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Antimicrobial magnetic *Glycyrrhiza glabra* nanocomposite for decolouration of water through adsorption and photodegradation

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A sustainable hybrid magnetic nanocomposite based on *Glycyrrhiza glabra* (GG), GG/ γ -Fe₂O₃, was synthesized via one-pot co-precipitation method, and efficiently utilized for adsorption and photocatalytic degradation of two toxic model dyes, Congo red (CR) and Nile blue (NB) dyes from water. The characterization of the GG/ γ -Fe₂O₃ was performed by using FT-IR, P-XRD, BET-BJH, FE-SEM-EDX, TEM, SAED, XPS, TGA, UV-visible, and PL techniques. The GG/ γ -Fe₂O₃ showed significant inhibition of bacterial and fungal growth. The inhibition statistics towards gram-(+) and gram-(−) bacteria, and fungal strains were found superior as compared to the naive plant material. The influence of adsorption parameters, on dye removal efficiency, was appraised via batch methodology. The fitting of isothermal and kinetic datasets into their respective models indicated that the adsorptive removal process was governed by the Freundlich isotherm and pseudo-second order kinetics. The Langmuir saturation capacity for CR and NB was found to be 47.50 and 15.36 mg g^{−1}, respectively. The spontaneous and physical sorption of CR and NB was delineated to be exothermic and endothermic, respectively, from 30 to 50 °C. The band gap of the GG/ γ -Fe₂O₃ were found 1.69 eV (indirect), and 2.30 eV (direct) which established its semiconducting design, with CR solar-degradation efficiency of 92.7%, following pseudo-first-order kinetics. The degradation intermediates and mechanism have been investigated from radical quenching experiments and high-resolution LC-MS. The GG/ γ -Fe₂O₃ exhibited structural integrity and excellent regeneration, supported by post-treatment FT-IR analysis. The reproducibility of the optimum experimental dataset under realistic conditions, including real wastewater, co-existing ions, and dye mixtures, revealed potent application of multifunctional and cost-effective GG/ γ -Fe₂O₃ for the efficient removal of both cationic and anionic water contaminants, as well as for reducing microbial loads.

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1 Introduction

The increasing level of water pollution, owing to industrialization and agricultural expansion, is of grave environmental concern.¹ Untreated or partially-treated aqueous wastewater, from various industries, is interspersed with mainstream water resources, which is detrimental to human life and aquatic organisms. Dyes are a significant class of recalcitrant toxic water contaminants emanating alongside various pigments and by-products from many industries.² From over 11 800 commercially available dyes/pigments, the annual global consumption is estimated at around 19 million metric tons. Textile (42.6%),

paint and coating (27.8%), plastic (16.3%), and paper, cosmetics and ink (13.3%) industries are the major consumers of dyes.³ Around 10–15% industrial dyes are released into the environment during manufacturing and processing operations.⁴ Congo red, CR, a highly water-soluble anionic diazo dye is utilized in textile, paper, plastic, and printing industries.⁵ It is considered mutagenic, teratogenic, genotoxic, neurotoxic, cytotoxic, cutaneous, and carcinogenic.^{2,6} The short-term ingestion of CR can lead to skin, eye, gastrointestinal irritation, and possible blood clotting.⁷ Likewise, Nile blue, NB, is a cationic azine dye that finds application in the textile industry for dyeing cotton, wool, and other fabrics.^{8,9} It can cause sleepiness, stimulation of the digestive tract, chills, respiratory tract allergy, redness, dryness/irritation of eyes/mouth/throat/skin, dermatitis, lung cancer, and even chromosomal aberrations.^{8,10,11} The natural decomposition of such types of dyes is extremely difficult mainly due to their persistency, non-biodegradability, hydrophilicity, and stability.^{12,13} Additionally, dyes alter water transparency, impede sunlight penetration into the water bodies, fluctuate the water quality parameters, and

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cumulate the oxidative stress, which in turn severely affects the aquatic biota owing to decreased photosynthetic action.¹⁴ It is thereby imperative to amputate water resources of these hazardous pollutants, rendering water safe for human consumption.

Numerous techniques have been employed to clean dye-polluted water.¹⁵ However, the conventional treatment methods are cumbersome, expensive, time and energy-consuming, show low removal efficiency and residual discharge.¹⁶ Adsorption and photocatalytic degradation, of pollutants, have caught attention of many researchers, being simple, environment-friendly alternative, with minimum sludge formation, and high mineralization efficiency.¹⁷

Over last few decades, a variety of materials have been developed for the adsorptive removal of toxic dyes which include nanogels,^{18,19} metal-oxide nanocomposites,^{20–23} metal-organic frameworks,²⁴ plant-based materials,^{10,25} and activated carbon/biochar^{26,27} because of their ease of preparation, inexpensiveness, effectiveness over a wide range of pollutants, and porous structure with high adsorption capabilities and kinetics. However, restricted functionality, regeneration, and imitation to real environmental scenarios amidst competing conditions limit their practical application. Moreover, the complete removal of some azo-dyes (*e.g.*, CR) is rather difficult because of their complex aromatic structure, thermodynamic stability and non-biodegradability.¹¹ The secondary by-products formed being more toxic than the parent materials, render the synthesis of novel visible-light responsive photocatalysts and porous nanocomposites inevitable.²⁸

Therefore, adsorption coupled with heterogeneous photocatalysis has received considerable attention as an economical, rapid and reliable treatment option. Many nanostructured metal oxides, preferably iron oxides such as magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$)^{6,29–31} and their hybrid nanocomposites^{13,32} have evinced considerable interest for the removal of pernicious dyes, owing to surface defects, high surface area to volume ratio, intrinsic reactivity of surface functional sites, wide light response range, narrow band gap, chemical stability, low-cost, non-toxicity, biocompatibility, and abundance. Further, the surface modification of nanoparticles by compositing with plant residues (biomass) substantially reduces their strong tendency to agglomerate. Compositing also prevents premature surface saturation during treatment and acts as a solid-phase co-substrate to support oxide nanoparticles.^{33,34} Additionally, the presence of pathogens, like bacteria and fungi, in wastewater, may cause severe health hazards, leading to various chronic and acute respiratory, gastrointestinal, and skin-related disorders.³⁵ Therefore, in addition to synergistic dye adsorption and photodegradation, the antipathogenic activity of the synthesized composite is vital to reduce the microbial loads of the polluted water.^{36–38} *Glycyrrhiza glabra* (GG), commonly called licorice, is a traditional medicinal plant, possess therapeutic and pharmacological activities,³⁹ and is a proficient bio-sorptive material because of its active oxygenous functional surface sites.⁴⁰ It is a naturally abundant, biodegradable, and renewable bioresource, particularly, valued for its rich phytochemical composition, which bequeath antimicrobial and antioxidant potential.³⁹ The amalgamation of GG and $\gamma\text{-Fe}_2\text{O}_3$ into a hybrid composite enhances

removal efficiency, surface active sites, structural stability, and recovery using magnetic separation to efficaciously treat wastewater for charged contaminants, and even microbes. It is a step forward towards circular bioeconomy, repurposing waste plant/agro-biomass to enhance resource efficiency, and minimize ecological impact to synthetic chemicals, promoting sustainable environmental remediation.⁴¹ Moreover, research indicates use of iron oxide nanoparticles, particularly Fe_2O_3 as iron micronutrient fertilizer for improved soil texture and plant growth. It gradually increases the level of iron in soil over time.^{42,43} Thus, water enriched with GG and $\gamma\text{-Fe}_2\text{O}_3$ together can enhance soil and water dynamics after treatment.

Several synthetic strategies, including green synthesis, hydrothermal, microemulsions, sol-gel, thermal decomposition, and co-precipitation, have been developed for the production of $\gamma\text{-Fe}_2\text{O}_3$ -based nanocomposites.³³ Of these, co-precipitation is simplest, most cost-efficient, allows for better control of size and morphology, composition, stability, reproducibility, functionality, and can produce a large amount of product in a single batch.⁴⁴

G. glabra (biomass and biochar) has been previously explored for water remediation,^{45–48} however, much attempts have not been made towards its modification into nanocomposite. Moreover, no study has schematically delved into the multifunctional approach considering adsorption, photodegradation, and antimicrobial tendency of GG composites in real wastewater conditions.

Altogether, the present study outlines co-precipitation mediated synthesis of an inexpensive advanced multifunctional magnetic hybrid nanocomposite, GG/ $\gamma\text{-Fe}_2\text{O}_3$, which was characterized using FT-IR, P-XRD, BET-BJH, FE-SEM-EDX, TEM, SAED, XPS, TGA, UV-visible, and PL techniques. The GG/ $\gamma\text{-Fe}_2\text{O}_3$ was explored for investigating its potential to decolourize wastewater by removing model CR and NB dyes. Different operational conditions (dosage, initial dye concentration, contact time, initial water pH and temperature) have been optimized. The sorption data was fitted into various isotherm and kinetic models, and thermodynamic equations for proposing plausible mechanism. The adsorption and degradation performance of the GG/ $\gamma\text{-Fe}_2\text{O}_3$ towards real wastewater, and in presence of competing ions, and dye mixtures have been thoroughly investigated. The stability, and regeneration potential have also been investigated. Lastly, the antibacterial and antifungal activities of the naive GG and GG/ $\gamma\text{-Fe}_2\text{O}_3$ against Gram-negative, *E. coli* (ATCC-25922), and Gram-positive, *S. aureus* (MTCC-902), bacterial strains, and fungal stain, *C. albicans* (SC-5314 and ATCC-90028), have also been investigated.

2 Materials and methods

2.1. Reagents and materials

The chemicals and instruments used for the synthesis and characterization of GG/ $\gamma\text{-Fe}_2\text{O}_3$ have been depicted in Tables S1 and S2, respectively.

2.2. Preparation of GG/ $\gamma\text{-Fe}_2\text{O}_3$

The GG roots were washed several times with deionized water to leach out solid or water-soluble impurities, oven-dried, and subjected to physical pre-treatment through



pulverization and sieving to a variable grain diameter (mesh) size of 60–200. Such pre-treatment downsizes particle dimensions and increases the available specific surface area⁴⁹ for the growth of γ - Fe_2O_3 nanoparticles on powdered GG following a slightly modified simple one-pot coprecipitation method.^{50,51} 1.0 g of GG powder was dispersed in 100 mL of distilled water (DW) and ultrasonicated for 15 min to prepare a homogeneous suspension. The suspension was stirred, over a magnetic stirrer, followed by the addition of 100 mL of 0.5 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.25 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ each, and was subjected to continuous stirring for 30 min at 50–60 °C. This was followed by the addition of 2 M NaOH solution dropwise until the suspension turned alkaline (~10–11 pH). The obtained brownish-black precipitate was allowed to settle, collected using a magnetic-separation method, and washed with deionized water, multiple times, followed by ethanol. It was oven-dried at 70 °C, calcined at 200 °C for 2 h, sieved, and stored in glass bottle. The schematic representation of the synthesis of GG/ γ - Fe_2O_3 is depicted in Scheme 1.

2.3. Point of zero charge (ZPC)

The ZPC, pH at which the surface possesses zero charge,⁵² was determined by following a slightly modified salt addition method.⁵³ A brief setup of a series of 100 mL Erlenmeyer flasks comprising double of the optimized dosage of GG/ γ - Fe_2O_3 in 20 mL of 0.2 M KNO_3 solutions, having pH variation in the pH range 2–10 were prepared and agitated for 24 h at 200 rpm. The final pHs of all solutions were recorded, and the point of intersection of the initial and final pHs curves established pH_{ZPC} of the GG/ γ - Fe_2O_3 .

