessment.

Effect of Initial Dye Concentration of Methyl Orange

The underlying grouping of color plays a vital part in adsorption peculiarities.

The surmising of the underlying centralization of MG in the Arrangements on the pace of adsorption on Well-suited CuO NPs was examined. The trial boundary was completed with fixed adsorbent measurement ideal pH and steadily kept up with temperature. Color range 10-50 (mg/L) was contemplated and yield is portrayed in Fig.-11. The adsorption limit of GS-Able CuO NPs diminished with expanding introductory color focus 10 to 50 mg/L. The greatest adsorption of 98.94% was verified for (10mg/l) and afterward, the rate of evacuation declined the adsorption came to achieve the balance. It implies that the adsorption is exceptionally subject to introductory centralization of Methyl Orange. Since the adsorbent portion is fixed, there is a proper number of dynamic sites that subsequently rate evacuation decline with expanding focus. At low starting centralizations of MG color somewhat high rate of sorption was noticed. Because of the great proportion of adsorbent surface restricting destinations to the color focus, implying that a lesser number of color particles were seeking the accessible restricting locales on the adsorbent.[32] The expansion in the underlying convergence of the color upgrades the collaboration between the color atoms and the outer layer of the adsorbent.

Effect of Contact Time

Equilibrium time may maybe of the primary limit in the arrangement of a proficient waste treatment system and its effect on the adsorption of MG-dye on potential CuO NP's is presented. These trials have been done at a variety of seasons of contact (30-150 minutes). After each contact time, one example was eliminated and separated right away and the filtrate was investigated (Fig.-12). The sum adsorbed colors first quickly expanded, and afterward progressively diminished until the balance was reached. This is maybe because of the underlying accessibility of the most extreme number of dynamic locales which gets soaked with time.

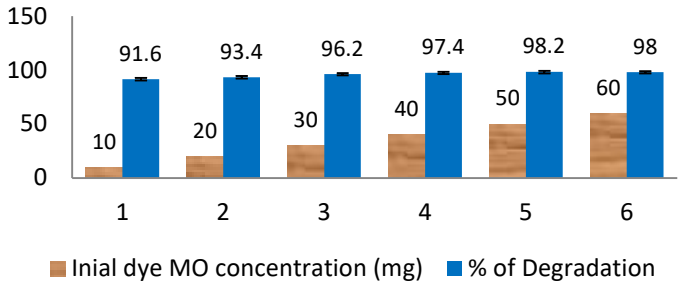

Fig.-11: Effect of Initial Concentration of MG Dye on the Adsorption of GS-APTCuO NP's

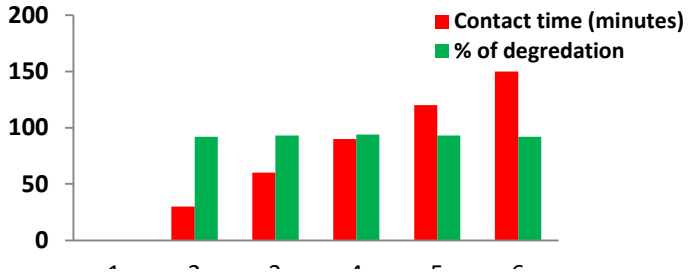

Fig.-12: Effect of contact time on the adsorption of MG onto GS-CuO NP's

The evacuation effectiveness was viewed as at the scope of 95.47.1 to 98.8% when the time ascends from 30 to an hour separately and afterward, bit by bit diminished with expanding time from 60 to 150 minutes. The outcome showed that the pre-arranged adsorbent has a short balance time which shows the adsorbent has a sufficient number of dynamic sites for a given focus. Truth be told short balance time is recommendable from the perspective of water treatment advances.

Effect of Temperature

The temperature can impact the adsorption rate. In this research the effect of temperature on MG-dye adsorption was investigated is the extent of 298-328 K (Fig.-13). The adsorption of color diminished when increment of temperature. The rate of expulsion adsorption diminished from 98.97% to 97.76% with the temperature expanded from 298K to 328K. The reduced variety of adsorption at maximum temperature was due to the incapacitating consistency between powerful sites on the adsorbent and adsorbate. A sharp decrease after 298 K in surface development at maximum temperature. From that point on, shows that the adsorption cycle is exothermic and MG variety adsorption onto CuO NPs happened essentially by physical adsorption.

Adsorption Kinetic-Studies

The pseudo-first and pseudo-2nd order were used to examine the adsorption efficiency of the CuO Np's.

