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Adsorption of Malachite Green Dye in Aqueous Solution Using Low-Cost Synthesis of Zinc Oxide Urea Formaldehyde Nanocomposite as Adsorbent

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Abstract: ***In recent decades, the world's fast industrialization has made water contamination the most serious problem in the world. Organic dyes, especially malachite green, are synthetic dyes used in the textile industries to dye silk, cotton, leather, wool, paper, etc. and consequently discharged into the water resources that pollute aquatic environments. The purpose of the research work is to study the efficiency of zinc oxide urea formaldehyde nanocomposite used as an adsorbent in the removal of malachite green dye from polluted wastewater. The main stages of this work include the synthesis of zinc oxide by the simple sol-gel method at room temperature. The synthesised nanoparticle was coated with urea formaldehyde to increase its efficiency. The characterization techniques such as XRD, FTIR, SEM, and BET of the synthesised nanomaterials show that the zinc oxide urea formaldehyde nanocomposite was successfully synthesised. The batch adsorption study of the dye onto the ZnO-UF nanocomposite was investigated with a UV-visible spectrophotometer. The application of this synthesised nanocomposites as an adsorbent successfully adsorbed more than 97% malachite green dye at a reducing dye strength of 40 PPM, doses of 0.35 g, and pH 8 within a 90-min equilibration time.***

Keywords: ***Adsorbent, Urea formaldehyde, Nanoparticles, Polluted Water, Malachite Green, Adsorption Isotherm, Textile Industry.***

I. INTRODUCTION

Water is paramountly important on our planet. But in recent decades, water pollution has been common all over the world with the rapid increasing population and vast development in different industries such as textiles, leather dyeing, cosmetics, paints, plastics, paper manufacturing, etc., which used dyes for colouring their products and also used large amounts of water and chemicals and subsequently discharged large amounts of coloured waste water, which were not degraded and hence pernicious to environmental health[1], [2]. Different types of dyes are widely used in several textile industries because of their favourable characteristics, such as their intense colour, water-soluble nature, and handy application[3]. It is estimated that approximately 10–20% of the used dyes are released into the water resources, and these dyes and their breakdown products are very hazardous for all living beings, causing serious diseases and disorders[4]. Therefore, the removal of dyes from the industrial-coloured waste water is very important before it is discharged into the aquatic ecosystem[1], [4]. Among the many synthetic dyes, malachite green (MG) is a very toxic dye. Malachite green dye is widely used in the acrylic, food, paper, and paint industries. It is also used in aquaculture as a therapeutic agent[2], [5]. The high-water solubility of MG causes water pollution and can result in mutagenesis, carcinogenesis, teratogenesis, respiratory diseases, damage to the central nervous system, digestive system, liver, kidney, spleen, lung, heart, skin, bones, and brain[6]. It can also cause infertility issues. So, it is mandatory to remove MG from aquatic resources[2]. Many methods, such as biological treatment, ultrafiltration, ion exchange, coagulation, membrane separation, oxidation, adsorption, etc., are available for the removal of organic and synthetic dyes[1], [5], [7]-[10]. But the major drawbacks of many of these methods are that they require high sludge production, are expensive and potentially hazardous to the environment, require handling and lead to residual toxic species, etc. This necessitates low-cost, economically efficient, and low-energy-use techniques for the treatment of dyes present in industrial waste water[4], [11], [12] Metal oxide-based compounds such as zinc oxide have attracted great attention as adsorbent materials due to their excellent surface area and high adsorption capacity. It is non-toxic and chemically stable. Hence, it has been utilised for wide-ranging applications[9], [13]-[16]. In the present work, zinc oxide was synthesised by the sol-gel method and coated with urea formaldehyde polymer to increase its efficiency. The synthesised zinc oxide urea formaldehyde nanocomposites are characterised by various spectroscopic techniques such as SEM, XRD, FTIR, and BET. And applied as a low-cost adsorbent to the adsorption of malachite green dye from industrial waste water.

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II. EXPERIMENTAL

A. *Materials*

Zinc Acetate Dihydrate (Zn (CH3COO)2.2H2O) ≥99% purity (Sigma Aldrich), Sodium Hydroxide (NaOH) ≥98% (Sigma Aldrich), Ethanol (CH2COOH) (analytical grade), and double distilled water. Zinc acetate dihydrate was used as a precursor, and ethanol was used as a reagent. Distilled water was used as a solvent medium. All the aqueous solutions were prepared using double-distilled water.