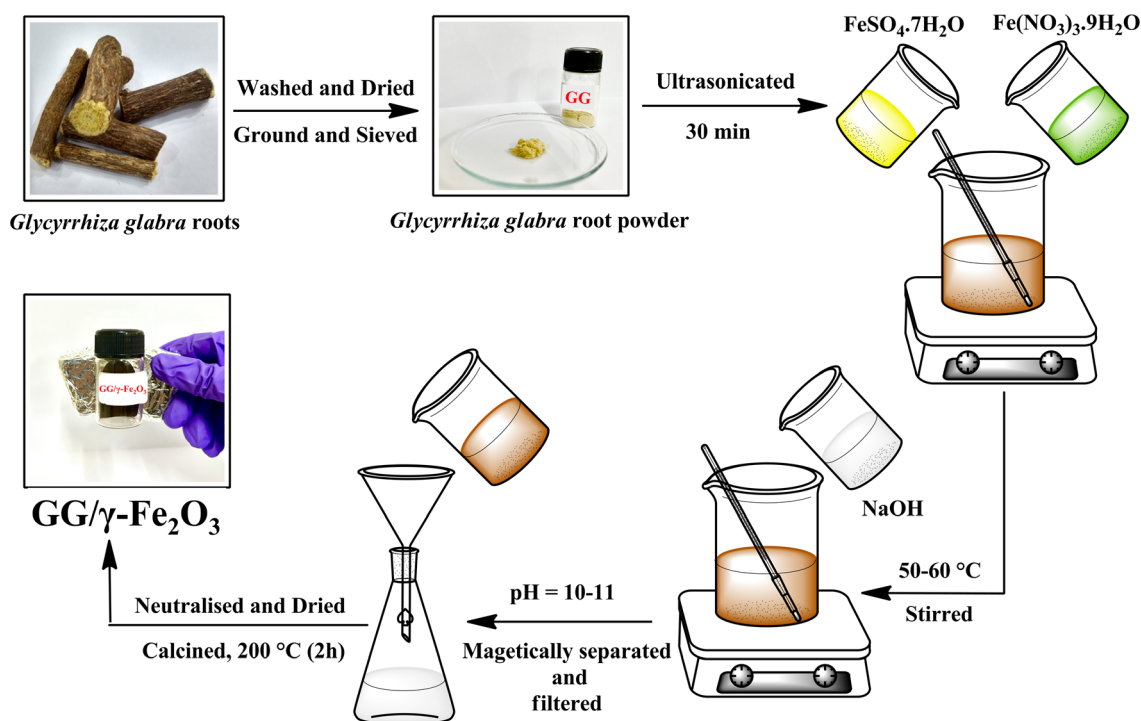
2.4. Antimicrobial activity

The antibacterial activities of the GG and GG/ γ - Fe_2O_3 were investigated using *in vitro* 96-well microtiter assays against *E. coli* and *S. aureus* bacteria. The broth micro dilution method was followed for the determination of the minimum inhibitory concentration (MIC), and minimum bactericidal concentration (MBC).⁵⁴ Each test strain was cultivated overnight in nutrient broth, with the turbidity adjusted to 0.5 McFarland units in 100 μL of Mueller–Hinton broth. The GG and GG/ γ - Fe_2O_3 stock suspensions (5.0 mg mL^{-1}) were added to each well. Positive and negative controls were also added, and then the plates were incubated at 37 °C for 12 h. To obtain MBC values, 100 μL of turbidity-free tube content was cultured in Mueller–Hinton agar and incubated for 24 h at 37 ± 0.1 °C.⁵⁵

The antifungal efficacy of the GG and GG/ γ - Fe_2O_3 , in terms of MIC and minimum fungicidal concentration (MFC)⁵⁶ were determined against *C. albicans* (SC-5314) and *C. albicans* (ATCC-90028), as described in the literature.⁵⁷ Briefly, 100 μL of yeast peptone dextrose media (YPD) and GG and GG/ γ - Fe_2O_3 stock solutions (5 mg mL^{-1}) were added to the first well, which was then serially diluted. Following the addition of 100 μL of fungal inoculant as a suspension in each well, the plates were incubated at 28 °C for 24 h. Plates without GG and GG/ γ - Fe_2O_3 served as a negative control, while the antifungal drug, fluconazole, as a positive control. For both assays, the respective culture growth was noted as absorbance at 600 nm on Elisa plate reader. All experiments were conducted in triplicate simultaneously.

2.5. Batch adsorption study and statistical data analysis

The factors which affect the removal efficiency were optimized by varying GG/ γ - Fe_2O_3 dosage (0.5–3 g L^{-1}), dyes concentration



Scheme 1 Stepwise depiction of the synthesis of GG/ γ - Fe_2O_3 nanocomposite.



(5–30 mg L⁻¹), reaction time (15–120 min), solution pH (2–11), and temperature (30, 40, 50 °C). Briefly, in 100 mL Erlenmeyer flasks, CR and NB solutions (10 mL) having concentrations of 10 and 20 mg L⁻¹, respectively, were mechanically shaken at 200 rpm at 30 °C and natural pH with varying dosage for 120 min. The effect of temperature was investigated using the optimized dosage of GG/γ-Fe₂O₃ (2.0 g L⁻¹), and [CR] = 10 mg L⁻¹ and [NB] = 20 mg L⁻¹. The experiments were performed in triplicate, and the mean values have been reported.

The rationale for selecting the experimental variables and their transferability to real systems was supported by preliminary batch adsorption trials and relevant literature.^{53,58} The initial screening experiments, using 0.5–3 g L⁻¹ GG/γ-Fe₂O₃ for 5–30 mg L⁻¹ CR and NB, showed good adsorption results without causing saturation or particle agglomeration. The time of contact, 15–120 min, ensured sufficient sorbent–pollutant interactions and practical treatment duration, as evident from the kinetic investigation. The pH range 2–11 was chosen, considering the pH sensitivity of CR and NB dyes, to obtain the maximum adsorption. Further, the reproducibility, reliability, and statistical significance of the experimentally optimized variables were realized using one-way analysis of variance (ANOVA, Origin Pro 8.5), at the 0.05 level. The standard deviation (SD) values (Table S3) have been depicted as error in Fig. S3, while the complete statistical analysis is given in Table S4. The realized experimental variable range ensured an efficient sorptive system and statistically valid optimisation.

After adsorption and magnetic separation of the dye-loaded GG/γ-Fe₂O₃, the concentrations of residual dyes were determined at λ_{max} 498 nm for CR and 627 nm for NB using a UV-visible spectrophotometer (T80+ UV/VIS, PG instruments Ltd, Leicestershire, England). The following equations were employed for the evaluation of per cent removal [eqn (1)] and equilibrium adsorption capacity [eqn (2)] of the GG/γ-Fe₂O₃.⁵⁹

$$\text{Removal efficiency (\% removal)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$Q_e = (C_0 - C_e) \times \frac{V}{m} \quad (\text{mass balance relationship}) \quad (2)$$

where, *m* (g) is the mass of GG/γ-Fe₂O₃, *V* (L) is volume of CR or NB solution; *C*₀ and *C*_e are initial and final equilibrium concentrations of the dye solutions (mg L⁻¹), respectively; and *Q*_e (mg g⁻¹) is the equilibrium adsorption capacity of the GG/γ-Fe₂O₃.

2.6. Photocatalytic degradation

Photocatalytic activity of the GG/γ-Fe₂O₃ against CR was investigated at its optimized sorption conditions. 2.0 g L⁻¹ of nanocomposite was placed in 100 mL of 10 mg L⁻¹ CR solution in dark for 1 h, under constant stirring for attainment of adsorption–desorption equilibrium on the catalytic surface. It was followed by subsequent irradiation under sunlight with uninterrupted stirring for 0–160 min. 10 mL of the degraded supernatant dye solution was withdrawn at 20 min intervals, centrifuged, and analysed spectrophotometrically. The time-dependent UV-visible spectra (*A* vs. *λ*) were recorded from *λ*

250 to 600 nm, for different intervals of time, and photocatalytic degradation efficiency (% DE) was evaluated using the following equation⁶⁰ [eqn (3)]:

$$\begin{aligned} \text{Photocatalytic degradation efficiency (\% DE)} \\ = \frac{(C_0 - C_t)}{C_0} \times 100 \end{aligned} \quad (3)$$

where, *C*_{*t*} (mg L⁻¹) is the concentration of the dye solution at irradiation time *t*.

The kinetics of the degradation, and the rate constant of the process were computed by employing the following pseudo-first order kinetic relationship [eqn (4)]:

$$\ln\left(\frac{C_t}{C_0}\right) = \ln\left(\frac{A_t}{A_0}\right) = -kt \quad (4)$$

where, *k* is the pseudo-first order rate constant, while *A*₀/*C*₀ and *A*_{*t*}/*C*_{*t*} are the initial and final absorbance/concentration, respectively.⁶⁰

Further, radical trapping experiments were performed for the detection of active degradation species.⁶¹ 4.0 mL each of benzoquinone (BQ, 1 mM), isopropanol (IPA, 2:20 vol/vol), and ethylenediaminetetraacetic acid (EDTA, 10 mM) scavengers were introduced to 100 mL, 10 mg L⁻¹ CR solution, and used to trap superoxide radicals (O₂⁻), hydroxyl radicals (OH[•]), and holes (h⁺), respectively. Lastly, a plausible mechanism, for the photodegradation of CR, has been proposed in accordance with the liquid chromatography-high resolution mass spectrometry (LC-HRMS) results.

2.7. Real wastewater analysis and effect of co-existing ions

The adsorption and photodegradation tendency of GG/γ-Fe₂O₃ towards actual real water sample were evaluated using sewage water (SW, collected from sewage treatment plant, Batla House, New Delhi), RO water (RO), and tap water (TW) spiked with 10 mg L⁻¹ CR and 20 mg L⁻¹ NB dye concentrations, under optimized conditions, at their natural pH. Such water samples have ample co-existing ions which might compete with the charged organic water contaminants for sorptive sites, interfering with their removal. Thereby, 10 mM of various inorganic anions (Cl⁻, NO₃⁻, SO₄²⁻, and CO₃²⁻), and cations (Na⁺, Ca²⁺) were selected to investigate the adsorption and degradation effect of GG/γ-Fe₂O₃ for CR and NB.

2.8. Adsorption selectivity in dye mixture

Real wastewater might contain a mixture of organic dyes, and the advancement of new materials for targeted adsorption relies on their selectivity. The adsorption selectivity of 2.0 g L⁻¹ GG/γ-Fe₂O₃ for CR and NB dyes was justified through single-dye system, their binary mixture, and of their mixture in a quaternary setup of two anionic (A) and two cationic (C) dyes each. The concentrations of all anionic dyes were taken as 10 mg L⁻¹, and cationic dyes as 20 mg L⁻¹.

2.9. Regeneration study

The reusability analysis of the spent GG/γ-Fe₂O₃ is significant for commercial application to diminish the overall treatment

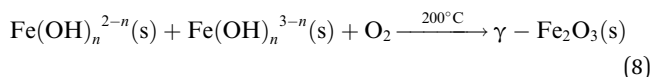
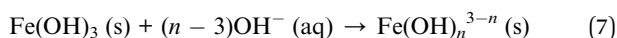
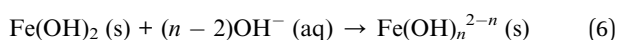
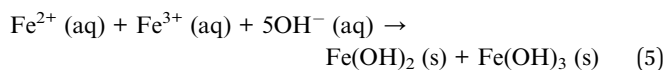


cost, promoting a sustainable and efficient water treatment process. For regeneration, 2.0 g L⁻¹ of CR/NB-loaded GG/γ-Fe₂O₃ nanocomposite was dispersed in 10 mL of ethanol and the suspensions were agitated in a water bath shaker at 30 °C at 200 rpm for 4 h. The spent GG/γ-Fe₂O₃ was washed until neutral pH, dried, and subjected to subsequent reusability–regeneration cycles. The percentage removal of dyes were determined spectrophotometrically in each cycle using eqn (1). The stability of spent GG/γ-Fe₂O₃ was established *via* FT-IR analysis post adsorption of CR and NB after a considerable number of adsorption–desorption cycles.

