

Sustainable Nanotechnology: Utilizing Ananas Comascus peel extract Iron Oxide Nanoparticles (AC-Fe₂O₃ -NPs) for Enhanced Congo Red dye Adsorption Using Response Surface Methodology (RSM)

Sivakumar Bandaru¹ , Velaga P V S Sai Pranai², Pulipati King³ , Meena Vangalapati^{4*}

ABSTRACT

The synthesis approach focuses on minimizing the use of hazardous chemicals, utilizing nanotechnology for the remediation of toxic pollutants in wastewater, and ensuring that the synthesized Nanoparticles exhibit minimal environmental impact. In the present study, Ananas comosus extract was employed for the synthesis of Iron Oxide Nanoparticles due to its excellent adsorptive properties and the presence of phytochemicals such as flavonoids, phenolics, and steroids. These bioactive compounds act as natural reducing and stabilizing agents, leading to the formation of Ananas Comosus iron oxide Nanoparticles (AC-Fe₂O₃-NPs). The synthesized AC-Fe₂O₃-NPs were characterized using SEM–EDX, XRD, and FTIR techniques to investigate their surface morphology, elemental composition, crystalline structure, and functional groups. The adsorption process was adopted to evaluate the removal efficiency of Congo Red dye (CR) dye from aqueous solutions. Various experimental parameters, including solution pH, initial dye concentration, temperature, adsorbent dosage, and contact time, were examined and optimized. The equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherm models, which showed good correlation with the experimental adsorption results for Congo Red dyedye onto Ananas Comosus Iron Oxide Nanoparticles.

Keywords Ananas comosus extract, Iron oxide Nanoparticles (AC–Fe₂O₃–NPs), Phytochemicals, Adsorption, Congo Red dyedye, Wastewater treatment, Nanotechnology, SEM–EDX, XRD, FTIR, Langmuir isotherm, Freundlich isotherm, Environmental remediation, Bio-reduction.

¹Research Scholar Chemical Engineering, AUCE(A), Visakhapatnam, AP, India.

²M. Tech Student Chemical Engineering, AUCE(A), Visakhapatnam, AP, India.

^{3,4*}Professor, Chemical Engineering, AUCE(A), Visakhapatnam, AP, India.

^{4*}**Corresponding Author:** Meena Vangalapati

Professor, Chemical Engineering, AUCE(A), Visakhapatnam, AP, India. (meenasekhar2002@yahoo.com)

1. INTRODUCTION

Industrial dye effluents are a major cause of water pollution, threatening ecosystems and human health. Wastewater from industries such as textiles, leather, and paper contains synthetic dyes that are chemically stable, non-biodegradable, and often toxic. Nanomaterial-based adsorbents, in particular, offer high surface areas, tunable properties, and strong adsorption capacity. Increasingly, research focuses on sustainable adsorbents from agricultural and food-processing bio-wastes [1,2]. Synthetic dyes are now major aquatic pollutants due to the textile industry's rapid expansion, which has increased wastewater discharge contaminated by dyes. While many remediation methods have been investigated, including photo-catalysis, oxidation, membrane filtration, and biological treatments, many of them have high operating costs, produce sludge, or are ineffective against stable dyes. Because of its simplicity, low cost, and high efficiency, adsorption continues to be the most reliable and cost-effective method for eliminating persistent organic contaminants [3]. Dyes are usually colored substances, used in many industries, such as textile, plastic, paper, and leather to color their products. Consequently, effluents of these industries contain dyes, some of which are carcinogenic and mutagenic [4]. Azo dyes are regularly used in various applications in food, pharmaceutical, paper, cosmetic, textile and leather industries [5]. Congo Red dye is seriously hazardous to aquatic living organisms and can cause human carcinogenesis. CR ($C_{32}H_{22}N_6Na_2O_6S_2$) is a benzidine-based anionic dye. It is the first synthetic dye produced that is capable of dyeing cotton directly. It is very sensitive to acids [6,7]. Anionic reactive dyes are widely used in the tannery, paper, and textile industries, distilleries, food companies, etc. Congo Red dye (CR) is a benzidine-based anionic bisazo dye known to metabolize to benzidine, a known human carcinogen. Congo Red dye is toxic to animals and plants and thus its introduction to water stream is of potential health, environmental, and ecological concern [8-11]. The Congo Red dye has been selected because of its high pollution degree in water. Considering the large, discharged volume and effluent combustion, the wastewaters from the textile industry are rated as the most polluting among all industrial sectors [12,13]. The most efficiency in recent years to removal of dyes pollutants is adsorption technique due to the procedure simplicity, ease of technique, operation, and its non-sensitivity to toxic materials. There are two different mechanisms of adsorption technique (physical and chemical) influenced by several factors, such as temperature, pH, adsorbate/adsorbent interaction, contact time, particle size, moreover, to reduce the procedure cost, lower-cost material in the adsorption processes [14]. Azo (around 70%) and anthraquinone (around 15%) compose the largest classes of dyes [15]. Many tropical nations, including Brazil, Indonesia, Vietnam, Malaysia, Thailand, and India, extensively produce pineapples. Brazil is the world's leading pineapple grower, producing an average of 2.2 million tonnes annually. The Asia area produces 46.7% of all pineapples worldwide [16,17]. Congo Red dye has an aromatic

structure that provides physicochemical, thermal and optical stability [18]. The long period ingestion of wastewater possessing Congo Red dye can severely destroy liver and blood circulatory system and leads to hematopoiesis in humans, and severe consequences appear in the form of numerous hazardous symptoms including nausea, vomiting, diarrhea, and difficulties in the breathing. On the flip side, Congo Red dye containing effluents can alter the odor as well as color of the water and become directly the major cause of the destruction of aquatic ecosystems [19]. Magnetite Nanoparticles have shown great potential in wastewater treatment [20]. Moreover, $1 \text{ mg} \cdot \text{L}^{-1}$ of most dyes exist in water, let alone the colored wastewater released from the textile processing unit with a dye content in the range of $10 \sim 200 \text{ mg L}^{-1}$ [21].

2. MATERIALS AND METHODS

Ananas Comosus peels were gathered from the local fruit market in Visakhapatnam, India.



Fig. 1. Peels of Ananas Comosus.

2.1 Chemicals Required:

Ferrous Sulphate (FeSO_4), Sodium Hydroxide (NaOH), Hydrochloric acid (HCl) and Distilled water.

2.2 Dye: Congo Red dye (CR)

2.3 Glassware:

1 litre beaker, Measuring jar, Pipette, conical flasks etc.,

2.4 Equipment:

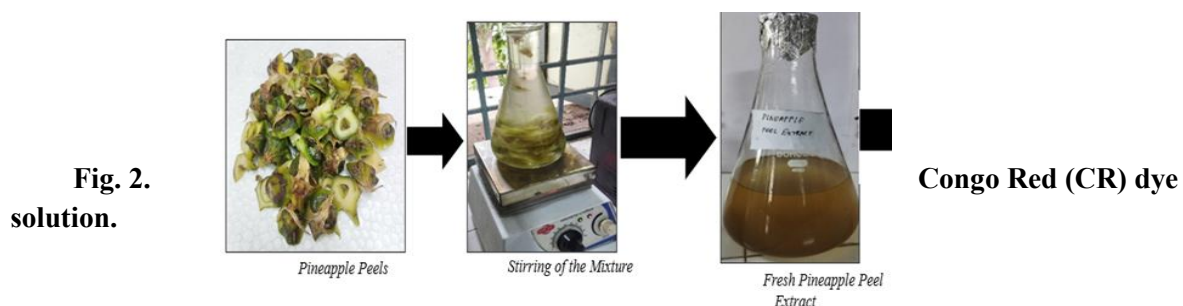
pH meter, Mechanical stirrer, Spectrophotometer, Orbital Shaker and Glass Ware etc.

2.5 Estimation of Dye:

2.5.1 Preparation of Dye Solution:

A stock dye solution of Congo Red with a concentration of 1000 mg L^{-1} was prepared by accurately dissolving 1 g of the dye in distilled water and making up the volume to 1000 mL in a volumetric flask. The stock solution was subsequently diluted serially with distilled water to obtain a series of

working dye solutions with concentrations ranging from 10 mg L^{-1} to 100 mg L^{-1} for experimental analysis.



2.6 Synthesis of Ananas Comosus Peel Iron Oxide Nanoparticles (AC-Fe₂O₃-NPs):

2.6.1 Preparation of Ananas Comosus Peel Extract:

Ananas comosus peels were collected from a nearby fruit market, thoroughly washed with distilled water, and dried in the sun. The dried peels were then ground to a fine powder. For each peel type, 40 g of powder was combined with 500 mL of distilled water and heated at 363 K for 40 minutes using a magnetic stirrer. After cooling, the mixture was filtered using filter paper. The resultant filtrate is used to make extract of Ananas Comosus.



Fig. 3. Preparation of Ananas Comosus Peel Extract.