B. *Synthesis of zinc oxide nanostructure*

For the preparation of zinc oxide nanoparticles by using the sol-gel method, zinc acetate dehydrate was used as a precursor, sodium hydroxide was used as a precipitating agent, double-distilled water was used as the solvent medium, and ethanol was used as a reagent.

In order to prepare a sol, 20 g of zinc acetate dehydrate was dissolved in 150 ml of double-distilled water, and 80 g of NaOH was dissolved in 100 ml of double-distilled water. The solutions were stirred with constant stirring for about 10 minutes each. After being well mixed, sodium hydroxide solution was added dropwise. A large amount of white slurry was formed, and then a burette was filled with 500 ml of ethanol and titrate dropwise into the solution containing both sodium hydroxide solution and zinc acetate dihydrate. After a reaction, a white precipitate was formed.

C. *Synthesis of Zinc oxide –Urea formaldehyde nanocomposite*

20 ml of 40% formaldehyde and 10 g of urea were mixed in a molar ratio of 2:1 (w/w) in a 250 ml beaker and stirred magnetically at 60 °C for 20 min, so that urea was dissolved in formaldehyde. In this mixture, 100 mg of zinc oxide were added while stirring. After 5 minutes, 0.5 ml of concentrated H_2SO_4 was added with continuous stirring. A white precipitate was obtained, which was washed with distilled water, dried in an oven, and placed in desiccators.

D. *Preparation of Dye Solution*

The malachite green dye stock solution was made by weighing 1.00 g of powdered malachite green dye. The dye was transferred quantitatively into a 1 L measuring flask, which was then filled with distilled water to achieve a dye concentration of 1000 mgL^{-1} in the solution. The stock dye solutions (1000 mgL^{-1}) were prepared separately and stored at 4 °C in distilled water. Dilution of the stock solutions with distilled water generated the working solutions.

E. *Estimation of Dye concentration*

The dye concentration and removal efficiency of ZnO-UF nanocomposite were estimated using a UV-Vis spectrophotometer (Schimadzu UV-Spectrophotometer, Model UV-1800). For the estimation of dye in synthetic effluent, absorbance was measured at 617 nm against blank, and malachite green was used as the standard effect of experimental parameters for malachite green dye removal using ZnO-UF nanocomposites.

III. RESULT AND DISCUSSION

A. *FT-IR Analysis*

The characterization of nanostructured zinc oxide was carried out using a Bruker ALPHA-E FTIR spectrometer in the department of organic chemistry at RTM Nagpur University Nagpur. Bonding between ZnO is in the range of 400 to 700 cm^{-1}. It means that the peak clearly represents the ZnO bonds.

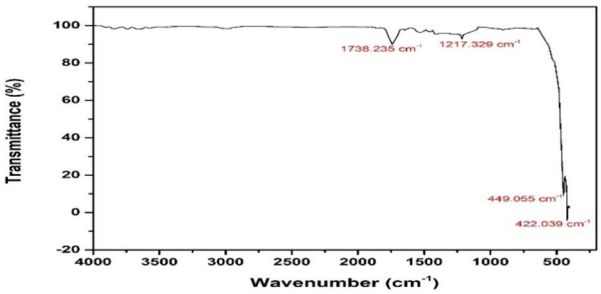


Fig.1 FTIR of ZnO

B. XRD Analysis

The XRD spectrum of prepared ZnO nanoparticles is shown in Fig. XRD analysis revealed that ZnO nanoparticles have a crystalline structure. The particle size of the prepared zinc oxide nanoparticle was calculated to be 22.97 nm based on the Debye-Scherrer equation using the full width at half maximum (FWHM) of the (101) peak[17], [18].

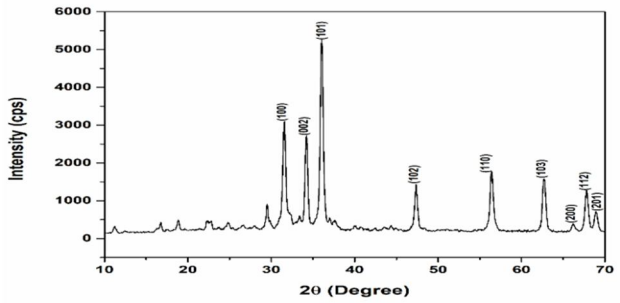


Fig. 2 XRD Spectra of ZnO

C. SEM Analysis

The morphology of the synthesised zinc oxide was homogeneous; figs. 3a and 3b show that the rod has a hexagonal structure with an approximate length and diameter of 2μ and 100 nm, respectively**.**