3 Result and discussion

3.1. Mechanism for preparation of GG/γ-Fe₂O₃

The mechanism of formation of GG/γ-Fe₂O₃ can be understood by considering the entrapment of Fe²⁺ and Fe³⁺ by oxygeneous groups (–OH and –COOH) at the GG surface through site-specific adsorption. The precipitating agent NaOH supplies enough OH⁻ which might have electrostatically attracted the adsorbed Fe²⁺ and Fe³⁺ yielding respective hydroxides, M(OH)_x that ultimately transformed into multiple hydroxyls bearing Fe(OH)_n²⁻ⁿ and Fe(OH)_n³⁻ⁿ species.⁶² Afterwards, dehydration and subsequent nucleation of these hydroxides, on porous GG surface, might have led to the formation of γ-Fe₂O₃, and later GG/γ-Fe₂O₃ *via* incorporation with the GG framework (Fig. S1). However, it may also be stated that the high concentration of NaOH, in the reaction mixture, might have also been responsible for driving the nucleation process towards the formation of tiny nuclei, leading to a decrease in the crystallite size of particles.⁶³ A theoretical mechanism depicting the formation of GG/γ-Fe₂O₃ can be proposed as [eqn (5)–(9)]:^{62,64,65}



3.2. Characterization

3.2.1. Fourier transform infrared spectroscopy. The Fourier transform infrared (FT-IR) analysis of the GG root powder specified the chemical composition and bonding of various functional groups, which results in the formation of the GG/γ-Fe₂O₃. The FT-IR spectrum of the GG {Fig. 1A(a)} showed a large number of peaks in the range 4000–650 cm⁻¹. A broad band, for O–H bonds due to alcoholic/phenolic compounds, like cellulose, hemicellulose or lignin, owing to intermolecular hydrogen bonding, was observed at 3362 cm⁻¹. It was followed by strong anti-symmetric and medium symmetric C–H stretching

frequencies of aliphatic –CH₃ and –CH₂ groups around 2930 and 2882 cm⁻¹, respectively.⁶⁶ The absorption peaks around 2136, 1637, and 1516 cm⁻¹ corresponded to the presence of benzene rings of flavonoids, phytosterols, *etc.*, appeared for stretching vibrations of C≡C, C=O in polyphenol carbonyl or carboxyl groups of flavonoids in conjugation with, or of C=C of aliphatic and aromatic systems.^{66,67} Moreover, the peak at 1637 cm⁻¹ also depicted the bending vibration of the O–H bond due to the entrapped moisture.⁶⁸ The peaks at 1423 and 1370 cm⁻¹ indicated the C–H bending vibrations due to –CH₃ and –CH₂ groups, respectively, from aliphatic chains or methoxy (O–CH₃) groups in lignocellulosic materials. The bands at 1246, 1152, and 1026 cm⁻¹ explicated deformational vibration of the C–O bond from acids, and/or ester functional groups of glycosides.^{66,69} While, the presence of flavonoids and saponins were confirmed by strong coupled vibrations at 849 and 762 cm⁻¹ due to out-of-plane bending deformations of C–H bond.⁶⁶ Thereby, the abundance of alcoholic, phenolic, carbonyl, carboxyl, and ester functional groups, on the GG surface, was quite evident.

The FT-IR spectrum of the GG/γ-Fe₂O₃ {Fig. 1A(b)} was scrutinized to discern the nature of interactions between GG surface functional groups and the integrated oxides. Slightly shifted and less intense peaks, with usual annotations to GG, were ascertained at 3378, 2925, 2854, 1624, 1462, 1381, 1022, 887, and 794 cm⁻¹. The peak at 1152 cm⁻¹ showed no shifting; however, some of the minor peaks got quenched, and some new peaks were spotted. This behaviour could be attributed to the possible increase in bond strength and formation of electrostatic and hydrogen bonds. Some new peaks, in the range 650–400 cm⁻¹, depicted the successful formation of GG/γ-Fe₂O₃ *via* metal–oxygen bond vibrations. Peaks at 623, 589, and 449 cm⁻¹ might be attributed to the Fe–O–C stretching vibrations which are characteristics of ν(Fe–O) stretching mode in iron oxides.^{68,70}

3.2.2. Powder-X-ray diffraction crystallography. The Powder-X-ray diffraction (P-XRD) patterns of GG and GG/γ-Fe₂O₃ (Fig. 1B) were analyzed in the angular range 5–90° (2θ). A broad peak around 22.48° (2θ) was observed for the GG corresponding to the (002) plane, characteristic peak of amorphous cellulosic material.⁷¹ However, the diffraction pattern of the GG/γ-Fe₂O₃ manifested distinct intense peaks at 18.14° (111), 30.1° (220), 35.54° (311), 43.46° (400), 53.98° (422), 57.16° (511), 62.76° (440), 70.9° (620), 73.98° (533), 78.86° (622) 21.14° (200), 23.78° (210), 26.10° (211), 32.24° (300), and 39.36° (320) due to the presence of γ-Fe₂O₃ (JCPDS PDF-04-0755). Moreover, a gradual change in colour from black to brownish black on heating exemplified the slow oxidation of magnetite to maghemite.⁷² The angular values ruled out the possibility of formation of other types of iron oxides, *i.e.*, hematite (α-Fe₂O₃), goethite [FeO(OH)], wüstite (FeO), *etc.*⁷³ Meanwhile, the occurrence of most intense peak at 35.54°, corresponding to (311) plane, was close to the standard angular value of 35.597° for γ-Fe₂O₃, signifying γ-Fe₂O₃ as the predominant crystalline phase in GG/γ-Fe₂O₃.²² On comparison of the two diffractograms (Fig. 1B) it was observed that GG/γ-Fe₂O₃ displayed peaks of both GG and γ-Fe₂O₃ at various 2θ levels. However, the intensity of diffraction peak at 22.48° for GG significantly got reduced in



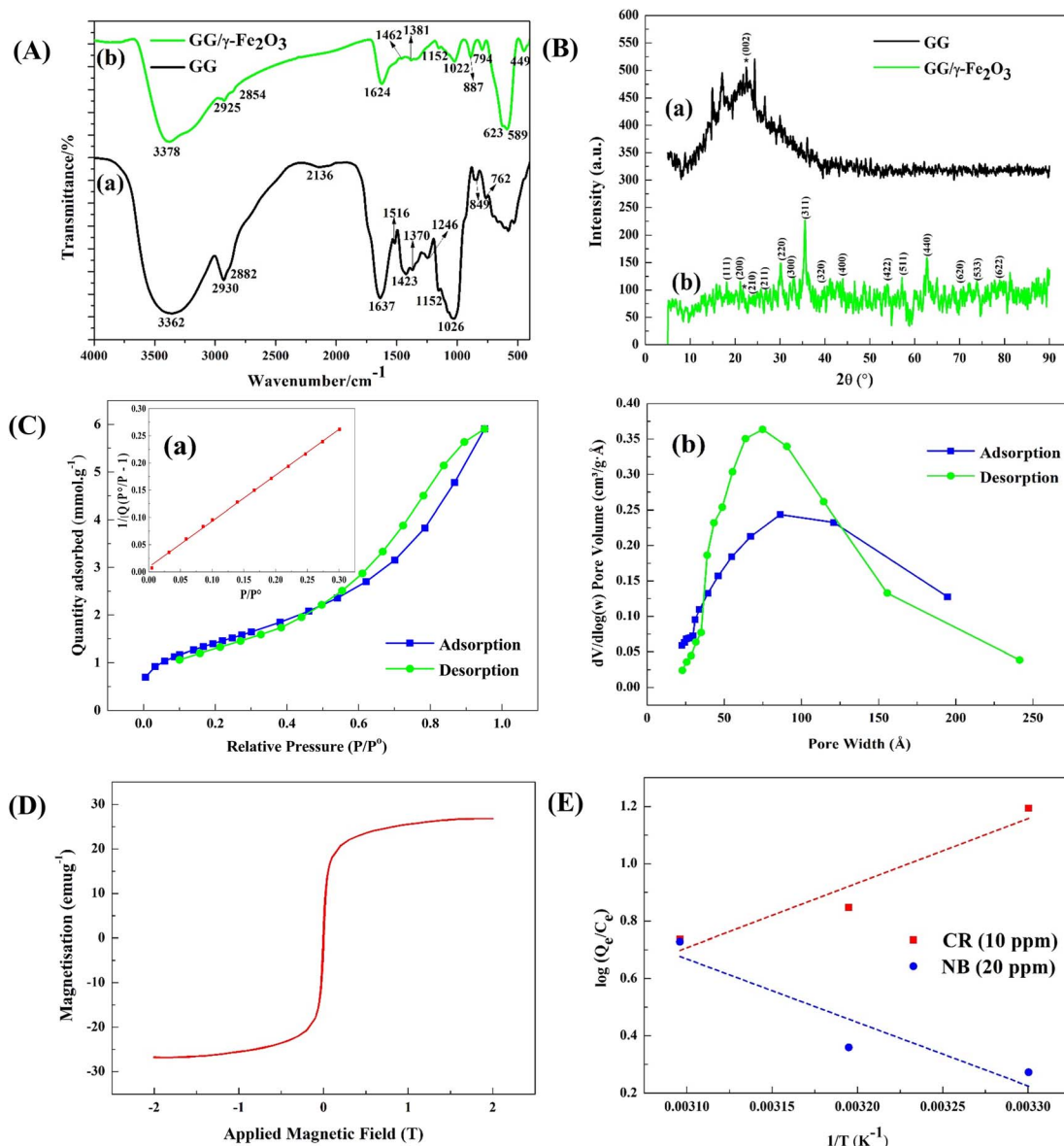


Fig. 1 (A) FT-IR spectra of (a) GG, and (b) GG/ γ -Fe₂O₃; (B) P-XRD analysis of (a) GG, and (b) GG/ γ -Fe₂O₃; (C) (a) BET, and (b) BJH curves; (D) M - H magnetization curve of GG/ γ -Fe₂O₃; (E) Van't Hoff plots.

GG/ γ -Fe₂O₃ owing to chemical interactions between its oxygenous functional groups and γ -Fe₂O₃ nanoparticles. The mean crystallite size, corresponding to prominent peaks of the XRD pattern, was estimated by fitting the angular data in the Debye-Scherrer equation (eqn (S1))⁷⁴ as 36.09 nm, confirming the nanostructure of high surface area, suitable for greater dye adsorption. Moreover, the nature and intensity of the peaks indicated low crystallinity of GG/ γ -Fe₂O₃.

3.2.3. BET and BJH analysis. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis was followed to determine surface area, average pore width, and single point total pore volume (of pores less than 413.690 Å width at $P/P^0 = 0.951$) of the GG/ γ -Fe₂O₃, which were found to be 114.454 m² g⁻¹, 71.549 Å, and 0.205 cm³ g⁻¹, respectively. The amount of the N₂ gas adsorbed by the GG/ γ -Fe₂O₃ decreased with reducing

pressure, and N₂ adsorption-desorption isotherm was similar to Type-IV, characteristic of a mesoporous structure {Fig. 1C(a)}.⁷⁵ The adsorption average pore size ($4 V A^{-1}$) distribution was centered at 75.251 Å, while the desorption average pore size ($4 V A^{-1}$) was found to be 70.258 Å from the BJH plot {Fig. 1C(b)}. The specific surface area and porosity of the GG/ γ -Fe₂O₃ were found to be appreciably high, indicating superior physical and textural characteristics.