2.6.2 Synthesis of peels of Ananas Comosus Iron oxide Nanoparticles (AC-Fe₂O₃-NPs):

The freshly produced peel extract was combined 1:1 with the 0.025 M FeSO₄ solution. The mixture was then stirred at room temperature for 30 minutes with a mechanical stirrer. After this time, the solution gradually darkened in hue, suggesting the production of Fe²⁺ ions. The pH of the mixture was determined and corrected to 8 by adding suitable amounts of 0.1 N NaOH and 0.1 N HCl. The solution was then agitated for an additional 60 minutes. After stirring, the mixture was centrifuged at 4000 rpm for 5 minutes. The resultant pellets were collected, placed on a tiny plate, and dried

in a vacuum oven at 800°C for 24 hours. After drying, the pellets were ground into AC-Fe₂O₃-NPs using a mortar and pestle.

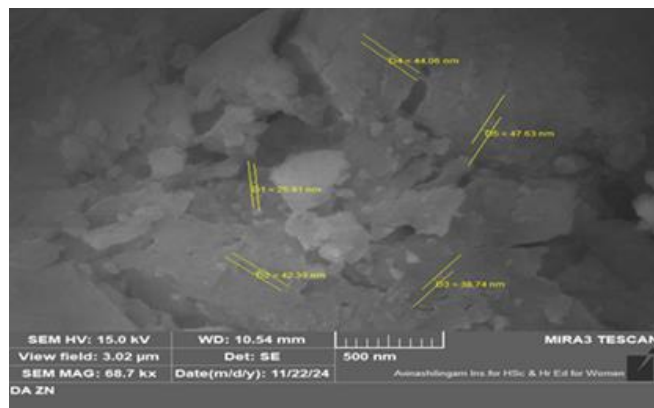


Fig. 4. Synthesis of AC-Fe₂O₃-NPs.

2.7 Characterization of peels of Ananas Comosus Iron oxide Nanoparticles (AC-Fe₂O₃-NPs)

2.7.1 Scanning Electron Microscope (SEM):

SEM image of AC-Fe₂O₃-NPs demonstrate the surface morphology of the produced materials that has uneven and aggregated surface features. The Nanoparticles appear generally spherical but have a wide size range, forming dense clusters as a result of agglomeration, which is presumably caused by magnetic interactions between Fe₂O₃ particles as shown in Fig. 5.

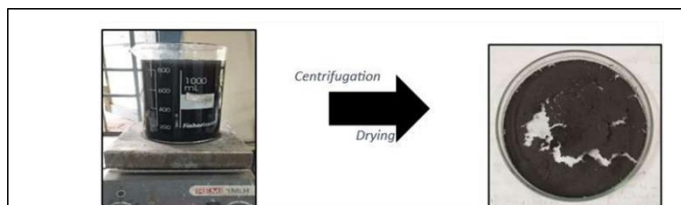
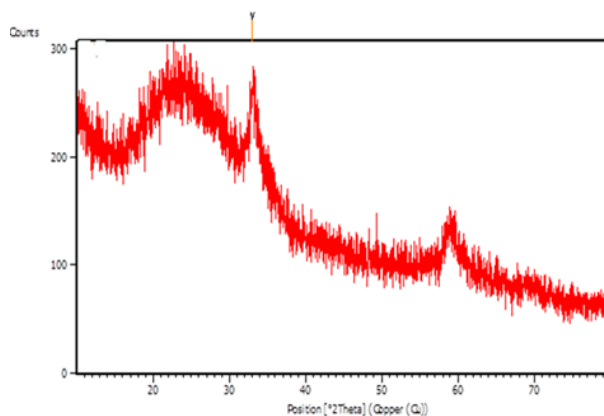


Fig. 5. SEM image for AC-Fe₂O₃-NPs.

2.7.2 X-ray Photoelectron Spectroscopy (XPS):

XPS scans of AC-Fe₂O₃-NPs demonstrate the existence of the main constituents Fe, O, and C, which are typical of iron oxide Nanoparticles generated from plant extracts. The Fe_{2p} peaks in the binding energy range of 710-725 eV confirm the production of Fe₂O₃ as shown in Fig. 6. A strong O1s signal at roughly 530 eV refers to lattice oxygen associated with Fe-O bonding. The C1s peak, which is near 285 eV, is caused by carbon-containing molecules and phytochemicals found in peel extracts, which serve as natural reducing and stabilizing agents during nanoparticle production. Overall, the XPS data confirm the effective production of AC-Fe₂O₃-NPs and demonstrate the presence of surface functional groups generated from plant extracts.



• Fig. 6. XPS analysis for AC-Fe₂O₃-NPs.

2.7.3 X-ray Diffraction Analysis (XRD):

Sample of AC-Fe₂O₃-NPs peaks broad shape suggests that tiny crystallite-sized Nanoparticles have formed. The exceptional purity of the biosynthesized iron oxide Nanoparticles is confirmed by the lack of any secondary or contaminant peaks. The Ananas comosus peel extract contains organic capping agents that affect particle development and aid in preventing agglomeration, which may cause slight changes in peak intensity and width as in the below Fig. 7. Overall, the XRD examination confirms that crystalline Fe₂O₃ Nanoparticles were successfully formed.

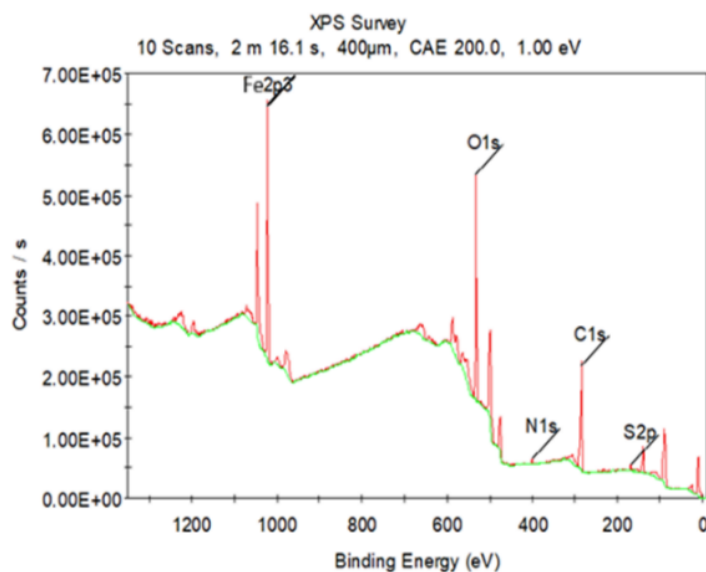


Fig. 7. XRD analysis for AC-Fe₂O₃-NPs.

2.7.4 . Thermogravimetric Analysis (TGA):

The TGA curve for AC-Fe₂O₃-NPs exhibits three distinct stages of weight loss, showing heat decomposition behavior as shown in Fig. 8. The initial weight loss below 150°C is caused by the removal of physically adsorbed moisture and volatile components from the nanoparticle surface. The second considerable weight loss between 200 and 400°C is due to the destruction of organic

phytochemicals and biomolecules in the Ananas comosus peel extract, which served as reducing and stabilizing agents. A minor and gradual mass loss over 450°C implies the removal of residual organic matter and possible structural changes within the Fe₂O₃ framework. TGA results show that the biosynthesized AC-Fe₂O₃-NPs have outstanding thermal stability and purity.

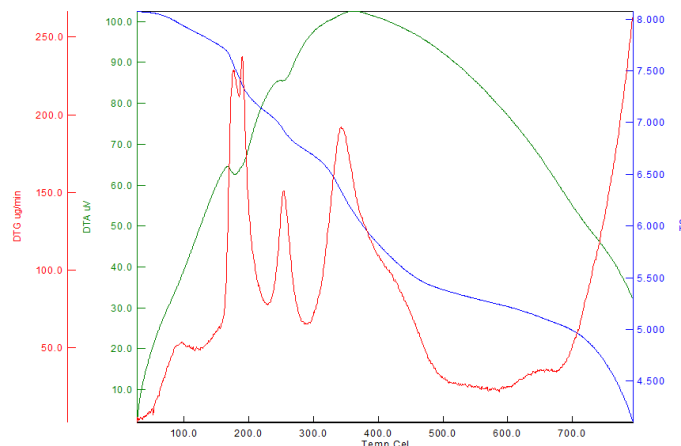


Fig. 8. TGA curve for AC-Fe₂O₃-NPs.

2.7.5 Brunauer-Emmett-Teller (BET) Analysis:

AC-Fe₂O₃-NPs had a reduced BET surface area of 3.647 m²/g, indicating bigger and densely packed nanoparticle aggregates with negligible porosity. The BJH desorption study shows a reduced surface area of 9.586 m²/g and a low pore volume of 0.011 cc/g. The average pore diameter is 3.781 nm, which is in the lower mesoporous range and most likely results from inter-particle voids rather than intrinsic porosity. The high BET C constant (17.902) and excellent correlation coefficient ($r = 0.999882$) indicate strong adsorbate-adsorbent interactions and consistent monolayer adsorption behavior. Overall, AC-Fe₂O₃-NPs create dense, low-surface-area structures.