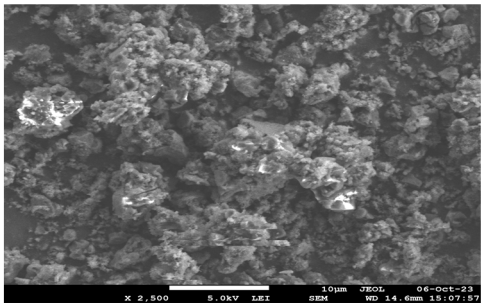


Fig. 3a SEM OF ZnO

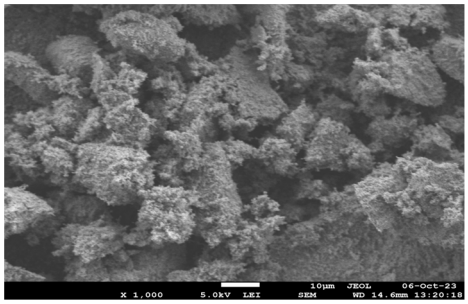


Fig 3b. SEM of ZnO

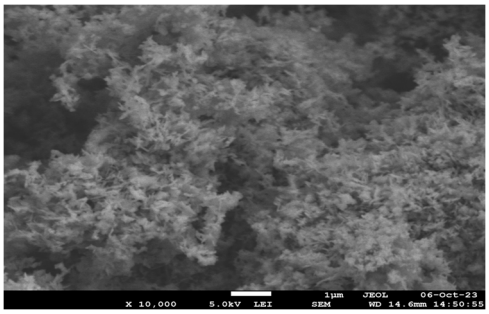


Fig. 3c SEM of ZnO-UF

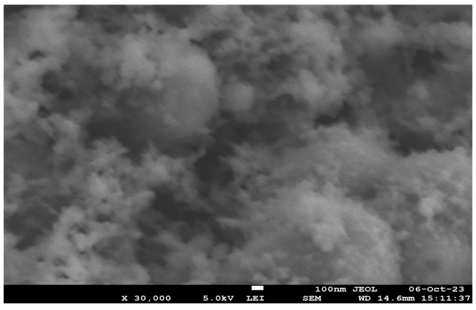


Fig. 3d SEM of ZnO-UF

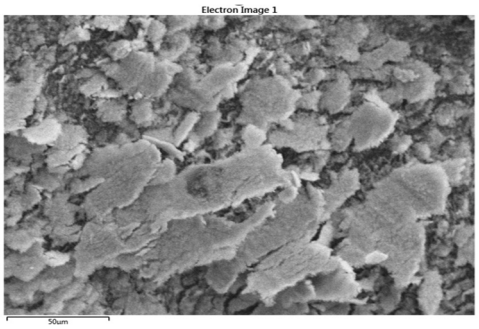


Fig.3e EDX OF ZnO

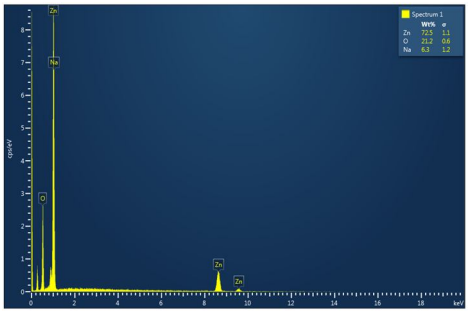


Fig. 3f EDX of ZnO

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D. BET Analysis

From the multipoint BET data, the surface area of the synthesised zinc oxide is 20.336 m^2/g, and the average pore radius is 3.19742e+o1 A.