3.2.4. Vibrating sample magnetometry. The magnetic hysteresis, M - H curve, recorded *via* vibrating sample magnetometry (VSM), indicated the magnetic nature of the GG/ γ -Fe₂O₃ in field strength of -2 T to +2 T (Fig. 1D). An S-shaped curve was observed, which suggested superparamagnetism, at room temperature mainly of the single magnetic domains of the nanoparticles in the material.⁷⁶ The saturation magnetic



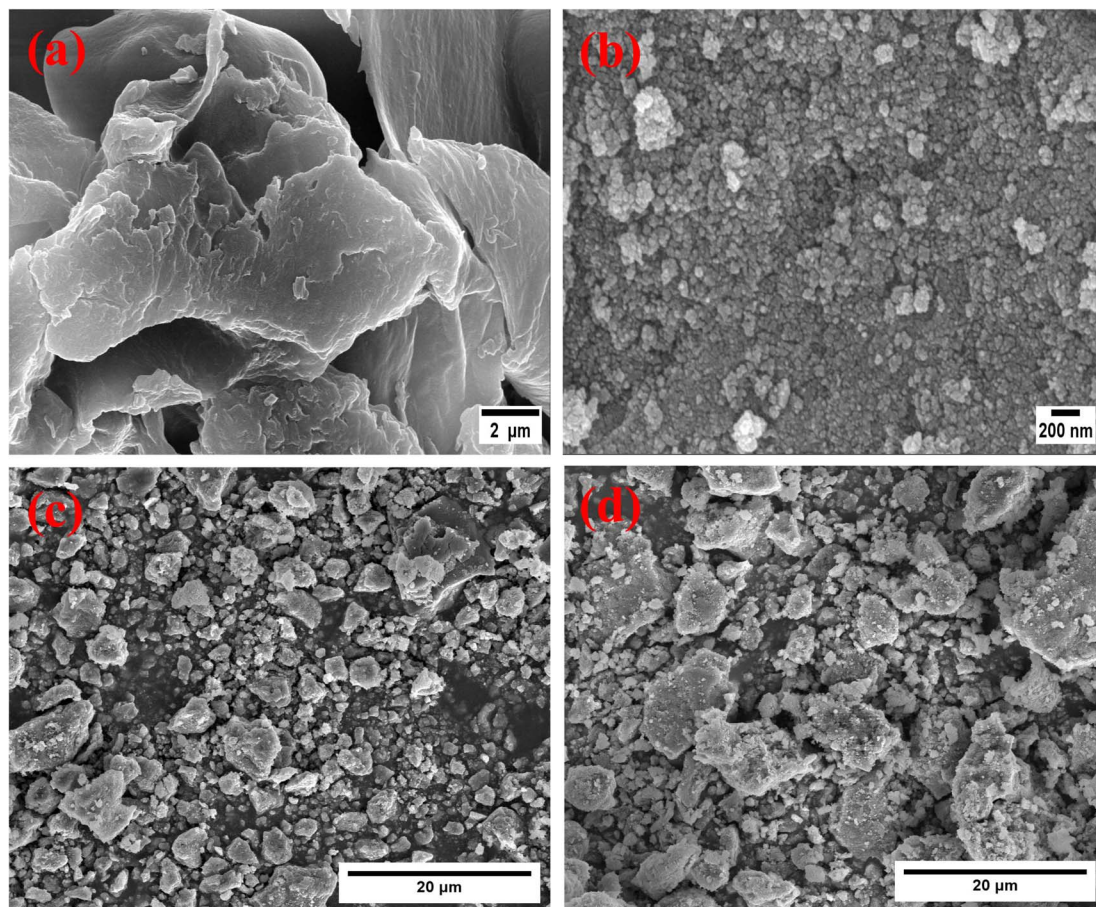


Fig. 2 FE-SEM images of (a) GG, (b) GG/ γ -Fe₂O₃, (c) GG/ γ -Fe₂O₃ before adsorption, and (d) GG/ γ -Fe₂O₃@CR.

moment, M_s , of the GG/ γ -Fe₂O₃ was found to be 26.827 emu g⁻¹, which is modest for the easy magnetic separation of the nanocomposite from the treated water.

3.2.5. FE-SEM-EDX and TEM. Field emission scanning electron microscopy (FE-SEM) imaging revealed a smooth and even surface of GG (Fig. 2a) and the introduction of heterogeneity and roughness in the GG/ γ -Fe₂O₃ surface due to clustering of irregular oxide nanoparticles (Fig. 2b and c). An enhancement in overall contending porosity and surface area was observed in GG/ γ -Fe₂O₃ for increased CR and NB uptake. The CR accumulation on the GG/ γ -Fe₂O₃ surface (Fig. 2d) caused abatement of even surface with significant accretion making the surface inhomogeneous. Elemental composition of the GG and GG/ γ -Fe₂O₃ were ascertained from the energy dispersive X-ray spectroscopy, EDX, and elemental mapping (Fig. 3a and b). The normalized atomic percentage of 67.70% C, and 32.30% O were detected for GG, while the composition fluctuated to 23% C, 64% O, and 13% Fe owing to the nanostructured growth of γ -Fe₂O₃ on GG framework. The analysis suggested the presence of C, H and O due to GG, while increase in % O, decrease in % C, and presence of iron was due to formation of nanostructured Fe(III) oxide which deposited in the form γ -Fe₂O₃.

Transmission electron microscopy (TEM) (Fig. 4a and c) provided a clear indication of the average size distribution of

the GG/ γ -Fe₂O₃ particles. The mean particle size of the GG/ γ -Fe₂O₃ (Fig. 4b) was estimated around 31.92 nm, which is in line with the XRD result (Fig. 1B). The contrast between the brighter GG framework and darker patches of γ -Fe₂O₃ corresponded to the uniform deposition, entrapment, and random dispersion of nanoparticles throughout. Moreover, the TEM images confirmed the amorphous and heterogeneous nature of GG/ γ -Fe₂O₃. The lattice fringes with protuberant electron diffraction rings in the selected area electron diffraction (SAED) pattern (Fig. 4d) indicated an amorphous nature with slight crystallinity of γ -Fe₂O₃ nanoparticles in GG/ γ -Fe₂O₃.⁷⁷ The d -spacing values and corresponding Miller indices of the six diffraction rings (Table S5) aligned with the XRD findings.

3.2.6. X-ray photoelectron spectroscopy. The chemical environment and the elemental valence states were further investigated through X-ray photoelectron spectroscopy (XPS) analysis of the GG/ γ -Fe₂O₃ (Fig. 5). The co-existence of elements Fe, O, and C was confirmed, which was consistent with the EDX data. The high-resolution narrow spectrum of Fe 2p (Fig. 5b) matches the core-level binding energies of the spin-orbit doublets Fe 2p_{3/2} and Fe 2p_{1/2}, centered at 710.4 and 724 eV, which is characteristic of Fe³⁺ in γ -Fe₂O₃. The Fe³⁺ 2p_{3/2} can be deconvoluted into two distinct sub peaks at 710.2 and 712 eV for Fe³⁺ in octahedral and tetrahedral sites, respectively.⁷⁸ Further,



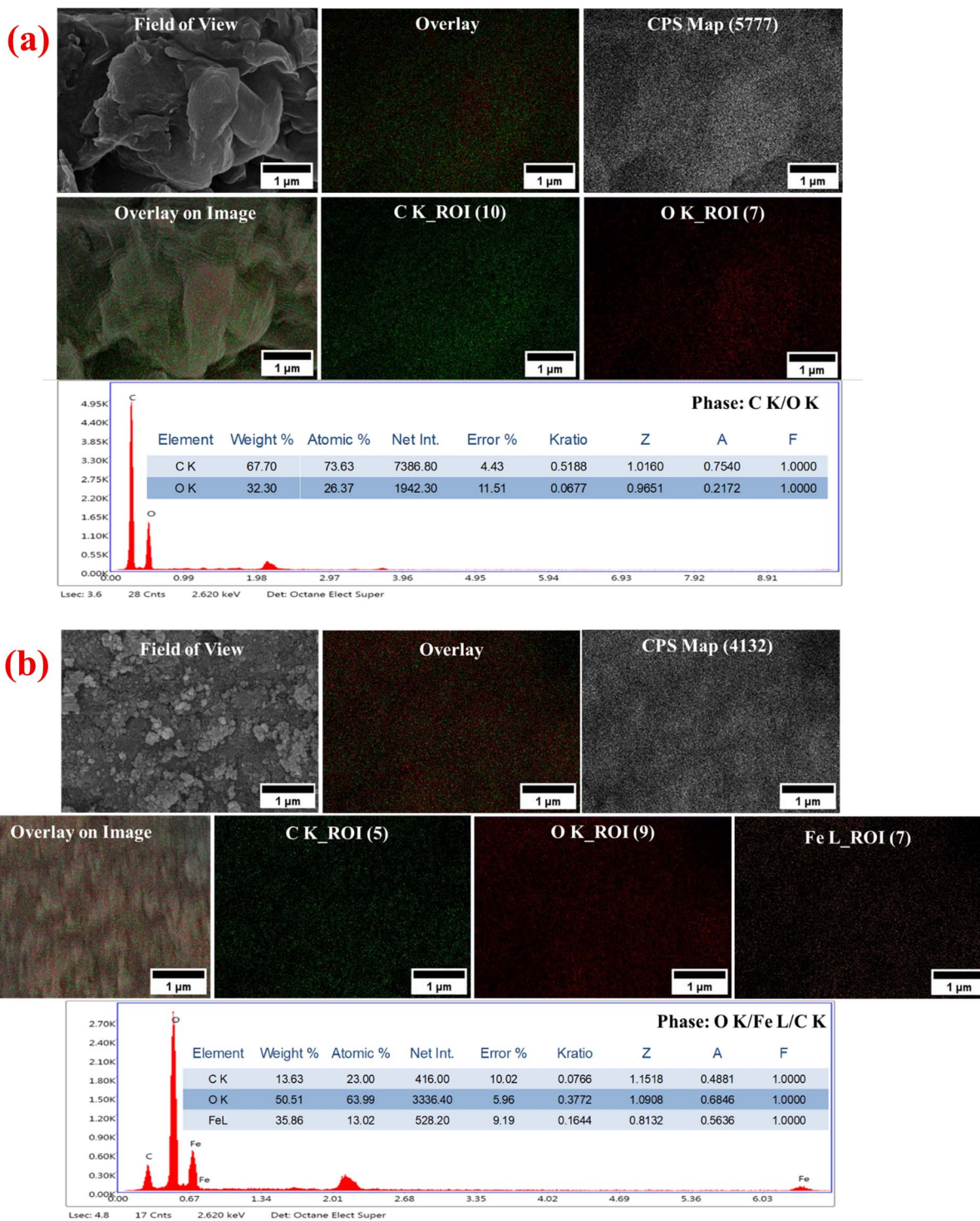


Fig. 3 EDX and mapping of (a) GG and (b) GG/ γ -Fe₂O₃.

shake-up satellite peaks for Fe 2p_{3/2} at 718.9, and Fe 2p_{1/2} at 733⁷⁹ were indicative of transition of Fe-3d electrons to empty 4s orbital during ejection of core 2p photoelectrons.⁷⁸ Moreover, the O 1s scan of GG/ γ -Fe₂O₃ (Fig. 5c) validated the prevalence of Fe–O bonds *via* peak at binding energy 529.6 eV; and the peak at 531 eV was assigned to C–O–Fe bond linkage between GG carbon framework and γ -Fe₂O₃.⁸⁰ An additional peak at 532 eV

was attributed to the C–O units (C–OH/C–O–C) in oxygen-containing functional groups.⁸¹ Lastly, the C 1s XPS spectrum (Fig. 5d) exhibited three fitted peaks of C–C/C=C, C–O, and O–C=O centered at 284.6, 286.18 and 288.2 eV.⁸² These results validated the FT-IR established functional groups and the formation of new metal–oxygen bonding interactions in the GG/ γ -Fe₂O₃ nanocomposite.