3. Results and Discussions:

3.1 Adsorption of CR Dye onto Peels of Ananas Comosus Iron Oxide Nanoparticles (AC-Fe₂O₃-NPs):

Batch tests were carried out to explore the impact of important process parameters such as agitation time, adsorbent dosage, solution pH, initial dye concentration, and temperature on Congo Red dye (CR) dye adsorption. This section analyzes experimental findings from employing peels of Ananas comosus-based iron oxide Nanoparticles (AC-Fe₂O₃-NPs) as an adsorbent. The research involve equilibrium, kinetic, and thermodynamic evaluations aimed at understanding the mechanisms that drive dye adsorption. Furthermore, process conditions were optimized using response surface methods to determine the most effective parameters for increasing dye removal efficiency.

3.1.1 Effect of agitation time:

The subsequent studies used a 25-minute agitation time as shown in Fig. 9. With an initial dye concentration of 20 mg/L, dye clearance increased from 56% to 78% for Congo Red dye as contact time increased from 5 to 25 minutes.

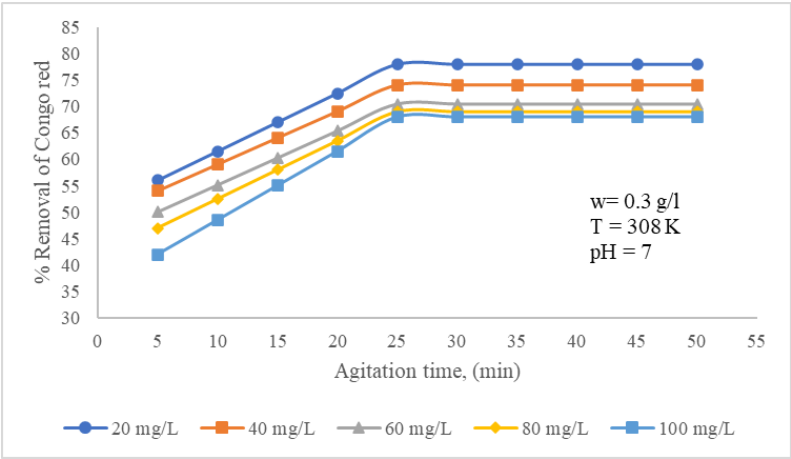


Fig. 9. Effect of agitation time on % dye removal of CR using AC-Fe₂O₃-NPs.

3.1.2 Effect of adsorbent dosage:

When the adsorbent dosage increased from 0.1 to 0.3 g/L at an initial dye concentration of 20 mg/L, dye removal improved from 57.5% to 78% for CR in Fig. 10. This improvement in removal effectiveness is related to the adsorbent's increased surface area, which provides more accessible adsorption sites.

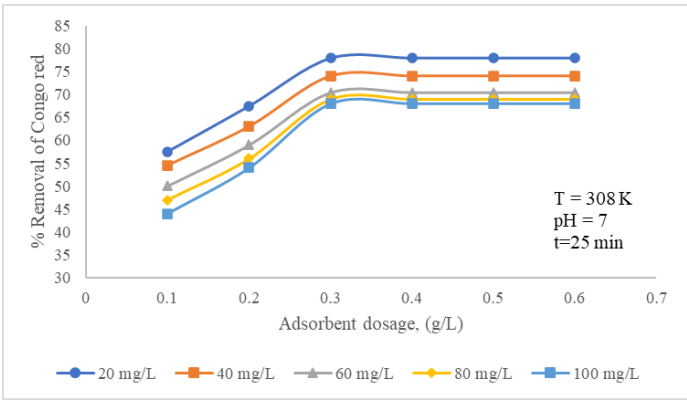


Fig. 10. Effect of adsorbent dosage on % dye removal of CR using AC-Fe₂O₃-NPs.

3.13 Effect of solution pH:

When pH was elevated from 2 to 6, dye removal for CR increase significantly and reached maximum efficiency. However, as pH increased from 6 to 9, dye removal declined as in Fig. 11.

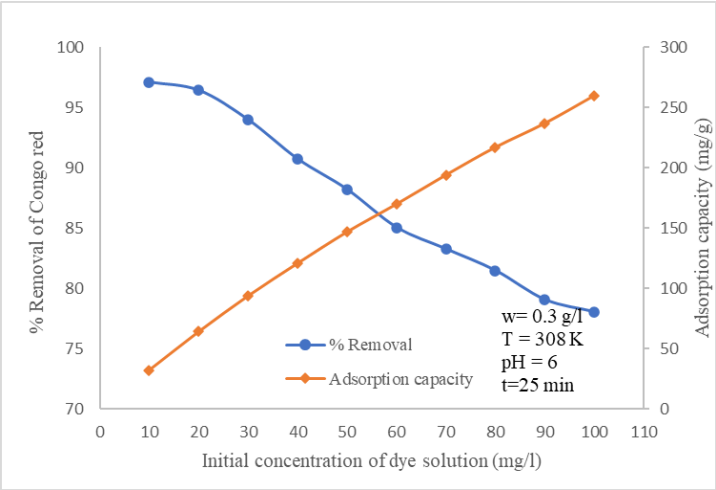


Fig. 11. Effect of solution pH on % dye removal of CR using AC-Fe₂O₃-NPs.

3.14 Effect of Initial concentration of dye:

The percentage of dye removal decreased from 97.13% to 78.05% for CR, when the original dye concentration was increased from 10 to 100 mg/L as shown in Fig. 12.

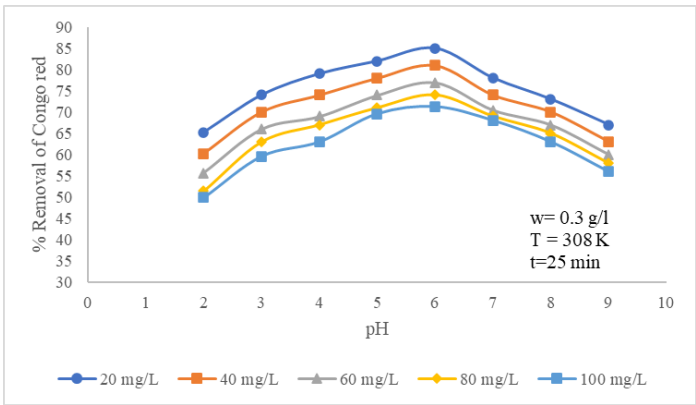


Fig. 12. Effect of solution Initial dye concentration on adsorption capacity and % dye removal of CR using AC-Fe₂O₃-NPs.

3.1.5 Effect of temperature:

At an initial concentration of 20 mg/L, the percentage of dye elimination increase with temperature; for CR Dye, it grew from 85% at 308 K to 96.5% at 328 K from Fig. 13.

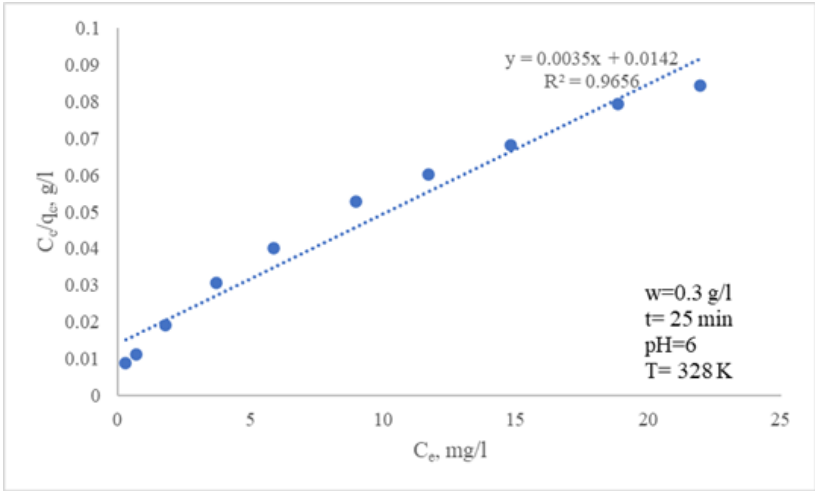


Fig. 13 Effect of temperature on % dye removal of CR using AC-Fe₂O₃-NPs.

3.2 Equilibrium Studies:

3.2.1 Langmuir Adsorption Isotherm:

The Langmuir model in linear form is given in (Eq. 1)

$$\frac{C_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{1}{q_{max}} C_e \tag{1}$$

Fig. 14 displays the Langmuir Plots (C_e / q_e versus C_e) for the adsorption of CR Dye at 328K . Langmuir isotherm constants and correlation coefficients values are listed in Table 1.