IV. BATCH STUDY

A. Effect of initial malachite green dye concentration

Fig. 4 shows the effect of initial concentration on the removal of malachite green dye by using zinc oxide urea formaldehyde nanocomposite. The efficiency of dye removal decreased when the initial dye concentration was increased from 10 to 100 ppm. The swift adsorption at the initial contact time can be attributed to the huge accessibility of the adsorption position on the surface of metal oxides, and the adsorption rate decreases, probably due to the steady pore diffusion of the solute ion into the bulk of the adsorbent. Also, at high concentrations, the accessible site of sorption decreases. This behaviour is connected with the competitive dispersion process of the dyes through the channels and pores in metal oxides. This combative will latch the inlet of the channel on the surface and forbid the dyes to pass enormously inside the metal oxide. i.e., the adsorption occurs only on the surface of metal oxide. As the concentration of the aqueous solution increases, the rate of adsorption decreases. As the initial malachite green concentration increases from 10 mg/l to 100 mg/l, the equilibrium removal of malachite green decreases from 97% to 84%. Optimisation of concentration was done by selecting the maximum removal of malachite green at low concentration. The effect of other parameters such as various numbers of doses, variation in contact time, and variation in pH was determined by selecting a concentration of 40 ppm as optimum.

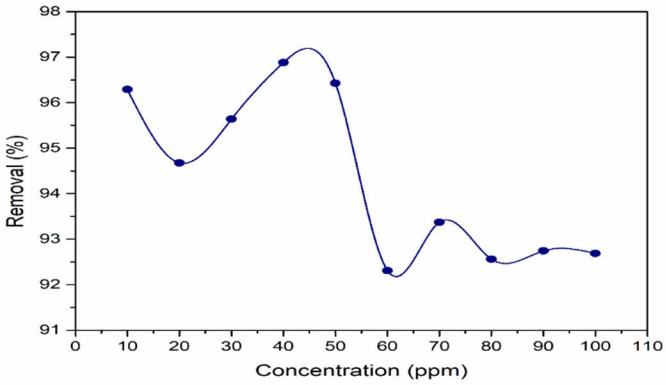


Fig. 4 Effect of initial concentration

B. Effect of contact time on adsorption

Fig. 5 clearly shows that, as the contact time increases, the adsorption of dye also increases. At equilibrium, all the active sites for the adsorption of the adsorbent get blocked, and there is no vacant side available for the adsorption of dye. The maximum dye removal efficiency was studied by varying the contact time from 10 to 100 min with an optimised initial dye concentration and an optimised nanocomposite dosage. The dye removal efficiency of 97.61% was obtained at 90 min. Hence, the contact time of 90 minutes was construed as optimal.

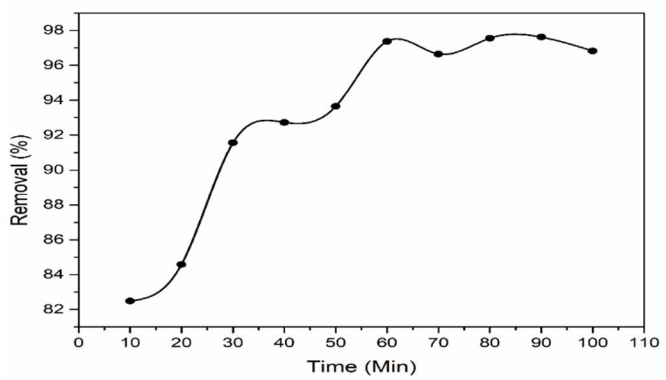


Fig. 5 Effect of contact time

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C. Effect of ZnO-UF nanocomposite Dosage on Adsorption

Fig. 6 clearly shows that, as the amount of adsorbent dose increases, the adsorption rate also increases. The optimised initial MG dye concentration of 40 PPM was maintained as constant by varying the adsorbent dosage of ZnO-UF nanocomposite from 0.05 to 0.5 mg. The dye removal efficiency increased with an increase in the dosage of nanocomposite as adsorption, from 84% to 96%. Maximum dye removal of 97.88% was obtained with a nanocomposite dosage of 0.35 mg. Probably, this occurs due to the increase in the vacancy of surface-active sites resulting from the increased adsorbent dose and agglomeration of the adsorbent. For the next parameter, the minimum dose with maximum adsorption was taken as 0.35 g with 97.88% adsorption of malachite green.