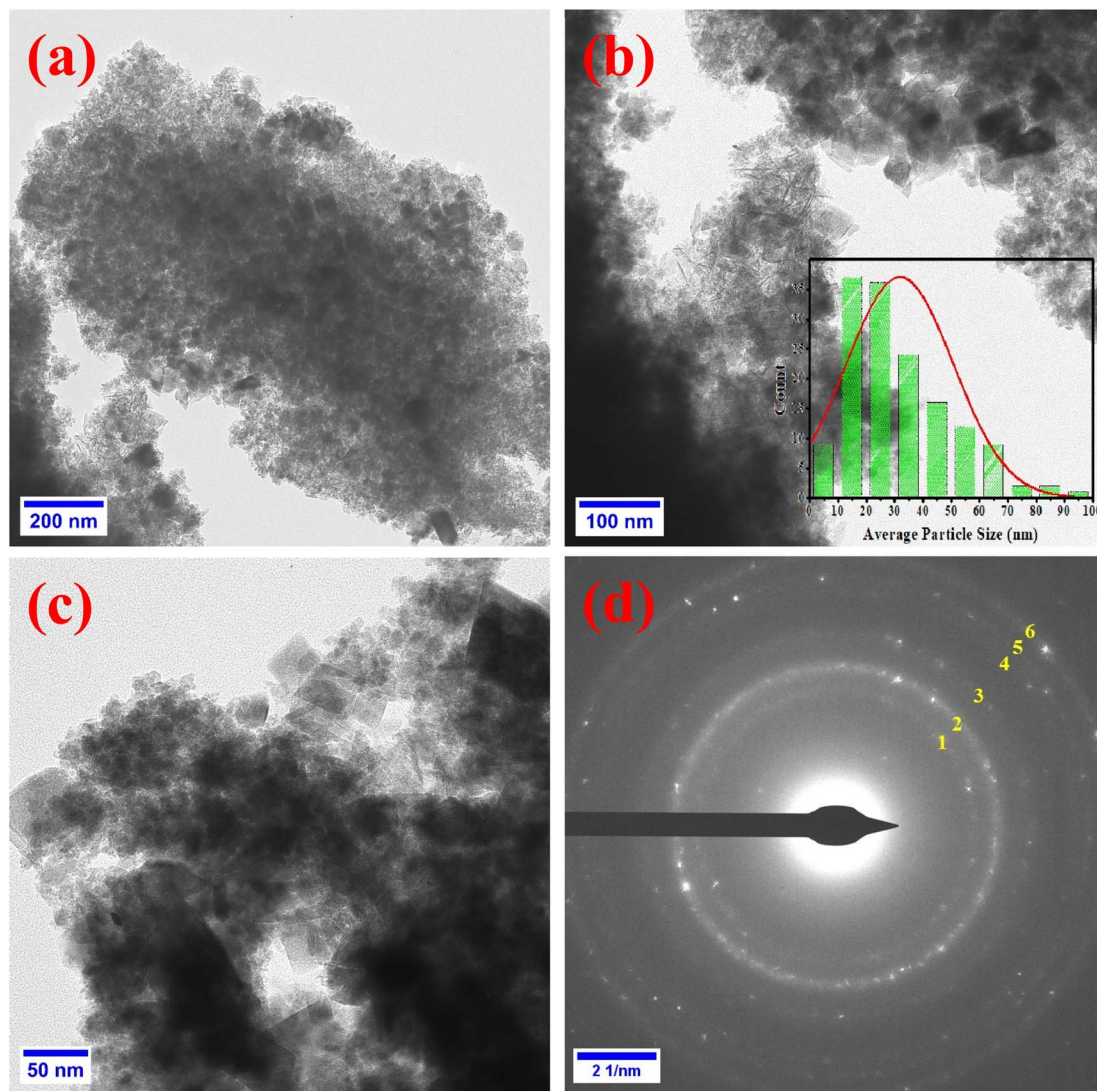


Fig. 4 (a)–(c) represent TEM images, and (d) the SAED ring pattern of GG/ γ -Fe₂O₃.

3.2.7. Thermogravimetric analysis (TGA). The weight loss curve of the GG/ γ -Fe₂O₃, due to thermal decomposition (Fig. 5e), shows gradual weight loss of 6.13% from room temperature to around 190 °C, related to the removal of residual surface water molecules. The primary decomposition of the sample occurred around 200–470 °C, accompanying biomass pyrolysis.⁸³ A slight weight change was observed at higher temperature, more than 470 °C due to phase transition.⁸⁴ The residual weight percent of 77.63% was realized, indicating high structural and thermal stability of the nanocomposite.

3.2.8. Optical properties of GG/ γ -Fe₂O₃. The UV-visible spectroscopic analysis of the GG/ γ -Fe₂O₃ (Fig. S2a) showed peaks between 320–420 nm, which are typically associated with the surface plasmon resonance of iron in γ -Fe₂O₃.⁸⁵ The band gap energy, E_g , is crucial for predicting the photochemical and photophysical characteristics of material that is used for photocatalytic dye degradation. γ -Fe₂O₃ based semiconductors have been known to exhibit both indirect [$O^{2-}(2p) \rightarrow Fe^{3+}(3d)$] and direct [$Fe^{3+}(3d) \rightarrow 3d$] transitions.^{86–88} The indirect and

direct transition band gap of the GG/ γ -Fe₂O₃, were determined by the Tauc plot, and found 1.69 and 2.30 eV, respectively (Fig. S2b and c). These band gap energy values established its semiconducting nature.

The photoluminescence (PL) spectra of the GG (Fig. S2d), GG/ γ -Fe₂O₃ and pure γ -Fe₂O₃ (Fig. 5f) were acquired at an excitation wavelength of 325 nm to comprehend the charge carrier separation efficiency and the recombination rate of electron–hole pair. The emission varied from 350 to 800 nm, with broad and intense emission bands centered at \sim 480 nm and \sim 565 nm in pure γ -Fe₂O₃ nanoparticles which might be due to exciton emission, and radiative recombination of mobile and trapped electrons on octahedral and tetrahedral sites of γ -Fe₂O₃, respectively.⁸⁹ However, the intensity of the peaks reduced significantly in GG/ γ -Fe₂O₃, confirming the hampering of recombination of photogenerated charge carriers. The PL spectra of GG was of highest intensity, which reduced drastically on combination with γ -Fe₂O₃.



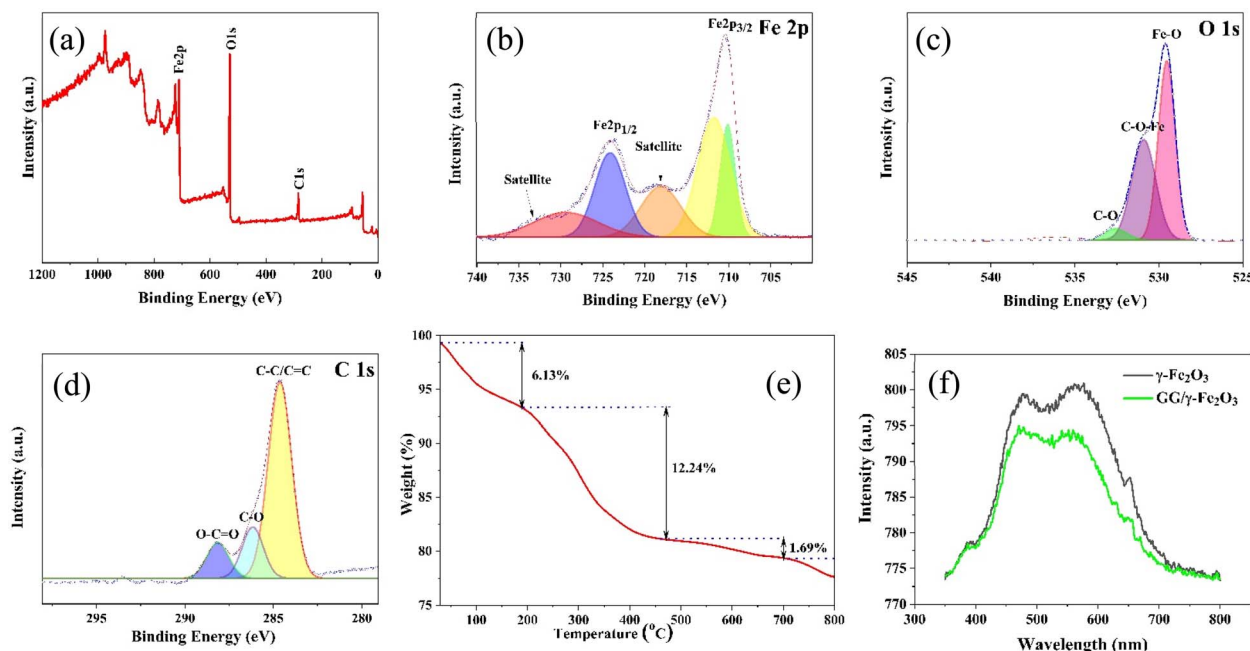


Fig. 5 (a) The full survey scan, and high-resolution spectra of (b) Fe 2p, (c) O 1s, (d) C 1s of GG/ γ -Fe₂O₃; (e) TGA of GG/ γ -Fe₂O₃; (f) PL spectra of γ -Fe₂O₃ and GG/ γ -Fe₂O₃.

3.3. Inhibition of growth of microorganisms

The GG and GG/ γ -Fe₂O₃ exhibited dose-dependent inhibition of pathogenic bacteria. The MICs of GG were found to be 550.25 ± 1.85 and 425.5 ± 1.25 $\mu\text{g mL}^{-1}$, whereas for GG/ γ -Fe₂O₃, these values were found to be 250 ± 3.15 and 200 ± 2.62 $\mu\text{g mL}^{-1}$, for *E. coli* and *S. aureus*, respectively (Table S6). The lower MIC values of the GG/ γ -Fe₂O₃ against both Gram-negative and Gram-positive bacteria, in comparison to GG, suggested the superiority of GG/ γ -Fe₂O₃ for treating bacterial pathogens in wastewater. The GG and GG/ γ -Fe₂O₃ generally showed more antibacterial effects against Gram-positive bacteria, due to differences in cell composition and thickness, compared to Gram-negative bacteria. The findings were aligned with previous studies that also indicated the antimicrobial potential of the GG.^{90,91}

In addition, the GG and GG/ γ -Fe₂O₃ also exhibited significant antifungal activity against two *Candida albicans* strains. The GG exhibited MICs of 300.85 ± 8.58 $\mu\text{g mL}^{-1}$ and 320.74 ± 5.65 $\mu\text{g mL}^{-1}$, while GG/ γ -Fe₂O₃ showed MICs of 131.25 ± 2.56 $\mu\text{g mL}^{-1}$ and 125 ± 1.15 $\mu\text{g mL}^{-1}$, for *C. albicans* (SC5314) and *C. albicans* (ATCC90028), respectively, and separately (Table S7). The lower MIC and MFC values of the GG/ γ -Fe₂O₃ indicated a more efficient and potent antifungal nature. Thereby, it could be justified that the enhanced antibacterial and antifungal activity of the GG/ γ -Fe₂O₃ could be attributed to the combined effect of phytochemical contents in GG and iron oxide nanoparticles, which might have diffused and interacted with the bacterial and fungal lipid layer within their cell membrane.⁹²

3.4. CR and NB sorption investigation

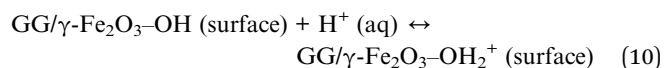
3.4.1. Influence of operational parameters on the dye removal efficiency of GG/ γ -Fe₂O₃. At first, with increase of GG/ γ -

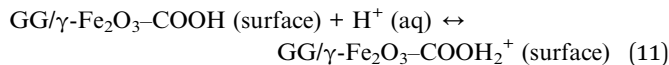
Fe₂O₃ dose, from 0.5 to 2.0 g L⁻¹, a relative increase in adsorption of CR, from 68.58 to 90.49%, and NB, from 68.92 to 95.90%, was observed (Fig. S3a). The observation could be justified due to the enhancement of the overall specific surface area of GG/ γ -Fe₂O₃, which is highly porous in nature. The FT-IR spectrum confirmed the presence of oxygenous adsorptive sites on the GG/ γ -Fe₂O₃ surface which increased up to 2.0 g L⁻¹ for both dyes. Following, at higher doses, the reduction in the amount of CR and NB against largely available adsorption active sites saturated the surface.^{22,93}

2.0 g L⁻¹ of the GG/ γ -Fe₂O₃ efficaciously removed around 97% CR from 10 mg L⁻¹ solution and 79% NB from the 20 mg L⁻¹ solution. At higher concentrations, the percentage adsorption reduced slightly to 96% and 72% for 30 mg L⁻¹ CR and NB, respectively (Fig. S3b). This observation could be attributed to the saturation of the available active sites on the otherwise fixed amount of GG/ γ -Fe₂O₃, which prevented further adsorption. Thus, as low as 10 mg L⁻¹ CR and 20 mg L⁻¹ NB concentrations were optimized, since the released dye concentration in industrial effluent is not too high.