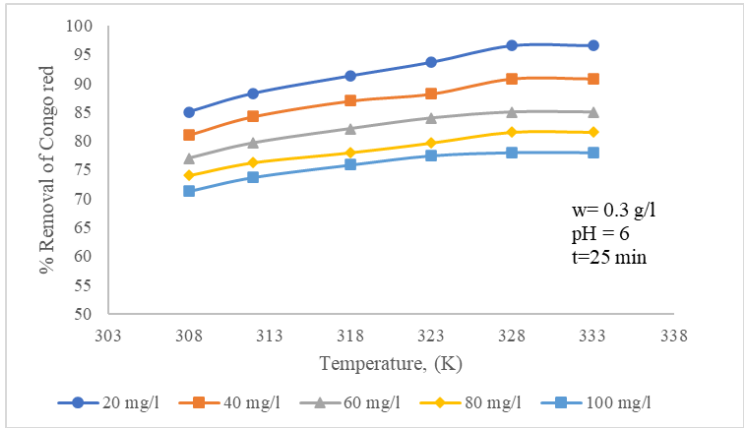


Fig. 14. Langmuir isotherm for adsorption of CR Dye onto AC-Fe₂O₃-NPs adsorbent.

3.2.2 Freundlich isotherm:

The linear form of Freundlich isotherm is mentioned in Eq. 2

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

Fig. 15 displays the Freundlich Plots ($\ln q_e$ versus $\ln C_e$) for the adsorption of CR Dye at 328K. Freundlich isotherm constants and correlation coefficients values are listed in Table 1.

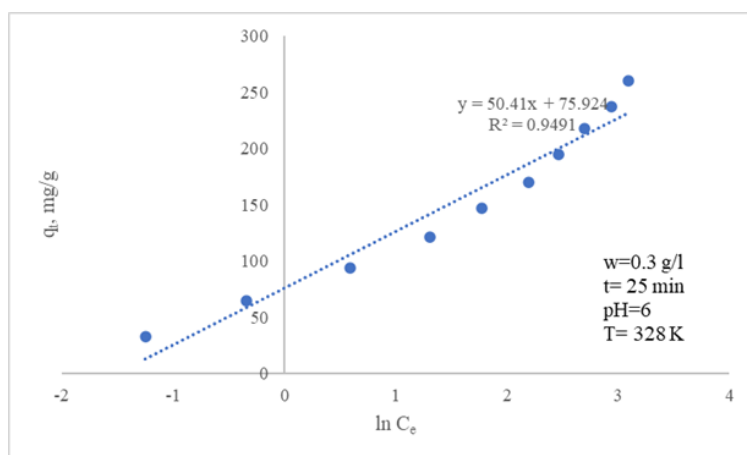


Fig. 15. Freundlich isotherm for adsorption of CR Dye onto AC-Fe₂O₃-NPs adsorbent.

3.2.3 Temkin isotherm:

The linear form of Temkin equation is given in Eq. 3

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (3)$$

Where, $B_T = RT/b$, R-universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), b-related to heat of adsorption (J mol^{-1}), T-absolute temperature (K) and A_T is the equilibrium binding constant (Lg^{-1}) and q_e (mg/g) and C_e (mg/L) are the amount of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively.

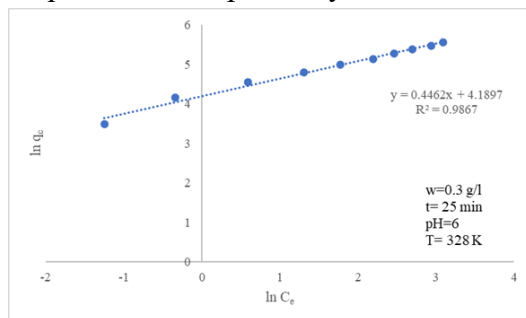


Fig. 16. Temkin isotherm for adsorption of CR Dye onto AC-Fe₂O₃-NPs adsorbent.

Fig. 16 illustrates the Temkin isotherm plots (q_e versus $\ln C_e$) for the adsorption of Congo Red dye(CR) dye at 328 K. The corresponding Temkin isotherm constants and correlation coefficient (R^2) values derived from the linear plots are summarized in Table 1, confirming the applicability of the Temkin model to describe the adsorption behavior under the studied conditions.

Table.1: Adsorption isotherm constants for removal of Congo Red dye(CR) Dye using AC-Fe₂O₃-NPs as adsorbent.

Isotherm model	Constants	CR Dye
Langmuir	k_L (L/mg)	0.247
	$q_{\max}$ (mg/g)	212.76
	R_L	0.066
	R^2	0.9656
Freundlich	k_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	49.5
	1/n	0.4462
	R^2	0.9867
Temkin	A_T (lg ⁻¹)	4.508
	B (J mol ⁻¹)	37.807
	R^2	0.9491

3.3 Kinetic studies

3.3.1 Pseudo-first-order model:

The pseudo-first-order kinetic equation is given in Eq. 4

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, then the equation becomes, (eq. 5)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

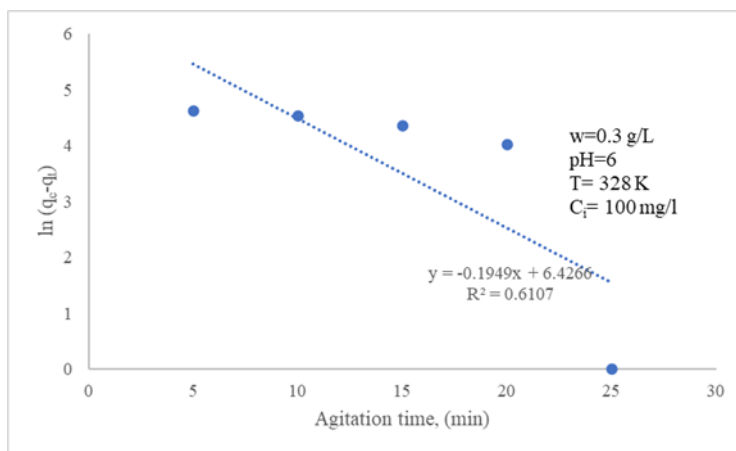


Fig. 17. Pseudo-first-order kinetics for adsorption of CR Dye onto AC-Fe₂O₃-NPs adsorbent.

From Fig. 17, was evaluated by plotting $\ln(q_e - q_t)$ versus time (t) under conditions of an initial dye concentration of 100 mg/L, solution pH of 6 for CR Dye, adsorbent dose of 0.3 g/L, temperature of 328 K, and agitation at 150 rpm.

The equilibrium adsorption capacity (q_e) and the first-order rate constant were calculated from the intercept and slope of the plots and are summarized in Table 2.

3.3.2 Pseudo-second-order model:

The pseudo-second-order equation is expressed in the form,

$$\frac{dq}{dt} = k_2[q_e - q_t]^2 \quad (6)$$

Where, q_t is the amount of dye adsorbed at time t (mg/g); q_e is the adsorption capacity at equilibrium (mg/g); k_2 is the equilibrium rate constant of pseudo-second-order sorption (g/mol-min); and t is the time (min).

After definite integration by applying the initial conditions $q = 0$ at $t = 0$ and $q = q_t$ at $t = t$, the equation becomes, Eq. 7

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

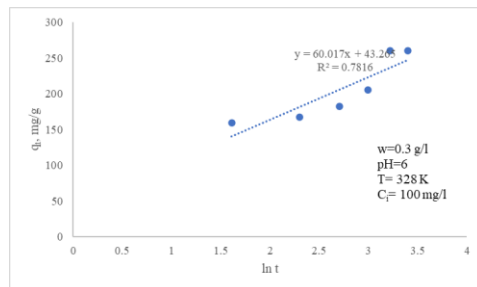


Fig. 18. Pseudo-second-order kinetics for adsorption of CR dye onto AC-Fe₂O₃-NPs adsorbent.

3.3.3 Elovich model:

The Elovich model describes the type of adsorption mechanism (physical and chemical). It is expressed as follows in Eq. 8

$$\frac{dq}{dt} = \alpha e^{-\gamma q} \quad (8)$$

Where α is initial rate and γ represents the extent of surface coverage and activation energy required for chemisorption (g/mg). Integrating the above equation between the boundary conditions $q=0$ at $t=0$ and $q=q$ at $t=t$, the following relationship is obtained, as expressed in Eq. 9.

$$q = \frac{1}{\gamma} \ln(\alpha\gamma) + \frac{1}{\gamma} \ln t \quad (9)$$

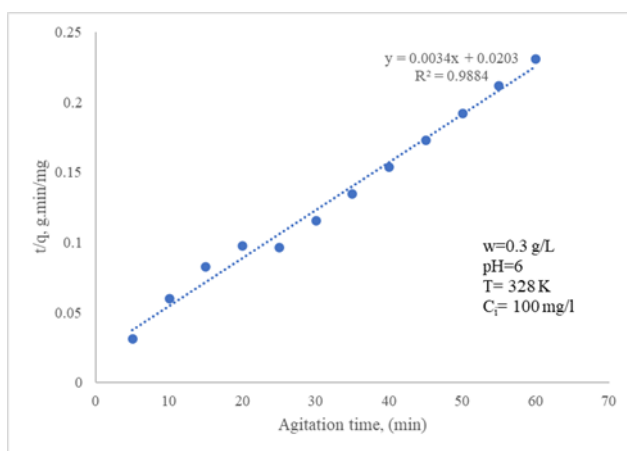


Fig. 19. Elovich model for adsorption of CR dye onto AC-Fe₂O₃-NPs adsorbent.