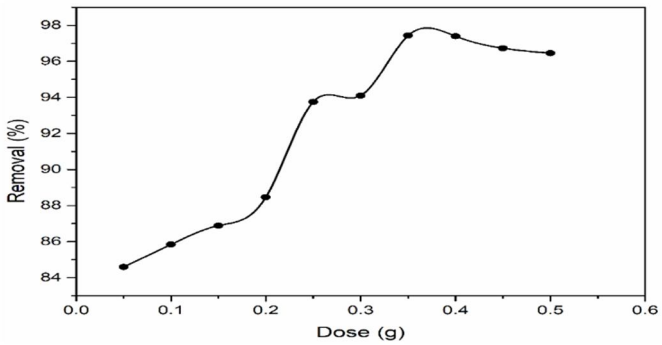


Fig. 6 Effect of Doses

D. Effect of pH on Adsorption

The pH of the solution is one of the most important factors that affects the adsorption of the dye by nanocomposite. The pH factor affects the chemistry of both adsorbent and adsorbate. The effect of pH on the adsorption of malachite green dye onto the zinc oxide urea formaldehyde was studied at pH 4–10 for an initial dye concentration of 40 mg/l. From Fig. 4, it was observed that the percentage of adsorption of dye increased with increased pH of the solution. It is noticeable that the maximum (97.83%) removal of malachite green is observed at pH 8. The pH was set as required with 0.1 M hydrochloric acid or 0.1 M sodium hydroxide. During the reaction, the pH factor not only affects the surface charge of the adsorbent but also the speciation and degree of ionisation of the adsorbent.

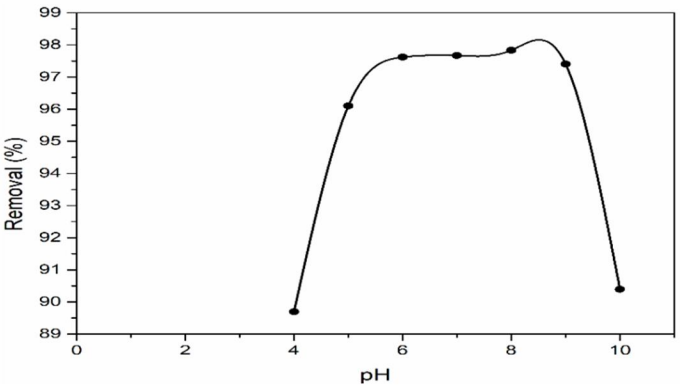


Fig. 7 Effect of pH

V. ADSORPTION ISOTHERM

The experimental adsorption equilibrium data were assessed to explore the mechanism of adsorption onto zinc oxide urea formaldehyde nanocomposite using two adsorption models, such as the Langmuir and Freundlich models, in their formats from the slopes and intercepts of which the correlated constants are assessed (tables 1 and 2). By fitting the investigational data to both of these isotherm models and taking into consideration the higher values of correlation coefficients ($R^2 \sim 1$), it is deduced that the Langmuir isotherm model is the best suitable model to explain the malachite green adsorption onto zinc oxide urea formaldehyde nanocomposite.

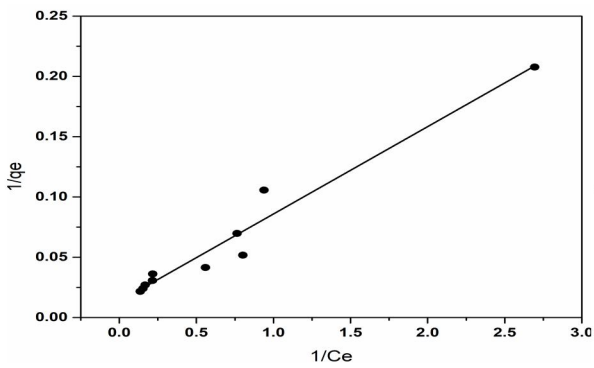


Fig. 8 The Langmuir adsorption isotherm

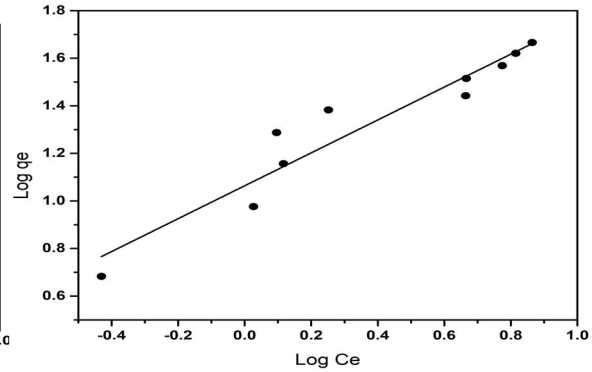


Fig. 9 The Freundlich adsorption isotherm

TABLE I

Langmuir Adsorption Parameter

Intercept	0.01335
Slope	0.07246
q_{max}(mg/g)	74.90636704
K_L	0.18423958
R_L	0.11948
R^2	0.95482