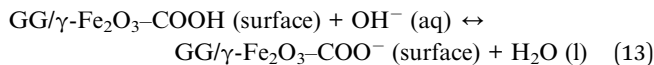
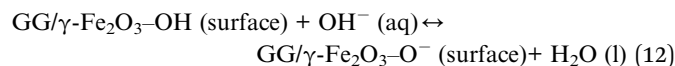
pH of water influence electrostatic interactions, directs the surface charge of solid, and the extent of ionization of dyes in water.⁹⁴ Numerous surface functional sites (-COOH, -OH) are subjected to modification, *i.e.*, either through protonation or deprotonation at pH below and above ZPC, bestowing either positive (-COOH₂⁺, -OH₂⁺) or negative (-COO⁻, -O⁻) charge to the surface, respectively, as depicted below [eqn (10)–(13)]:

At acidic pH





At alkaline pH



The GG/ γ -Fe₂O₃ showed higher uptake capacity for CR in acidic medium, however, an insignificant gradual decrease in percentage sorption was observed on transition to neutral conditions, which further steepened in alkaline environment, *i.e.*, 59.07% at pH = 11.⁹⁵ Moreover, NB removal was at its lowest (40.36%) in highly acidic conditions (pH = 2) and increased significantly from pH 4 to 8. The maximum adsorption of NB onto GG/ γ -Fe₂O₃ was obtained at pH 11 (Fig. S3c).

The sorption trend of GG/ γ -Fe₂O₃ can be explained on the basis of the ZPC of 6.9, indicating a nearly amphoteric surface (Fig. S4). In acidic pH (pH < ZPC), the GG/ γ -Fe₂O₃ exhibited greater CR adsorption owing to extensive electrostatic interactions between the protonated positively charged GG/ γ -Fe₂O₃ surface and negatively charged CR ions. Additionally, around pH 8, hydrogen bonding between surface functional groups of the GG/ γ -Fe₂O₃ and -NH₂ group in CR was majorly governing its uptake.²² Conversely, at higher pH, the coulombic repulsion between the negatively charged deprotonated surface and the anionic CR relinquished its uptake.

Reversibly, the cationic NB exhibited favourable sorption at higher pH (pH > ZPC) following deprotonation of the GG/ γ -Fe₂O₃ surface by OH⁻, bestowing negative charge to the surface. Moreover, the extensive protonation of the GG/ γ -Fe₂O₃ at low pH (pH < ZPC) decreased the sorption of positively charged NB. Further, there might be a sense of competition between H⁺/H₃O⁺ and NB ions for binding sites at low pH, resulting in slower NB sorption. Therefore, a combination of electrostatic and hydrogen bonding interactions might be responsible for the adsorptive removal of CR and NB by GG/ γ -Fe₂O₃.

Monitoring of contact time, for 10 mg L⁻¹ CR and 20 mg L⁻¹ NB sorption onto 2.0 g L⁻¹ GG/ γ -Fe₂O₃, elucidated a continuous increment in the percentage adsorption with increasing time (Fig. S3d). The adsorption of CR and NB by GG/ γ -Fe₂O₃ proceeded in two phases: an instantaneous initial fast phase, followed by a later slow phase. The rate of removal of CR and NB showed a steady increase till 60 min (optimum time), removing nearly 88% CR and 93% NB within the first 15 min, increasing gradually to 94% CR and 96% NB removal at 60 min, after which the transport rate diminished, and nearly became constant for a prolonged time of contact. The trend can be explained based on of the availability of abundant vacant active sites (with COO⁻ and OH⁻ groups) initially, providing an easy pathway for interaction between dye molecules and 2.0 g L⁻¹ GG/ γ -Fe₂O₃. With time, the need for specific pathways subjugated the adsorption rate onto the partially available or later filled sites, attaining equilibrium.⁹⁶

3.4.2. Effect of temperature and thermodynamics. The CR removal by the GG/ γ -Fe₂O₃ decreased with increasing temperature, which can be attributed to an increase in mobility and a decrease in diffusion rates of CR into pores.⁹⁷ Furthermore, with an increase in temperature, the weakly-bonded CR ions might have escaped from their binding sites in response to bond breakage. For instance, weak hydrogen bonds are susceptible to breakage upon receiving energy at 40 and 50 °C, resulting in reduced adsorption capacity at higher temperatures.⁹⁸ Thereby, CR adsorption onto GG/ γ -Fe₂O₃ surface was exothermic in nature.⁹⁹ On the other hand, NB adsorption showed an increase with the rise in temperature, indicating an endothermic process.¹⁰⁰ The activation of GG/ γ -Fe₂O₃ surface at high temperatures made the adsorptive sites readily available for NB sorption.⁹⁷

Adsorption thermodynamics was studied by appraising the changes in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG). Substituting the experimental data in thermodynamic equations (eqn (S2) and (S3))^{101,102} delivered negative values of ΔG , *i.e.*, -6.928, -5.076, and -4.552 kJ mol⁻¹ for 10 mg L⁻¹ CR, and -1.579, -2.151, and -4.501 kJ mol⁻¹ for 20 mg L⁻¹ NB sorption, at 30, 40, and 50 °C, respectively (Table 1). These values indicated the thermodynamic feasibility of CR and NB sorption onto GG/ γ -Fe₂O₃ within the tested temperature range. Besides, ΔG , between 0 and -20 kJ mol⁻¹, suggested physisorption of CR and NB dyes onto the surface of GG/ γ -Fe₂O₃.¹⁰³ The surface charge significantly influences the thermodynamics of physical adsorption by altering the interaction energy, electrostatic interactions around ZPC, and strength of the weak bonding (van der Waals) interactions between the dye molecules and the interface, posing substantial impact on the overall extent of adsorption.^{104,105} The balance between physisorption and electrostatic interactions drives the whole sorption process. The electrostatic attractions enhance physisorption and make ΔG more negative, while electrostatic repulsions decrease physisorption and increase the ΔG value. On increasing temperature, the order of ΔG for CR removal became less negative, while a corresponding increase in negative value was observed for NB removal, suggesting a decrease in the adsorption rate in the former and a corresponding increase in the latter. For NB adsorption, a higher negative ΔG at elevated temperatures indicated greater spontaneity and affinity due to electrostatic interactions between NB and GG/ γ -Fe₂O₃ at 50 °C. This indicated endothermic adsorption of NB which could be justified from the positive value of ΔH (+42.408 kJ mol⁻¹). Moreover, a positive ΔS (+0.144 kJ mol⁻¹ K⁻¹) value suggested good affinity of NB towards GG/ γ -Fe₂O₃, and increased randomness at the dye-adsorbent interface (Table 1). Van't Hoff plot (Fig. 1E) produced negative ΔH , -43.146 kJ mol⁻¹, confirming exothermic thermodynamics for CR adsorption. Moreover, for CR sorption, the plot also showed a decrease in randomness, $\Delta S = -0.120$ kJ mol⁻¹ K⁻¹, at the interface, indicating adsorption accompanied by a corresponding reduction in the degrees of freedom at the solid-liquid interface. It might be due to a probable increase in affinity between CR and GG/ γ -Fe₂O₃ surface through van der Waals, electrostatic and



Table 1 Non-linear isotherm and thermodynamic parameters for CR and NB adsorption onto GG/γ-Fe₂O₃

Parameter	CR			NB			
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C	
Langmuir isotherm $Q_e = \frac{Q_0 b C_e}{1 + b C_e}$	Q_0 (mg g ⁻¹)	39.744	39.789	47.504	15.361	14.902	13.305
	b (L mg ⁻¹)	0.412	0.188	0.118	0.259	0.365	1.508
	R_L	0.195	0.347	0.459	0.162	0.120	0.032
	R^2	0.986	0.994	0.993	0.996	0.980	0.990
	χ^2	0.284	0.113	0.112	0.036	0.221	0.142
Freundlich isotherm $Q_e = k_F C_e^{1/n}$	k_F [(L mg ⁻¹) ^{1/n} (mg g ⁻¹)]	11.455	6.261	5.092	3.544	4.313	7.063
	$1/n$	0.756	0.778	0.815	0.529	0.481	0.351
	n	1.323	1.286	1.227	1.892	2.077	2.845
	R^2	0.996	0.998	0.998	0.990	0.997	0.953
	χ^2	0.082	0.029	0.039	0.099	0.037	0.653
Temkin isotherm $Q_e = \beta_T \ln(k_T C_e)$	k_T (L mg ⁻¹)	11.712	4.559	3.453	3.002	5.633	17.264
	b_T (kJ mol ⁻¹)	0.547	0.532	0.541	0.793	0.928	0.993
	R^2	0.891	0.925	0.921	0.981	0.950	0.997
	χ^2	2.149	1.336	1.359	0.196	0.554	0.038
	k_{D-R}	0.628	1.452	2.019	3.004	2.552	0.474
D-R isotherm $Q_e = Q_{D-R} \exp \left[-k_{D-R} \left(\ln \left(1 + \frac{1}{C_e} \right) \right)^2 \right]$	Q_{D-R} (mg g ⁻¹)	15.894	14.158	13.849	9.853	10.506	11.185
	E_{D-R} (kJ mol ⁻¹)	2.248	1.527	1.336	1.028	1.152	2.758
	R^2	0.902	0.892	0.881	0.843	0.809	0.928
	χ^2	1.931	1.926	2.031	1.607	2.130	0.993
	ΔG (kJ mol ⁻¹)	-6.928	-5.076	-4.552	-1.579	-2.151	-4.501
ΔH (kJ mol ⁻¹)		-43.146			+42.408		
ΔS (kJ mol ⁻¹ K ⁻¹)		-0.120			+0.144		

hydrogen bonding interactions. However, the magnitude of ΔH , less than 80 kJ mol⁻¹ for both CR and NB adsorption, supported weak physical interaction with GG/γ-Fe₂O₃ surface.¹⁰⁶

3.4.3. Modelling of adsorption isotherms. The sorption data, at 30, 40, and 50 °C for CR and NB (5–30 mg L⁻¹), and 2.0 g L⁻¹ GG/γ-Fe₂O₃, were fitted into different isotherm models to decipher the corresponding isotherm parameters, which delineate the surface characteristics, interactions, and sorption capacity (Table 1). The non-linear regression analysis was conducted using OriginPro 8.5 software. The statistical treatment of experimental data concerning error analysis and conformity to various models was performed using correlation coefficient (R^2) and reduced chi-square (χ^2), represented by eqn (14) and (15).

$$R^2 = \frac{\sum_{i=1}^N \left(Q_{e(\text{cal})} - \bar{Q}_{e(\text{meas})} \right)_i^2}{\sum_{i=1}^N \left[\left(Q_{e(\text{cal})} - \bar{Q}_{e(\text{meas})} \right)_i^2 + \left(Q_{e(\text{cal})} - \bar{Q}_{e(\text{meas})} \right)_i^2 \right]} \quad (14)$$

$$\chi_{\text{red}}^2 = \frac{1}{N-p} \sum_{i=1}^N \left[\frac{\left(Q_{e(\text{meas})} - Q_{e(\text{cal})} \right)^2}{Q_{e(\text{cal})}} \right]_i \quad (15)$$

where $Q_{e(\text{cal})}$ and $Q_{e(\text{meas})}$ are the calculated (theoretical) and measured (experimental) adsorption capacities (mg g⁻¹), respectively, $\bar{Q}_{e(\text{meas})}$ (mg g⁻¹) is the average of $Q_{e(\text{meas})}$, p represents the number of model parameters, and N is the number of experimental data points.