The rate constants for the Elovich model were determined from the slope and intercept of the straight-line plots of q versus $\ln t$, as shown in Fig. 19.

The calculated Elovich parameters for the adsorption of CR dye onto AC-Fe₂O₃-NPs are summarized in Table 2.

3.3.4 Intra-particle diffusion model:

The Weber-Morris intra-particle diffusion model is expressed as in Eq. 10

$$q = K_{id}t^{1/2} + I \quad (10)$$

where q is the amount of dye adsorbed at time t , K_{id} is the intra particle diffusion rate constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$), and I is the thickness of the boundary layer. The higher the value of I , the greater the contribution of surface sorption in the rate-controlling step.

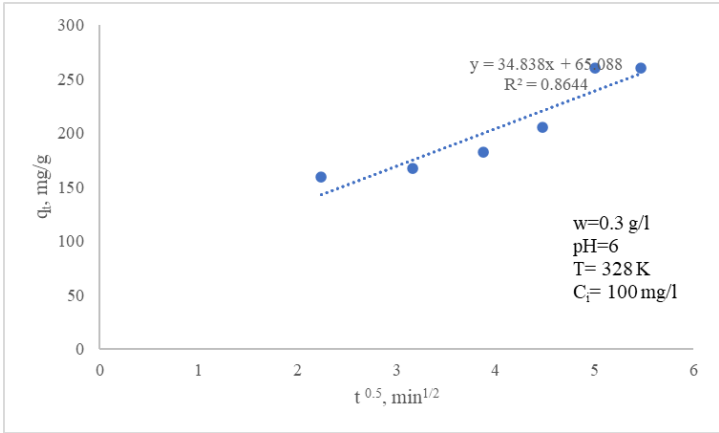


Fig. 20. Intra-particle diffusion model for adsorption of CR Dye onto AC-Fe₂O₃-NPs adsorbent.

The intra-particle diffusion rate constants (K_{id}) for CR Dye are listed in Table 2 respectively. Fig. 20 display the plots of intra-particle diffusion. The fact that the respective straight lines do not pass through the origin suggests that intra-particle diffusion is not the sole rate-controlling mechanism. Therefore, the overall adsorption is likely governed by a combination of intra-particle diffusion and surface adsorption mechanisms, with intra-particle diffusion playing a predominant role.

Table.2: Kinetic model parameters for CR Dye removal using AC-Fe₂O₃-NPs.

Concentration, mg/L	Pseudo-first-order kinetics		
	k_1 (L/min)	q_e (mg/g)	R^2
100	0.1834	413.18	0.618
	Pseudo-second-order kinetics		
	k_2 (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2
	0.0046	217.39	0.9884
	Elovich model		
	γ (g/mg)	α (mg/g.min)	R^2
	0.0222	92.542	0.7816
	Intra-particle diffusion model		
	$K_{id1}, \text{mg/g.min}^{1/2}$	$I_1, \text{mg/g}$	R^2
	26.129	48.816	0.864

3.4 Thermodynamic studies

The enthalpy changes ΔH° and entropy change ΔS° of the adsorption were estimated from the following Eq. 11

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

(11)

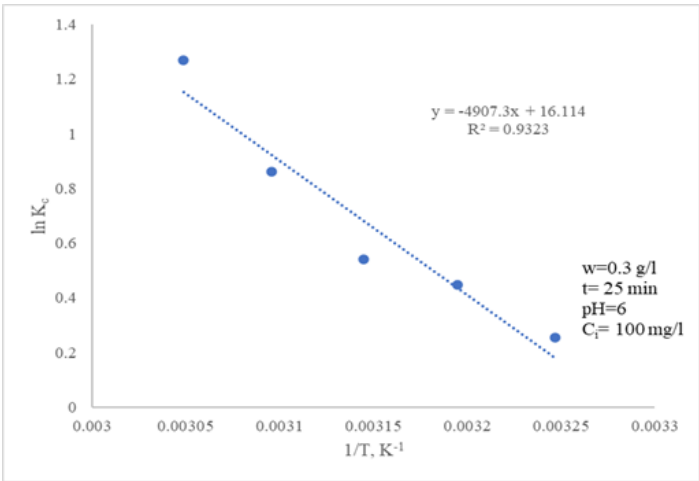


Fig.21. Thermodynamic studies for adsorption of CR dye onto AC-Fe₂O₃-NPs adsorbent.

Thermodynamic studies of the adsorption of CR dye into AC-Fe₂O₃-NPs were carried out over a temperature range of 308 to 328 K, with an initial dye concentration of 100 mg/L. The changes in enthalpy (ΔH°) and entropy (ΔS°) were calculated from the slope and intercept of the linear Van't Hoff plots of $\ln K_c$ versus $1/T$ Fig. 21. The resulting data are summarized in Table 3, with correlation coefficients (R^2) of 0.9323 for CR dye. The negative ΔG° values at all studied temperatures indicate that the adsorption process is spontaneous and thermodynamically feasible.

Table.3: Thermodynamic parameters for CR dye adsorption using AC-Fe₂O₃-NPs adsorbent.

Temperature, K	CR dye		
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)
308	-6.5318	24.53	89.02
313	-11.6883		
318	-14.2927		
323	-23.1214		
328	-34.6033		

3.5 Characterization of Peels of Ananas Comosus-Iron Oxide Nanoparticles (AC-Fe₂O₃-NPs) using FTIR analysis:

3.5.1 Fourier Transform Infrared Spectroscopy (FTIR) for AC-Fe₂O₃-NPs before and after adsorption with CR dye:

From Fig. 22, the spectrum of AC-Fe₂O₃-NPs exhibits broad absorption around 3425 cm⁻¹, attributed to the O–H stretching vibration of surface hydroxyl groups and adsorbed moisture. The bands observed between 2850–2950 cm⁻¹ correspond to aliphatic C–H stretching vibrations from residual phytochemicals acting as capping agents. A distinct band at 1630 cm⁻¹ is due to H–O–H bending of water molecules, while the prominent absorption near 550 cm⁻¹ represents the Fe–O stretching vibration, confirming the formation of iron oxide Nanoparticles.

After CR dye adsorption, noticeable spectral modifications were observed. The broad O–H band shifted slightly from 3425 cm⁻¹ to 3380 cm⁻¹, indicating hydrogen-bond interactions between dye molecules and surface hydroxyl groups. New and intensified bands around 1570–1500 cm⁻¹ and 1380 cm⁻¹ correspond to azo (–N=N–) and aromatic C=C stretching vibrations of the CR dye. The appearance of a peak at 1750 cm⁻¹ may be attributed to C=O stretching due to dye–nanoparticle complexation. Furthermore, the Fe–O stretching band shifted from 550 cm⁻¹ to 460 cm⁻¹, suggesting surface coordination or electrostatic binding of the dye molecules to Fe₂O₃ sites as shown in Fig. 23.

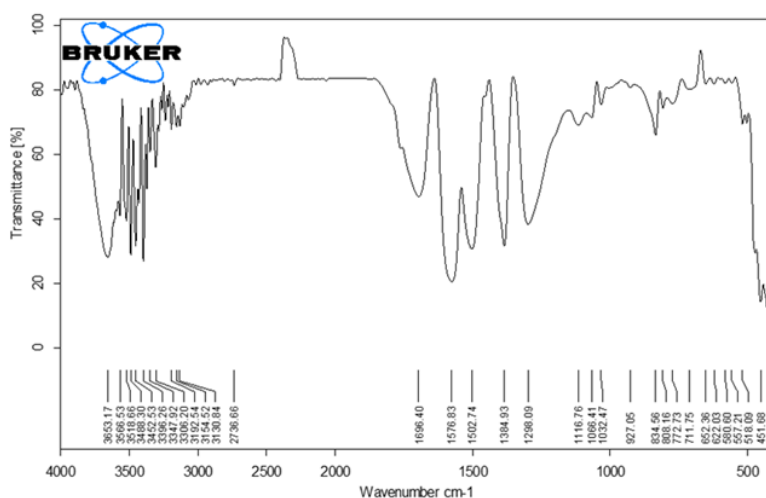


Fig. 22. FTIR spectra of Peels of Ananas Comosus-Iron Oxide Nanoparticles before adsorption with CR dye.