TABLE II

Freundlich adsorption parameter

Intercept	1.06367
Slope	0.69164
1/n	0.69164
K_f	11.57897
R^2	0.90862

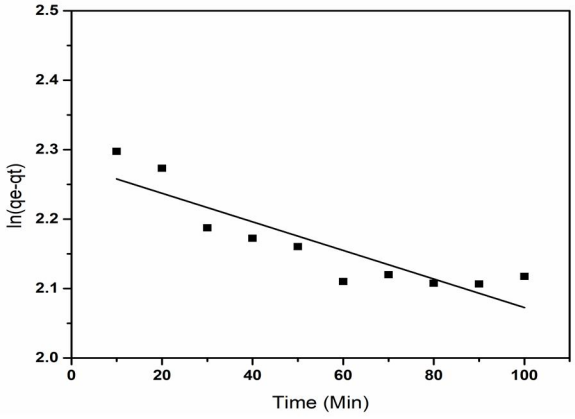


Fig. 10 Pseudo first order

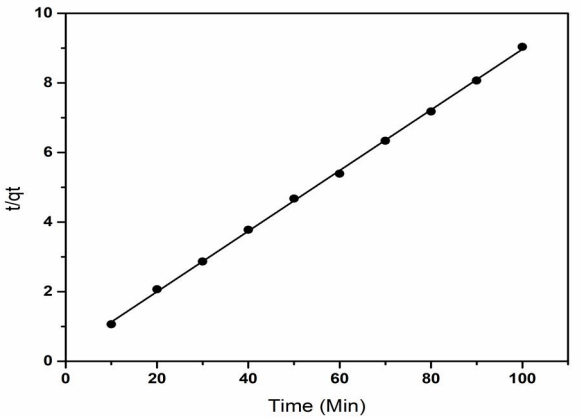


Fig. 11 Pseudo second order

TABLE III

Pseudo First Order Parameters

Intercept	2.27831
Slope	-0.00206
qe(mg/g)	9.760172
K_1	-0.0000206
R^2	0.76965

TABLE IV

Pseudo Second Order Parameters

Intercept	0.25436
Slope	0.0871
q_e(mg/g)	11.48106
qe^2	131.8147
K_2	0.029825
R^2	0.99945

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VI. ADSORPTION KINETIC

The kinetics of malachite green adsorption onto the zinc oxide urea formaldehyde surface were evaluated using different kinetic models, such as pseudo-first-order and pseudo-second-order. The varying parameters were calculated from the plots of the kinetic model equation (Tables 3 and 4). Among both of these models, the criteria for their applicability are the correlation coefficient (R^2) and the concurrence between the calculated and experimental values of $q_{e.}$ The higher values of $R^2 \sim 1$ and near about the same experimental and calculated values of q_e indicate that the system follows a pseudo-second-order kinetic model (tables 3 and 4).

VII. CONCLUSION

In this work, the aim is to synthesise zinc oxide by the simple sol-gel method and characterise it. The synthesised zinc oxide is encapsulated with polymer urea formaldehyde in the ratio 1:2 to increase its efficiency. The nanocomposite zinc oxide urea formaldehyde provides an economically cheap, efficient, and eco-friendly approach for the removal of malachite green from wastewater. The studied initial malachite green concentration, adsorbent dose, contact time, and pH affected the adsorption yield notably. The Langmuir isotherm gave a better fit into the adsorption isotherm than the Freundlich adsorption isotherm. The kinetic study of malachite green on zinc oxide urea formaldehyde was performed based on pseudo-first order and pseudo-second order. The resultant data indicate the applicability of the pseudo-second-order kinetic model. The present study shows that due to the coating of urea formaldehyde on zinc oxide, the properties and applications of the present material changed drastically, and it was applicable to water remediation techniques.

REFERENCES

[1] K. Y. Kumar, H. B. Muralidhara, Y. A. Nayaka, J. Balasubramanyam, and H. Hanumanthappa, “Low-cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution,” Powder Technol, vol. 246, pp. 125–136, Sep. 2013, doi: 10.1016/j.powtec.2013.05.017.

[2] R. Sarathi et al., “5 Journal of Chemical Reviews Photocatalytic Degradation of Malachite Green Dye by Metal Oxide Nanoparticles-Mini Review Photocatalytic Degradation of Malachite Green Dye by Metal Oxide Nanoparticles-Mini Review,” J. Chem. Rev, vol. 5, no. 1, 2023, doi: 10.22034/JCR.2023.