3.4.3.1. Langmuir isotherm. The Langmuir isotherm assumes homogeneous, one molecule per site, monolayer adsorption onto finite and degenerate adsorptive sites *via* physical or chemical forces, without lateral interactions.¹⁰⁷ Non-

linear Langmuir isotherm¹⁰⁸ expounded maximum adsorption capacities, Q_0 , in the range 39.744–47.504 mg g⁻¹ for CR (increasing) and 15.361–13.305 mg g⁻¹ for NB (decreasing) sorption, representing endothermic and exothermic adsorption, respectively, within 30–50 °C. This observation deviated from the thermodynamic interpretations. Moreover, the corresponding values of Langmuir constant, b , representing the extent of affinity in terms of binding energy was determined from the non-linear Langmuir isotherm plots (Fig. S5a and b), which decreased from 0.412 to 0.118 L mg⁻¹ for CR; increased from 0.259 to 1.508 L mg⁻¹ for NB removal, suggesting lower heat of adsorption/affinity of CR, and higher heat of sorption/affinity of NB with increasing temperature, which was also not in accordance with ΔS values. These interpretations suggested disagreement between the experimental data and the derived Langmuir parameters (Table 1).

In addition, the separation factor, $R_L \left(= \frac{1}{(1 + bC_0)} \right)$, specifies the shape of an isotherm and the reversibility of a process. If $0 < R_L < 1$, then the sorption is considered feasible and energetically favourable, whereas $R_L = 0$ implies an irreversible adsorption phenomenon, and $R_L = 1$ indicates linearity.¹⁰⁹ R_L values between 0 and 1 confirmed the energetically feasible adsorption of CR and NB onto the GG/γ-Fe₂O₃ surface within the tested temperature range.

3.4.3.2. Freundlich isotherm. The Freundlich isotherm assumes surface as heterogeneous and physical adsorption onto energetically non-uniform sites with explicit bond energies, resulting in multilayers *via* lateral interactions. It considers an exponential decrease in sorption energy upon surface coverage.¹¹⁰ Non-linear, Q_e vs. C_e , Freundlich plots, for



CR (Fig. 6a) and NB (Fig. 6b) adsorption onto GG/ γ -Fe₂O₃, demonstrated best-fit statistics to the experimental sorption data, in terms of R^2 nearest to unity. This extraction could be further confirmed from the texture of GG/ γ -Fe₂O₃ particles in the SEM micrographs (Fig. 2b) which indicated a heterogeneous multi-layer formation. The Freundlich parameter, k_F , decreased from 11.455 to 5.092 (L mg⁻¹)^{1/n} (mg g⁻¹) for CR, and increased from 3.544 to 7.063 (L mg⁻¹)^{1/n} (mg g⁻¹) for NB adsorption in the temperature range 30–50 °C, indicating low adsorption capacity for CR (exothermic), and high capacity for NB (endothermic) sorption at elevated temperatures. This conclusion was found in accordance with the thermodynamic data set, dictating the Freundlich isotherm fitting for both CR and NB dye removal data. The heterogeneity factor, n , obtained in the range 1–10 ($n > 1$) and $1 < 1/n < 0$ (Table 1), established favourable physical adsorption with strong interaction of CR/NB and the GG/ γ -Fe₂O₃ surface.¹¹⁰

3.4.3.3. Temkin isotherm. The Temkin isotherm considers heterogeneous solute–solid interactions. It assumes orderly distribution of binding energy to a certain extent, and linear decrease in adsorption enthalpy with surface coverage.¹¹¹ Non-linear plots of Temkin isotherm, for CR (Fig. S5c) and NB

(Fig. S5d) adsorption onto the GG/ γ -Fe₂O₃, produced parameters k_T (L mg⁻¹) and b_T (kJ mol⁻¹), where b_T ($=RT/\beta_T$) is associated with heat of adsorption, and β_T is the Temkin constant. The k_T corresponds to the maximum binding energy and is the binding constant. The respective decrease (from 11.712 to 3.453 L mg⁻¹) and increase (from 3.002 to 17.264 L mg⁻¹) in parameter k_T , from 30–50 °C, for CR and NB adsorption reinforced the exothermic and endothermic nature of the sorption processes, respectively. The considerable difference in k_T between 30 and 40 °C indicated significant variation in the binding capabilities for CR adsorption. Moreover, the closeness in b_T values for CR directed a similar extent of binding probability and constant sorption enthalpy at all temperatures. Conversely, for NB sorption, a notable increase in k_T was observed between 40 and 50 °C, indicating a change in bonding pattern. It can be stated that the reported typical range of bonding energy for ion exchange mechanism is between 8 and 16 kJ mol⁻¹,¹¹² however, the observed low values ($b_T < 8$ kJ mol⁻¹) indicated weak van der Waals interactions between CR/NB and GG/ γ -Fe₂O₃.

3.4.3.4. Dubinin–Radushkevich isotherm. The Dubinin–Radushkevich (D–R) isotherm illustrates pore-filling nature of

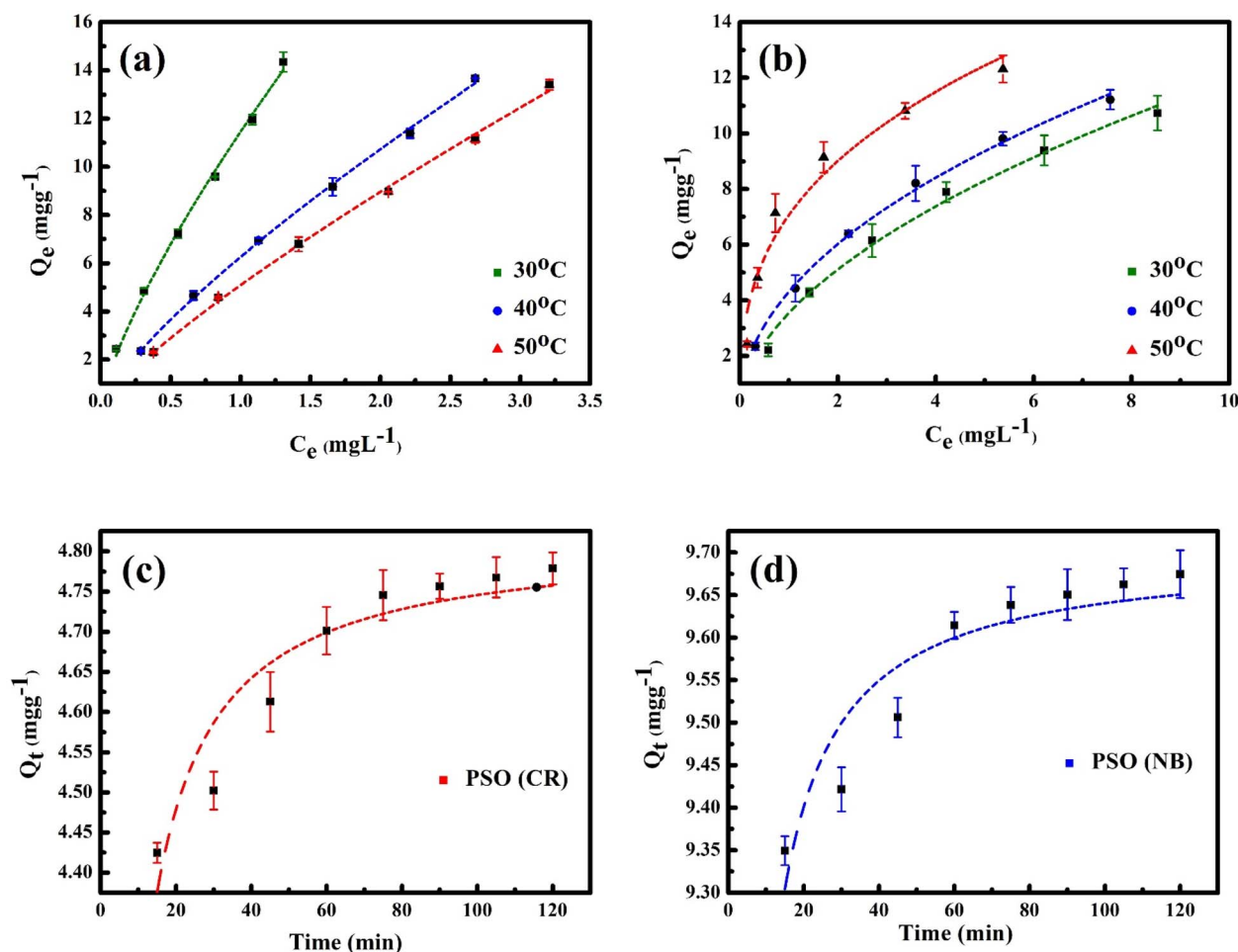


Fig. 6 Non-linear Freundlich isotherm plots for (a) CR, and (b) NB adsorption; non-linear pseudo-second order plots for (c) CR, and (d) NB adsorption.



sorption for intermediary to highly concentrated systems, and supports mechanism that follows heterogeneous Gaussian energy distribution onto specific adsorptive sites.¹¹³ The activity coefficients, k_{D-R} ($=\beta R^2 T^2$), for both CR and NB sorption at 30, 40, and 50 °C were interpreted, from non-linear Q_e vs. C_e D-R plots (Fig. S5e and f). A decrease in the maximum (theoretical) equilibrium monolayer sorption capacity, Q_{D-R} , (from 15.894 to 13.849 mg g⁻¹), and free energy, E_{D-R} (from 2.248 to 1.336 kJ mol⁻¹) with temperature was observed for CR sorption that indicated an exothermic nature, where $E_{D-R} = (2\beta)^{-0.5}$, and β (kJ⁻² mol²) is a constant related to adsorption energy. However, both Q_{D-R} and E_{D-R} values slightly increased in the range 9.853–11.185 mg g⁻¹ and 1.028–2.758 kJ mol⁻¹, respectively, with a rise in temperature from 30–50 °C, indicating endothermic NB adsorption onto the GG/ γ -Fe₂O₃. The D-R isotherm also gave low values of E_{D-R} , < 8 kJ mol⁻¹, suggesting physisorption of CR and NB onto the GG/ γ -Fe₂O₃ at three test temperatures.