(a) Pseudo 1st Order Analysis

The pseudo 1st order rate method of Lagergren's depends on solid capability and is usually stated as follows:

$$\text{Log } (q_e\text{-}q_t) = \log q_e - K_1/2.303t$$

Where qe is how much solute adsorbed at balance per unit Weight of adsorbed (mg/g), qt is how much solute adsorption whenever (mg/g), K is the adsorption predictable. This verbalization is the most

prominent kind of pseudo-first applies to the energy model. K-1 Values at various starting MG are not permanently set up from the plots of $\ln(q_e-q_t)$ versus t. Steady K1 and affiliation coefficient not permanently set up and summed up Table-2. The affiliation coefficient (R-2) respect acquired was decently hence, this model has extraordinarily horrifying relationship coefficients R-2 = 0.8027 the best fit information.

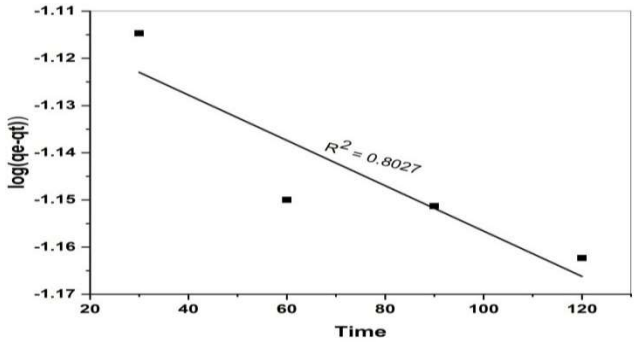

Fig.-13: Pseudo 2nd Order Kinetic Scheme Graph for Adsorption of MG-dye on GS-CuO NP's

(b) Pseudo 2nd Order Analysis

The energy information was examined utilizing the pseudo-second-request model which can be communicated as follows:

$$t/qt = 1/K_2\, qe_2 + t/qe$$

The plot of 1/qt versus t ought to give a straight connection from which qe and K2 are not set in stone from the slant and block of the plot.

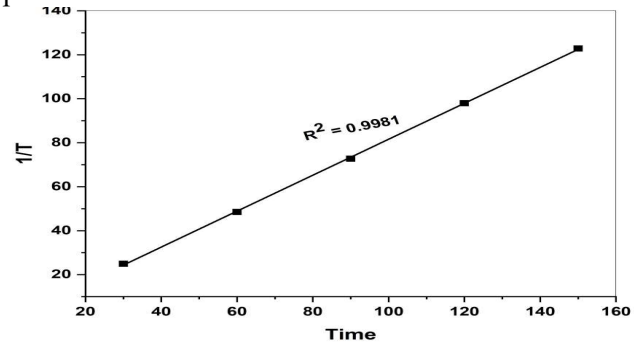

Fig.-14: Pseudo 2nd Order Kinetic Analysis for Adsorption of the MG-dye on GS-CuO

The pseudo-second-request rate steady K-2 is not entirely settled from the model as well as the relationship coefficient introduced in Table-3. The noticed R-2 (0.9981) values are exceptionally high for the pseudo 2nd order technique, where the upsides of qe are in great concurrence with q_e exp. It is consequently apparent that the pseudo 2nd order method is the suitable active scheme in depicting the adsorption cycle MG onto GS-CuO Np's.

Table-3: Adsorption kinetics of MG

Adsorption Kinetics	Parameters	Methyl Orange
Pseudo First Order	K_1 (min^{-1})	0.0012
	q_e (mg g^{-1})	0.0772
	R^2	0.8025
Pseudo Second Order	h (g^{-1} mg^{-1} min^{-1})	6.0050
	q_e (mg g^{-1})	1.2230
	R^2	0.9981

CONCLUSION

In this report, we examined a green, quick, one-pot blend of CuO NP's, CuCl2.2H2O was utilized as a wellspring of Cu, and tuber concentrate of Amorphophallus paeoniifolius was utilized as a lessening and settling specialist in this combination trail. The CuO NPs were described by UV-apparent, FT-IR, XRD, SEM-EDX, and TEM. The bunch exploratory, the impact of starting color focus, adsorbent measurement,

pH, contact time, and temperature individually. The aftereffects of the motor showed that the adsorption followed the pseudo-second-request for sorption of MG onto green blended CuO Np's. In the current work, the green method is tremendously honest, modest, economical, and eco-accommodating. The orchestrated nanoparticle could be a decent option for the removal of Methyl Orange (MO) from water-colored solutions such as tannery industry effluent, dye industries effluent, etc.

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CONFLICT OF INTERESTS

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

All authors significantly contributed to this manuscript, participated in reviewing and editing, and approved the final draft for publication. The authors' research profiles can be verified through their ORCID IDs listed below:

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