[3] A. A. Sabrin A, “Textile Dye Removal from Wastewater Effluents Using Chitosan-ZnO Nanocomposite,” J Text Sci Eng, vol. 05, no. 03, 2015, doi: 10.4172/2165-8064.1000200.

[4] D. Nayeri and S. A. Mousavi, “Dye removal from water and wastewater by nanosized metal oxides - modified activated carbon: a review on recent researches,” Journal of Environmental Health Science and Engineering, vol. 18, no. 2. Springer Science and Business Media Deutschland GmbH, pp. 1671–1689, Dec. 01, 2020. doi: 10.1007/s40201-020-00566-w.

[5] W. S. Al-Arjan, “Zinc Oxide Nanoparticles and Their Application in Adsorption of Toxic Dye from Aqueous Solution,” Polymers (Basel), vol. 14, no. 15, Aug. 2022, doi: 10.3390/polym14153086.

[6] A. A. Alanazi, “Investigation of malachite green removal using graphene oxide-zinc oxide composite from aqueous solution: synthesis, characterization and application,” Desalination Water Treat, vol. 293, pp. 243–252, May 2023, doi: 10.5004/dwt.2023.29519.

[7] S. Modi et al., “Recent and Emerging Trends in Remediation of Methylene Blue Dye from Wastewater by Using Zinc Oxide Nanoparticles,” Water (Switzerland), vol. 14, no. 11. MDPI, Jun. 01, 2022. doi: 10.3390/w14111749.

[8] P. Saravanan, R. Gopalan, and V. Chandrasekaran, “Synthesis and Characterisation of Nanomaterials,” 2008.

[9] V. Srivastava, D. Gusain, and Y. C. Sharma, “Synthesis, characterization and application of zinc oxide nanoparticles (n-ZnO),” Ceram Int, vol. 39, no. 8, pp. 9803–9808, Dec. 2013, doi: 10.1016/j.ceramint.2013.04.110.

[10] V. M. Muinde, J. M. Onyari, B. Wamalwa, and J. N. Wabomba, “Adsorption of malachite green dye from aqueous solutions using mesoporous chitosan–zinc oxide composite material,” Environmental Chemistry and Ecotoxicology, vol. 2, pp. 115–125, Jan. 2020, doi: 10.1016/j.enceco.2020.07.005.

[11] T. M. Tamer et al., “Formation of zinc oxide nanoparticles using alginate as a template for purification of wastewater,” Environ Nanotechnol Monit Manag, vol. 10, pp. 112–121, Dec. 2018, doi: 10.1016/j.enmm.2018.04.006.

[12] Z. Monsef Khoshhesab and S. Souhani, “Adsorptive removal of reactive dyes from aqueous solutions using zinc oxide nanoparticles,” Journal of the Chinese Chemical Society, vol. 65, no. 12, pp. 1482–1490, Dec. 2018, doi: 10.1002/jccs.201700477.

[13] R. Saravanan, V. K. Gupta, T. Prakash, V. Narayanan, and A. Stephen, “Synthesis, characterization and photocatalytic activity of novel Hg doped ZnO nanorods prepared by thermal decomposition method,” J Mol Liq, vol. 178, pp. 88–93, Feb. 2013, doi: 10.1016/j.molliq.2012.11.012.

[14] R. Saravanan et al., “ZnO/Ag nanocomposite: An efficient catalyst for degradation studies of textile effluents under visible light,” Materials Science and Engineering C, vol. 33, no. 4, pp. 2235–2244, May 2013, doi: 10.1016/j.msec.2013.01.046.