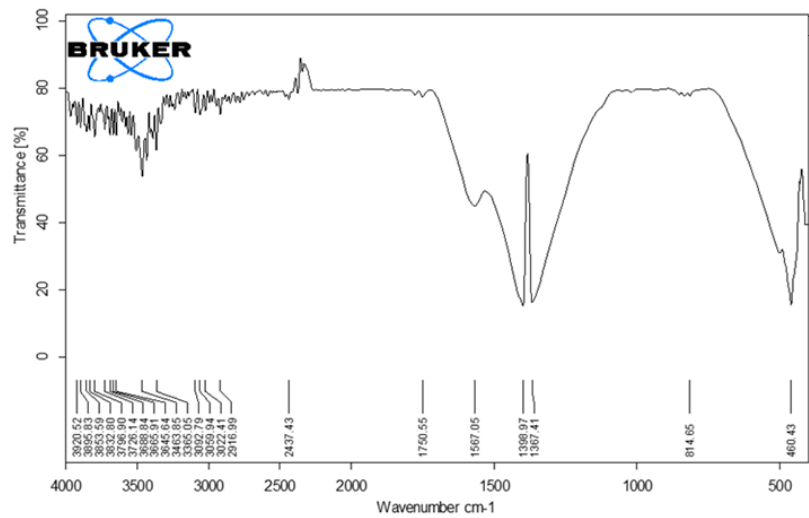


Fig. 23. Fourier Transform Infrared Spectroscopy (FTIR) for AC-Fe₂O₃-NPs after adsorption with CR dye.

3.6 Optimization of adsorption process parameters using Response Surface Methodology (RSM):

A Box Behnken Design (BBD) was used to explore the effect of experimental factors such as solution pH, adsorbent dosage, beginning dye concentration, and temperature on the percentage of CR dye removed using AC-Fe₂O₃-NPs. The reaction was given as the percentage of CR dye removed from the adsorbent. A box Behnken design with 29 tests, including 16 cube point runs, 5 center point runs, and 8 axial point runs, was used to optimize process parameters for CR dye adsorption from aqueous solution.

3.6.1 Optimization using Box Behnken Design (BBD):

The quadratic model is adopted in the current investigation. The regression equation for percent dye removal from CR dye is a function of pH (A), K (B), C_i (C), and w (D). The range of variables used in this design was determined based on the analysis of preliminary experiments and they are shown in Table 4.

Table.4: Levels of different process variables for optimization using BBD for the adsorption of CR dye onto AC-Fe₂O₃-NPs adsorbent.

Variable Name		Range and levels for CR dye		
		-1	0	+1
A	Solution pH	5	6	7
B	Temperature T, K	323	328	333
C	Initial dye Concentration C _i , mg/L	10	20	30
D	Adsorbent dosage w, g/L	0.2	0.3	0.4

The following equations represent multiple regression analysis of the experimental data for the adsorption of CR dye into AC-Fe₂O₃-NPs:

Equation in terms of coded factors for Congo Red (CR) dye:

$$\text{Removal of CR dye} = +96.500.2667A + 0.1333B + 0.9500C + 0.2833D + 0.1250AB + 0.2750AC + 0.2000AD - 0.1000BC - 0.0250BD - 0.2250CD - 1.91A^2 - 2.83B^2 - 3.86C^2 - 2.98D^2 \quad (12)$$

The greatest percentage of dye removal was projected to be 91.7% at the optimal values of the variables from RSM for CR dye, which are temperature 331 K, solution pH-6.4, adsorbent dosage of 0.25 g/L, and beginning dye concentration of 18 mg/L.

The predicted values on % dye removal of CR onto the adsorbent using the above Eq. 12 are given in Table 5 along with the experimental data. The coefficients of the regression model calculated are listed in Table 6 for the adsorption of CR dye, respectively.

The 'P' values are analyzed from Table 6. And it is found that the A, B, C, D, A², B², C², D², AB, AC, BC and BD have high significance to explain the individual and interaction effect of independent variables on CR dye.

Table.5: Experimental design matrix along with % dye removal of CR onto Peels of Ananas Comosus-Iron Oxide Nanoparticles (AC-Fe₂O₃-NPs) adsorbent.

Run no.	A, pH	B, T	C, C _i	D, w	% dye removal of CR	
					Experimental	Predicted
1.	6	333	10	0.5	79.5	87.64
2.	6	333	30	0.5	77.4	89.43
3.	6	328	30	0.4	93.9	93.9
4.	6	328	20	0.3	96.5	96.5
5.	7	323	20	0.5	82.5	89.63
6.	6	328	20	0.3	96.5	96.5
7.	6	323	20	0.6	81.6	87.19
8.	6	328	30	0.6	77.2	88.54
9.	6	323	10	0.5	80.2	86.17
10.	5	328	20	0.4	80.5	89.19
11.	7	333	20	0.5	81.5	87.93
12.	6	328	10	0.4	79.6	89.15

13.	6	333	20	0.4	82.9	88.52
14.	6	328	10	0.6	79.8	86.05
15.	6	328	20	0.5	91.4	87.96
16.	5	328	10	0.5	83.4	89.42
17.	7	328	30	0.5	79.4	88.26
18.	5	323	20	0.5	82.9	87.50
19.	6	323	20	0.4	83.6	89.36
20.	5	328	30	0.3	80.1	96.5
21.	6	328	20	0.5	91.4	93.90
22.	5	328	20	0.6	80.9	86.23
23.	6	328	20	0.5	91.4	93.90
24.	6	333	20	0.6	81.5	93.90
25.	5	333	20	0.5	79.8	86.29
26.	7	328	20	0.6	80.8	88.63
27.	7	328	20	0.4	81.1	87.18
28.	7	328	10	0.5	82.8	93.90
29.	6	323	30	0.5	78.5	88.48

Table.6: ANOVA table for model to predict % removal of CR dye onto AC-Fe₂O₃-NPs adsorbent using BBD.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	167.74	14	11.98	105.94	< 0.0001
A-pH	0.8533	1	0.8533	7.55	0.0157
B-Temperature	0.2133	1	0.2133	1.89	0.1912
C-Initial concentration	10.83	1	10.83	95.76	< 0.0001
D-Adsorbent dosage	0.9633	1	0.9633	8.52	0.0112
AB	0.0625	1	0.0625	0.5526	0.4695
AC	0.3025	1	0.3025	2.67	0.1242
AD	0.1600	1	0.1600	1.41	0.2541
BC	0.0400	1	0.0400	0.3537	0.5615
BD	0.0025	1	0.0025	0.0221	0.8839
CD	0.2025	1	0.2025	1.79	0.2022
A ²	23.62	1	23.62	208.87	< 0.0001
B ²	52.07	1	52.07	460.43	< 0.0001
C ²	96.56	1	96.56	853.82	< 0.0001
D ²	57.73	1	57.73	510.47	< 0.0001
Residual	1.58	14	0.1131		
Lack of Fit	1.58	10	0.1583		

Pure Error	0.0000	4	0.0000		
Cor Total	169.32	28			

df-degree of freedom; SS- the sum of squares; F- factor F; P- probability

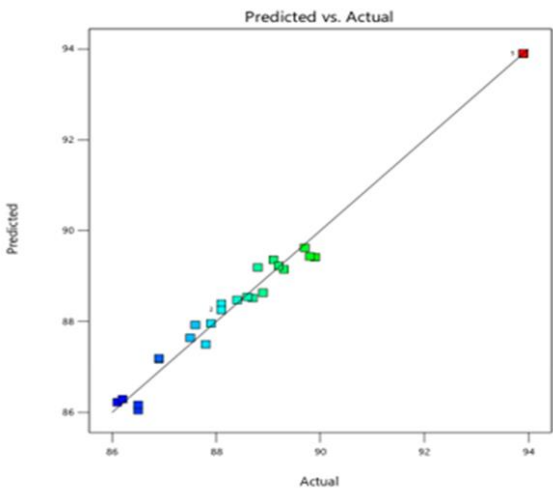


Fig. 24. Predicted values vs. actual values from BBD for CR dye (Parity plot).

3.6.2 Interaction effects of adsorption variables:

The Response Surface Graphs were plotted to know the interaction of the process variables and to determine the optimum level of each variable for maximum response. The Response Surface Curves for % of dye removal for CR shown in (Fig. 25-30).

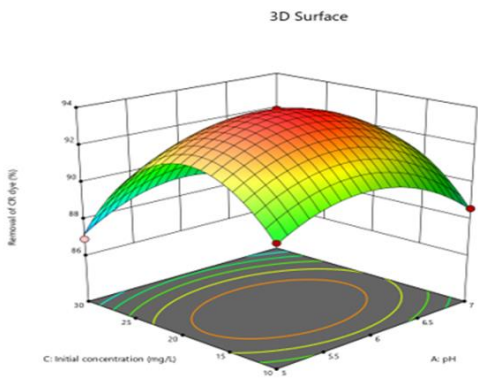


Fig. 25. Response surface plot of initial concentration vs solution pH on % dye removal of CR.

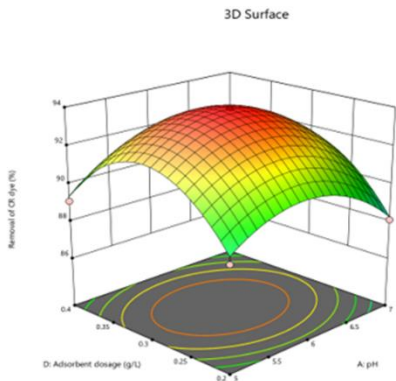


Fig. 26. Response surface plot of adsorbent dosage vs solution pH on % dye removal of CR.

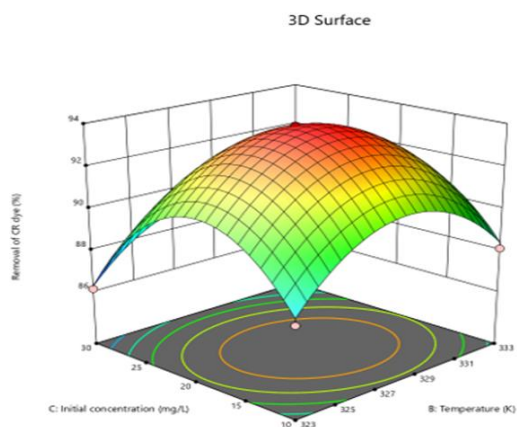


Fig. 27. Response surface plot of temperature vs solution pH on % dye removal of CR.

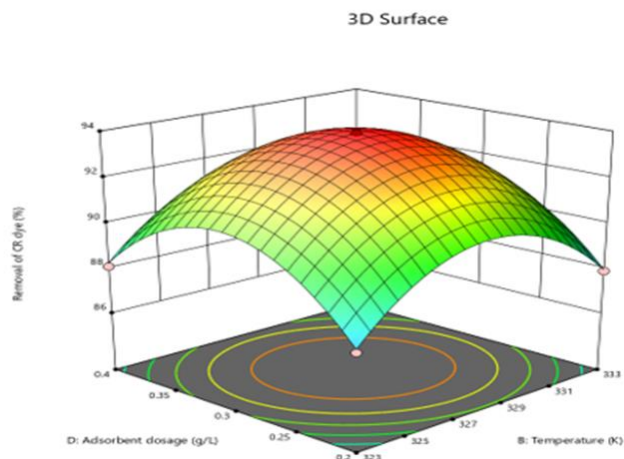


Fig. 28. Response surface plot of initial concentration vs adsorbent dosage on % dye removal of CR.

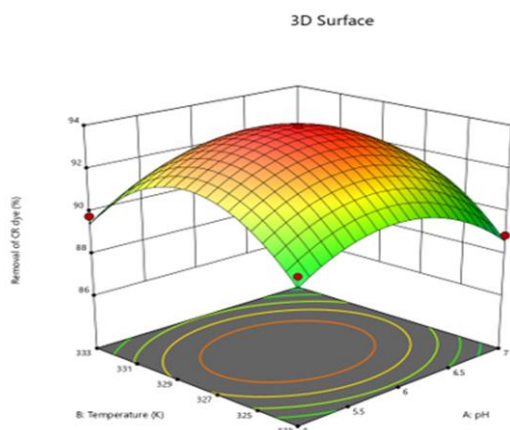


Fig. 29. Response surface plot of initial concentration vs temperature on % dye removal of CR.

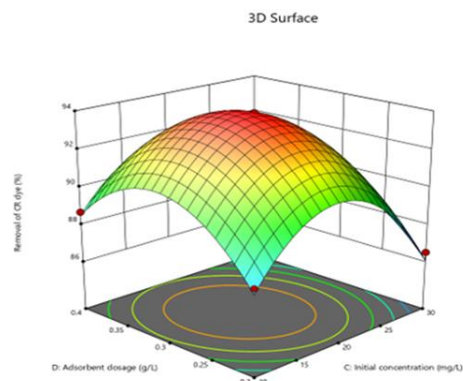


Fig. 30. Response surface plot of adsorbent dosage vs temperature on % dye removal of CR.

It is evident from (Fig. 25-30), that the % dye removal was increased with an increase in adsorbent dosage and temperature and decreased with an increase in dye concentration and solution pH.

The response surface contour plots are used to get better understanding of independent variables and their interaction on the dependent variable. It represents the interactive effect of any two variables on the response variable when the remaining variables are kept constant.

The shape of the response surface curve indicates good interaction of two variables and circular shape indicates no interaction between the variables. The elliptical shape of the response surface curve indicates good interaction of two variables and circular shape indicates no interaction between the variables. The maximum predicted % dye removal is indicated by the surface confined in the smallest ellipse in the contour

diagrams. (Fig. 31-36) represent the response surface contour plots on % dye removal versus interactive effects of all process variables for CR dye.

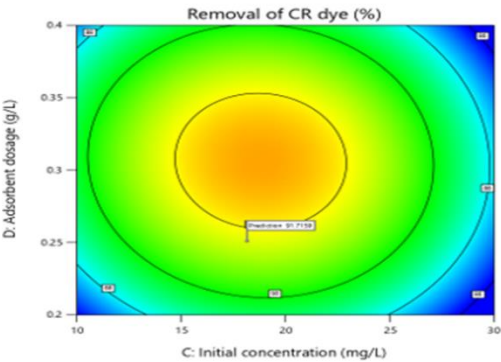


Fig. 31. Contour plot of initial concentration vs adsorbent dosage on % dye removal of CR.

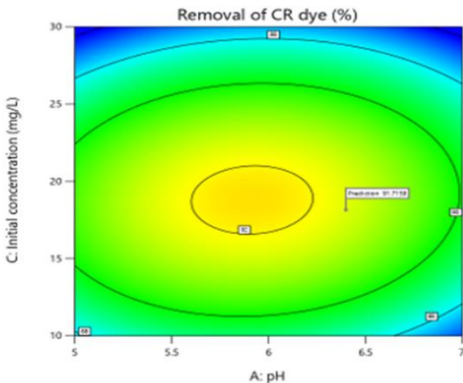


Fig. 32. Contour plot of initial concentration vs solution pH on % dye removal of CR.

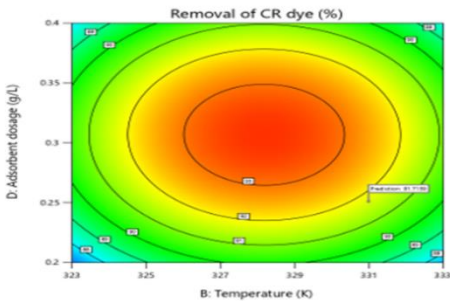


Fig. 33. Contour plot of temperature vs adsorbent dosage on % dye removal of CR.

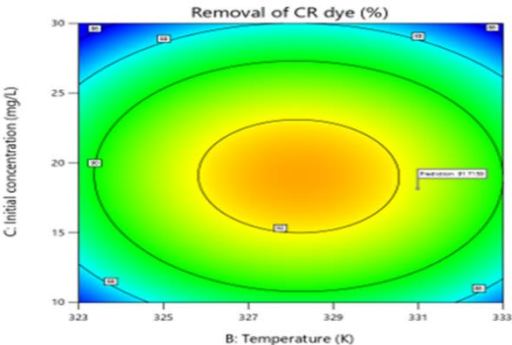


Fig. 34. Contour plot of initial concentration vs temperature on % dye removal of CR.

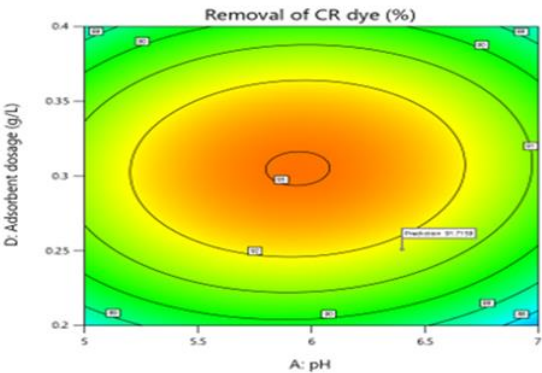


Fig. 35. Contour plot of adsorbent dosage vs pH on % dye removal of CR.

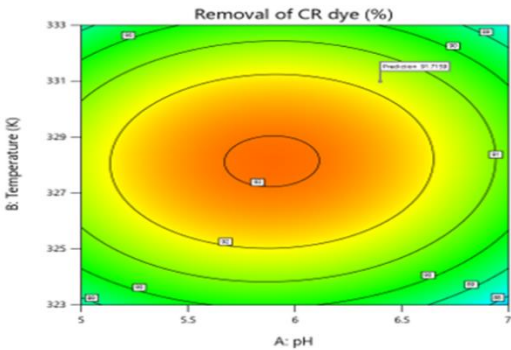


Fig. 36. Contour plot of solution pH vs temperature on % dye removal of CR.