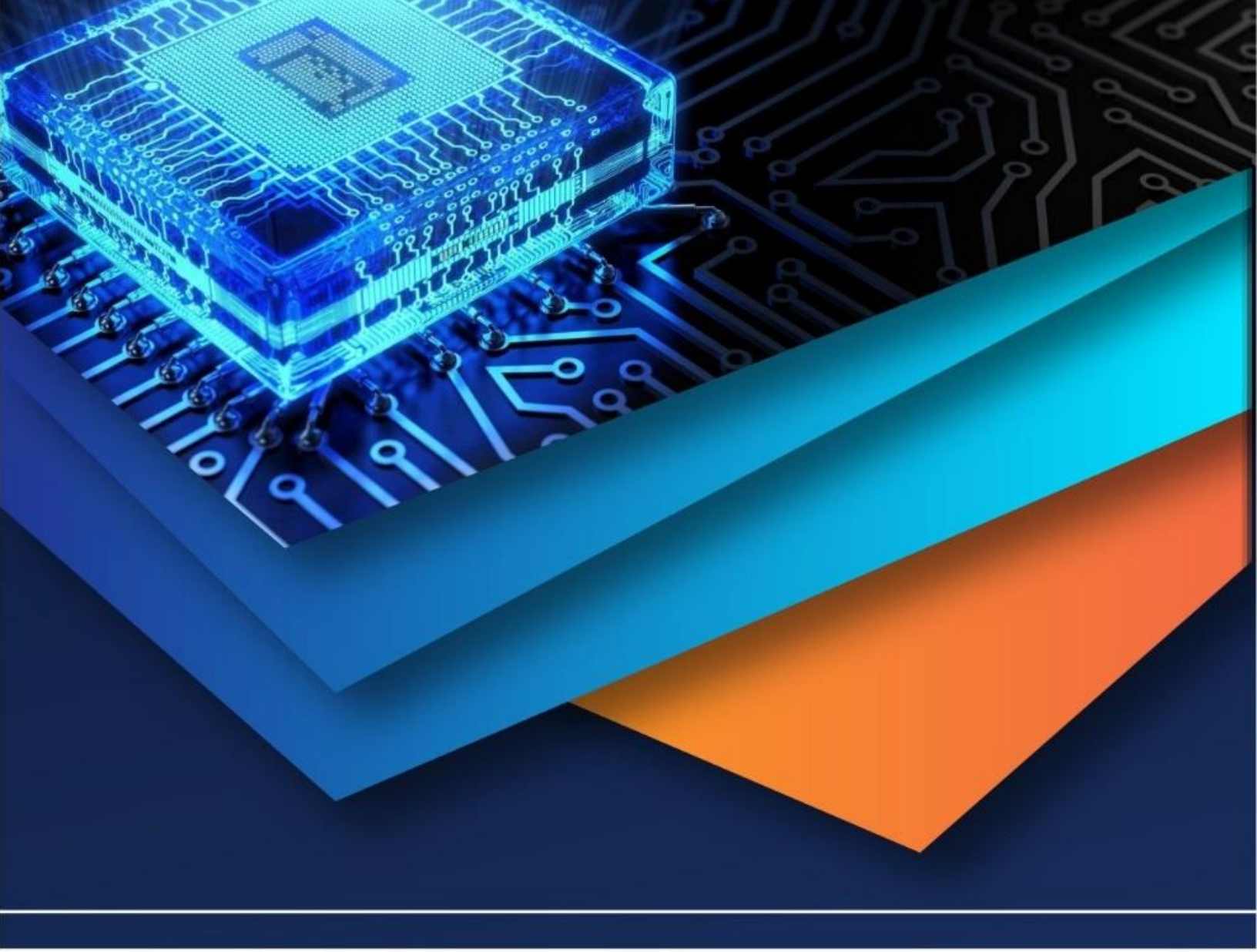
[15] R. Saravanan et al., “ZnO/Ag/CdO nanocomposite for visible light-induced photocatalytic degradation of industrial textile effluents,” J Colloid Interface Sci, vol. 452, pp. 126–133, Aug. 2015, doi: 10.1016/j.jcis.2015.04.035.

[16] R. Saravanan, V. K. Gupta, V. Narayanan, and A. Stephen, “Comparative study on photocatalytic activity of ZnO prepared by different methods,” J Mol Liq, vol. 181, pp. 133–141, May 2013, doi: 10.1016/j.molliq.2013.02.023

[17] M. Ghaedi, F. N. Azad, K. Dashtian, S. Hajati, A. Goudarzi, and M. Soylak, “Central composite design and genetic algorithm applied for the optimization of ultrasonic-assisted removal of malachite green by ZnO Nanorod-loaded activated carbon,” Spectrochim Acta A Mol Biomol Spectrosc, vol. 167, pp. 157–164, Oct. 2016, doi: 10.1016/j.saa.2016.05.025.

[18] J. N. Hasnidawani, H. N. Azlina, H. Norita, N. N. Bonnia, S. Ratim, and E. S. Ali, “Synthesis of ZnO Nanostructures Using Sol-Gel Method,” Procedia Chem, vol. 19, pp. 211–216, 2016, doi: 10.1016/j.proche.2016.03.095.

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