4. CONCLUSIONS

- This work looked into the removal of Congo Red (CR) dye from aqueous solutions utilizing iron oxide Nanoparticles derived from Ananas comosus peel extract (AC-Fe₂O₃-NPs). This adsorbent is studied using SEM, XRD, BET, XPS, and FTIR techniques, and their performance was assessed using batch adsorption studies confirmed with response surface methodology.
- AC-Fe₂O₃-NPs achieved a contact time of 25 minutes for Congo Red dye. For AC-Fe₂O₃-NPs, the ideal adsorbent dosage was found to be 0.3 g/L. The pH of the solution was important; pH 6 was ideal for Congo Red (CR) dye removal and the system's maximum adsorption efficiency was reached at 328 K.
- AC-Fe₂O₃-NPs showed performance with 97.13% removal at an initial dye concentration of 10 mg/L for Congo Red dye. The highest adsorption capacities for AC-Fe₂O₃-NPs were 260.18 mg/g, respectively.
- The Freundlich isotherm model best explained the adsorption behavior for AC-Fe₂O₃-NPs, according to equilibrium data analysis. This suggests a heterogeneous surface with multilayer adsorption involving both physisorption and chemisorption mechanisms.
- The adsorption process was accurately approximated by the pseudo-second-order model, according to kinetic studies. The computed enthalpy and entropy changes from thermodynamic analysis showed that the adsorption was endothermic, practicable, and spontaneous.
- The produced AC-Fe₂O₃-NPs have structural characteristics that were ideal for adsorption uses. Particles with irregular shapes and sizes smaller than 100 nm were found via SEM analysis. The crystalline nature and porous structure of the adsorbent, contribute to their large surface area, were verified by XRD, BET, and XPS investigations.
- Different functional groups (hydroxyl, carboxyl, and amino groups) on the adsorbent surfaces were detected by FTIR spectroscopy. These groups promoted dye molecule binding via chemical bonding and electrostatic interactions.
- The initial dye concentration, pH, adsorbent dose, and temperature were all successfully tuned for the AC-Fe₂O₃-NPs Response surface methodology employing Box-Behnken design. The statistical model's dependability for process optimization was validated by the outstanding agreement between the projected values from RSM and experimental outcomes.
- The results of the experiment clearly show that AC-Fe₂O₃-NPs are inexpensive, very effective adsorbents for eliminating Congo Red (CR) dye from wastewater. These bio-synthesized Nanoparticles are interesting options for sustainable wastewater treatment applications because of their excellent adsorption capacities and the use of agricultural waste as precursor materials.

5. REFERENCES

1. Sustainable synthesis and characterization of Zn–Al doped nanocomposites for removal of brilliant blue dye: optimization using a response surface methodology Sreenivas Matla, Gnanakumari Talathoti, Tamirat Lamaro Bate, Megersa Tadesse Adugna, Paruvu Yogitha, Boggala Reddemma, Pulipati King & Meena Vangalapati.
<https://doi.org/10.1038/s41598-025-25078-1> (2025).
2. J. Zolgharnein, Z. Choghaci, M. Bagtash, Sh. Feshki, M. Rastgordani & P. Zolgharnein (2016): Nano-Fe₃O₄ and corn cover composite for removal of Alizarin Red S from aqueous solution: characterization and optimization investigations, Desalination and Water Treatment.
<http://dx.doi.org/10.1080/19443994.2016.1177736>
3. Characterization and Optimization of Tamarindus indica Copper Nanoparticles (Ta-Cunps) for the Adsorptive Removal of Malachite Green Pampana Anil Kumar, Alpitha Suhasini J., Sarva Rao B., Pulipati King, D.Appala Naidu and Meena Vangalapati. <https://doi.org/10.46488/NEPT.2026.v25i03.B4401> (2025).
4. Tasneem Zehra, Namal Priyantha, Linda B.L. Lim & Erum Iqbal (2015) Sorption characteristics of peat of Brunei Darussalam V: removal of Congo Red dye from aqueous solution by peat, Desalination and Water Treatment, 54:9, 2592-2600. <https://doi.org/10.1080/19443994.2014.899929>
5. Kumar, S., Raut, S., Bandyopadhyay, P.: Fungal decolouration and degradation of azo dyes : A review. Fungal Biol. Rev. 30, 112–133 (2016).
<http://dx.doi.org/10.1016/j.fbr.2016.06.003>
6. Gülbahar Akkaya Saygılı, Synthesis, characterization and adsorption properties of a novel biomagnetic composite for the removal of Congo Red dye from aqueous medium, Journal of Molecular Liquids, Volume 211, 2015, Pages 515-526.
<https://doi.org/10.1016/j.molliq.2015.07.048>
7. Zepeng Liu, Jie Zhang, Liping Zhang, Ying Guan, Hao Ji, Yu Zhang, Hui Gao, Efficient removal of Congo Red dye and methylene blue using biochar from Medulla Tetrapanacis modified by potassium carbonate, Bioresource Technology, 376, 2023.
<https://doi.org/10.1016/j.biortech.2023.128912>
8. Rais Ahmad, Rajeev Kumar, Adsorptive removal of Congo Red dye from aqueous solution using bael shell carbon, Applied Surface Science, Volume 257, Issue 5, 2010, Pages 1628-1633.
<https://doi.org/10.1016/j.apsusc.2010.08.111>
9. Estevan D. Cruz, Juliano Missau, Simon R. Collinson, Eduardo H. Tanabe, Daniel A. Bertuol, Efficient removal of Congo Red dye using activated lychee peel biochar supported Ca-Cr layered double hydroxide, Environmental Nanotechnology, Monitoring & Management, 20, 2023.
<https://doi.org/10.1016/j.enmm.2023.100835>
10. Jegede, M.M., Durowoju, O.S. & Edokpayi, J.N. Sequestration of Congo Red dye from aqueous solution using raw and citric acid-modified Dicerocaryum eriocarpum biomass: isotherm, kinetics and thermodynamics. Appl Water Sci 14, 59 (2024).
<https://doi.org/10.1007/s13201-024-02114-5>
11. Kaur, Sumanjit, Seema Rani, and Rakesh Kumar Mahajan. "Adsorption kinetics for the removal of hazardous dye Congo Red dye by biowaste materials as adsorbents." Journal of chemistry 2013 (2013).
<https://doi.org/10.1155/2013/628582>
12. Moussa Abbas, Mohamed Trari, Kinetic, equilibrium and thermodynamic study on the removal of Congo Red dye from aqueous solutions by adsorption onto apricot stone, Process Safety and Environmental Protection, Volume 98, 2015, Pages 424-436.
<https://doi.org/10.1016/j.psep.2015.09.015>
13. Vijayakumar, G., Dharmendirakumar, M., Renganathan, S., Sivanesan, S., Baskar, G. and Elango, K.P. (2009), Removal of Congo Red dye from Aqueous Solutions by Perlite. Clean Soil Air Water, 37: 355-364.

- <https://doi.org/10.3390/md21050312>
14. Thabet, M.S. and Ismaiel, A.M. (2016) Sol-Gel γ -Al₂O₃ Nanoparticles Assessment of the Removal of Eosin Yellow Using: Adsorption, Kinetic and Thermodynamic Parameters. *Journal of Encapsulation and Adsorption Sciences*, 6, 70- 90.
<http://dx.doi.org/10.4236/jeas.2016.63007>
 15. Gholamreza Moussavi, Maryam Mahmoudi, Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO Nanoparticles, *Journal of Hazardous Materials*, Volume 168, Issues 2–3, 2009, Pages 806-812.
<https://doi.org/10.1016/j.jhazmat.2009.02.097>
 16. Nur Ayshah Rosli, Mohd Azmier Ahmad, Teh Ubaidah Noh, Nur Afiqah Ahmad, Pineapple peel–derived carbon for adsorptive removal of dyes, *Materials Chemistry and Physics*, 306, 2023.
<https://doi.org/10.1016/j.matchemphys.2023.128094>
 17. Le, Ha Vu Dao, Nghia Thi Bui, Ha Truc Kim Le, Phung Thi Le, Kien Anh Tuong Tran, An Thi Nguyen, Khoa Dang Mai Nguyen, Hanh Huynh Ho, Phuoc Hoang, Bacterial Cellulose Aerogels Derived from Pineapple Peel Waste for the Adsorption of Dyes, *ACS Omega* 2023, 8(37) 33412–33425.
<https://doi.org/10.1021/acsomega.3c03130>
 18. Gautam, Ravindra Kumar, et al. "Synthesis of bimetallic Fe–Zn Nanoparticles and its application towards adsorptive removal of carcinogenic dye malachite green and Congo Red dye in water." *Journal of Molecular Liquids* 212 (2015): 227-236.
<https://doi.org/10.1016/j.molliq.2015.09.006>
 19. Manzoor, K., Batool, M., Naz, F. et al. A comprehensive review on application of plant-based bioadsorbents for Congo Red dye removal. *Biomass Conv. Bioref.* 14, 4511–4537 (2024).
<https://doi.org/10.1007/s13399-022-02741-5>
 20. Ahmad, I.Z., Ahmad, A., Tabassum, H., Kuddus, M.: Applications of Nanoparticles in the treatment of wastewater. In: *Handbook of Ecomaterials*. pp. 275–299 (2019)
https://doi.org/10.1007/978-3-319-48281-1_37-1
 21. Shi, Y., Yang, Z., Xing, L., Zhang, X., Li, X., Zhang, D.: Recent advances in the biodegradation of azo dyes. *World J. Microbiol. Biotechnol.* 37, 1–18 (2021).
<https://doi.org/10.1007/s11274-021-03110-6>