Furthermore, the comparison of χ^2 , for various non-linear isotherms, established the lowest value for the Freundlich isotherm for both CR and NB sorption, in addition to the highest R^2 values for CR adsorption, and high values for NB adsorption as well. The fitting of experimental sorption data was more pronounced for the Freundlich isotherm compared to the Langmuir, Temkin, and D-R isotherms. Thereby, adsorption of both CR and NB from their aqueous solution onto GG/ γ -Fe₂O₃ was satisfactorily described by the Freundlich isotherm, reflecting physical nature of sorption on the energetically heterogeneous surface of GG/ γ -Fe₂O₃. Appearance of heterogeneity might be a result of non-homogeneous distribution of adsorptive sites on the GG/ γ -Fe₂O₃ surface, which was cross-referred and found in order with the SEM (Fig. 2b), and TEM micrographs (Fig. 4).

3.4.4. Investigation of sorption kinetics. An insight into the kinetics of the sorption reaction was devised from the dynamic parameters that regulate the overall rate of transportation of CR/NB ions from the aqueous phase onto the surface of GG/ γ -Fe₂O₃. The kinetic data, for 15–120 min duration at 30 °C for 10 mg L⁻¹ CR and 20 mg L⁻¹ NB solutions with 2.0 g L⁻¹ GG/ γ -Fe₂O₃, were monitored at intervals of 15 min, and then fitted into pseudo-first order (PFO), pseudo-second order (PSO), Elovich (Table 2), intraparticle diffusion (IPD), and Boyd's liquid film diffusion (LFD) models (Table S8). The adequacy of each model was examined from R^2 and χ^2 values [eqn (14) and (15)].

3.4.4.1. Pseudo-first order kinetic model. Lagergren and Ho's pseudo-first order kinetic model (PFO) assumes that the number of available or unoccupied adsorption sites is the sole governing parameter of the rate of reaction on the solid surface in a liquid–solid system. The parameters, k_1 (min⁻¹), PFO rate constant; Q_e and Q_t (mg g⁻¹), the equilibrium sorption capacity, and sorption uptake at time t , respectively, were determined from the non-linear plot of Q_t and t .¹¹⁴ The plots (Fig. S6a and b) produced comparable calculated and experimental Q_e values, but with inferior R^2 . The rate constant k_1 was found to be 0.183 and 0.241 min⁻¹ for CR and NB removal, respectively (Table 2).

3.4.4.2. Pseudo-second order kinetic model. Ho and McKay's pseudo-second order kinetic model (PSO) assumes that in addition to the adsorption surface sites, the concentration of

pollutant in the aqueous phase also determine the rate of the whole sorption process. At equilibrium, the rate-determining step (RDS) exemplifies the square of the difference between the total sorption sites and the unoccupied ones. The nature of chemical interaction between the pollutant and the surface sites controls the process.¹⁰³ Q_t vs. t plots (Fig. 6c and d) gave the pseudo-second order rate constant, k_2 (g mg⁻¹ min⁻¹), and equilibrium sorption capacity, Q_e .¹¹⁴ The parameters obtained from these plots showed fair agreement between the experimental Q_e (4.701 mg g⁻¹ for CR, and 9.614 mg g⁻¹ for NB) and calculated Q_e (4.817 mg g⁻¹ for CR, and 9.702 mg g⁻¹ for NB) values, greater R^2 , and lowest χ^2 values in comparison to PFO plots (Table 2). Therefore, there was a clear-cut indication in favour of site-specific chemical interactions between CR or NB and functional groups on the GG/ γ -Fe₂O₃ surface following PSO kinetics. This observation could be justified from the accuracy of the established resemblance between the PSO kinetic equation and the universal rate law for a chemical reaction,¹¹⁵ alongwith the FT-IR interpretations (Fig. 1A).

3.4.4.3. Elovich kinetic model. The Elovich model focuses on the chemical interaction between the functional sites on the liquid–solid interface. The model assumes energetically heterogeneous adsorption without sideways interaction.¹¹⁶ The Elovich coefficients, α (mg g⁻¹ min⁻¹) and β (g mg⁻¹), exemplify the initial rate of adsorption and desorption, respectively. Moreover, β also signifies the extent of surface coverage and corresponding energy of activation for the chemisorption process. The non-linear Q_t vs. t plots,¹¹⁷ for Elovich model (Fig. S6c and d), provided value of α parameter (1.995×10^8 mg g⁻¹ min⁻¹ for CR, and 3.867×10^{21} mg g⁻¹ min⁻¹ for NB) much greater than β (5.324 g mg⁻¹ for CR, and 5.802 g mg⁻¹ for NB) (Table 2), suggesting viability and feasibility of CR and NB sorption at the GG/ γ -Fe₂O₃ specific sites with higher rate of adsorption than desorption.

3.4.4.5. Adsorption mechanism. Various factors influence the adsorption mechanism, including the nature of the solid surface, active sites, functionality, charge, and structure of the dyes, as well as interactions between the solid and pollutant interfaces.¹⁰³ The shifting, weakening, and appearance of distinctive peaks in the FT-IR spectra of dye-loaded GG/ γ -Fe₂O₃, *i.e.*, GG/ γ -Fe₂O₃@CR, and GG/ γ -Fe₂O₃@NB when compared to the values for virgin GG/ γ -Fe₂O₃ (Fig. S7) indicated the prevalence of variable covalent/ionic/hydrogen bonding interactions, owing to involvement of O–H, C=O, *etc.* groups in bonding which influence the adsorption of CR and NB.⁶² For instance, the peak at 3378 cm⁻¹ in the GG/ γ -Fe₂O₃ shifted to a lower wavenumber, 3368 cm⁻¹ in the GG/ γ -Fe₂O₃@CR and 3354 cm⁻¹ in GG/ γ -Fe₂O₃@NB, due to extended hydrogen bonding.²⁷ Moreover, the peak at 1622 cm⁻¹ was assigned to O–H bending vibration in GG/ γ -Fe₂O₃ alongside N=N stretching of azo bonds in CR.¹¹⁸ However, no significant change in C–H stretching frequencies was discerned, and an additional peak at 1231 cm⁻¹ was ascertained for GG/ γ -Fe₂O₃@CR for S=O stretch due to the –SO₃⁻ group in CR.¹¹⁹ The strong molecular bonding interactions between γ -Fe₂O₃ and functional groups on GG (–OH, –CO–, –COOH), as indicated by FT-IR spectra and XPS analysis, contributed to its stability and prevented any leaching



Table 2 Kinetic parameters derived from non-linear kinetic plots for CR and NB adsorption onto GG/ γ -Fe₂O₃

Pollutant	Pseudo-first order $Q_t = Q_e(1 - e^{-k_1 t})$				Pseudo-second order $Q_t = \frac{k_2 Q_e^2 t}{(1 + k_2 Q_e t)}$					Elovich $Q_t = \frac{1}{\beta} \ln(\alpha \beta t + 1)$			
	Q_e (cal.) (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	χ^2	Q_e (exp.) (mg g ⁻¹)	Q_e (cal.) (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2	χ^2	α (mg g ⁻¹ min ⁻¹)	β (g mg ⁻¹)	R^2	χ^2
CR	4.701	0.183	0.484	0.009	4.701	4.817	0.137	0.876	0.002	1.995×10^8	5.324	0.960	7.227×10^{-4}
NB	9.598	0.241	0.435	0.009	9.614	9.702	0.161	0.854	0.002	3.867×10^{21}	5.802	0.952	7.311×10^{-4}

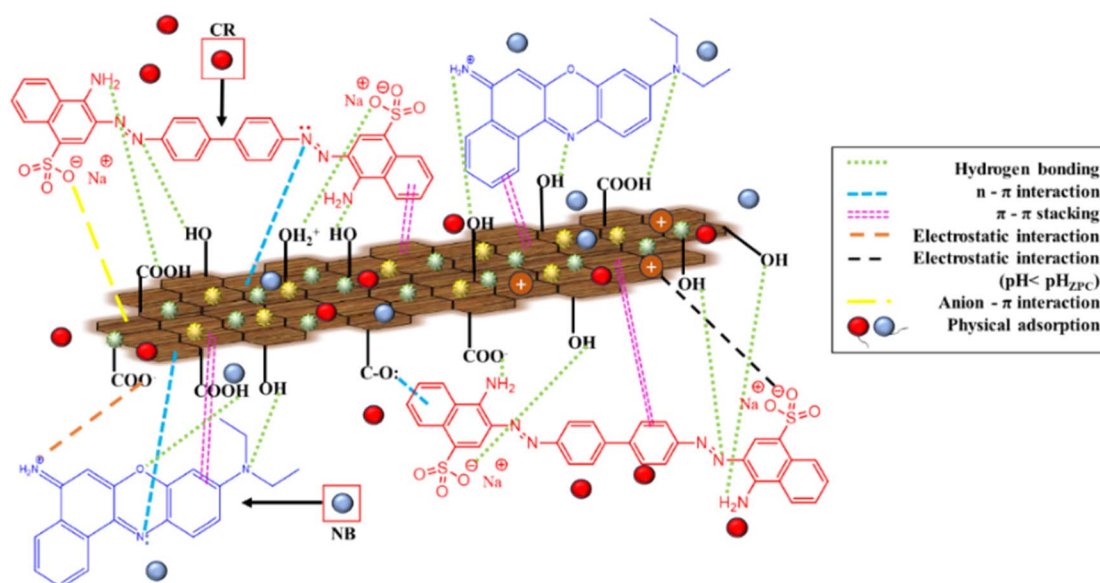
possibility of the composite in water during adsorption.⁶² Thus, the commendable adsorption performance of GG/ γ -Fe₂O₃ for both CR and NB might be the consequence of FT-IR established extensive functional sites on the GG/ γ -Fe₂O₃ surface, and their specific interaction through several interactive pathways. Furthermore, the presence of charge on dyes, and GG/ γ -Fe₂O₃ surface over and above the ZPC¹²⁰ might have also paved the way to additional weak physical, and non-specific bonding interactions, *viz.*, van der Waals, n- π , anion- π , and π - π stacking in addition to previously confirmed electrostatic and hydrogen bonding interactions (Fig. 7). The strength of these forces was confirmed from the bonding energy pattern obtained from the Temkin and D-R isotherms, alongside the thermodynamic investigations.

From a mechanistic viewpoint, analysis of steps governing the adsorption process becomes an indispensable task. A detailed exploration suggested that the adsorption process could be controlled by either a mass action mechanism or a chemical action (IPD/LFD). The former was realised as irrelevant considering physisorption to be a fast phenomenon.¹²¹ Thus, the kinetic data was fitted to the Webber-Morris and Boyd relationships to assert whether the diffusion mechanism underlying physisorption for CR and NB removal by GG/ γ -Fe₂O₃

followed (a) intraparticle diffusion (IPD), or (b) liquid film diffusion (LFD) kinetics, or (c) a simultaneous combination of both processes covering all the interior and exterior surface pores of the adsorbent by the pollutant ions.

3.4.5.1. Intraparticle diffusion. The Intraparticle diffusion (IPD) model is validated for those systems in which rapid adsorption takes place, such that the pollutant diffuses through the surface into the interstitial pores of the adsorbent, and binds through physical/chemical bonds, which is characterized as the RDS. This phenomenon is well understood by fitting adsorption data into the Weber and Morris equation¹²² [eqn (S4)].

The linear IPD plots, for both CR and NB, did not pass through the origin, which suggested that IPD was not the sole RDS (Fig. S8a and b).¹²³ Moreover, the plots depicted three linear regions for both dyes, the initial portion incorporated the diffusion of dyes into the exterior surface-active sites, followed by their gradual intrusion into the interstitial pores which later slowed down following unavailability of sorptive sites and diminished dye concentration, subjugating a three-step mechanism, and thus the multilinearity.¹²⁴ In addition, the value of intercept *C* (Table S8) for NB (9.178) was superior to that for CR (4.240), indicative of significant coverage at the boundary layer of GG/ γ -Fe₂O₃ on account of driving diffusion of NB.

Fig. 7 Plausible mechanism for the adsorption of CR and NB by GG/ γ -Fe₂O₃.

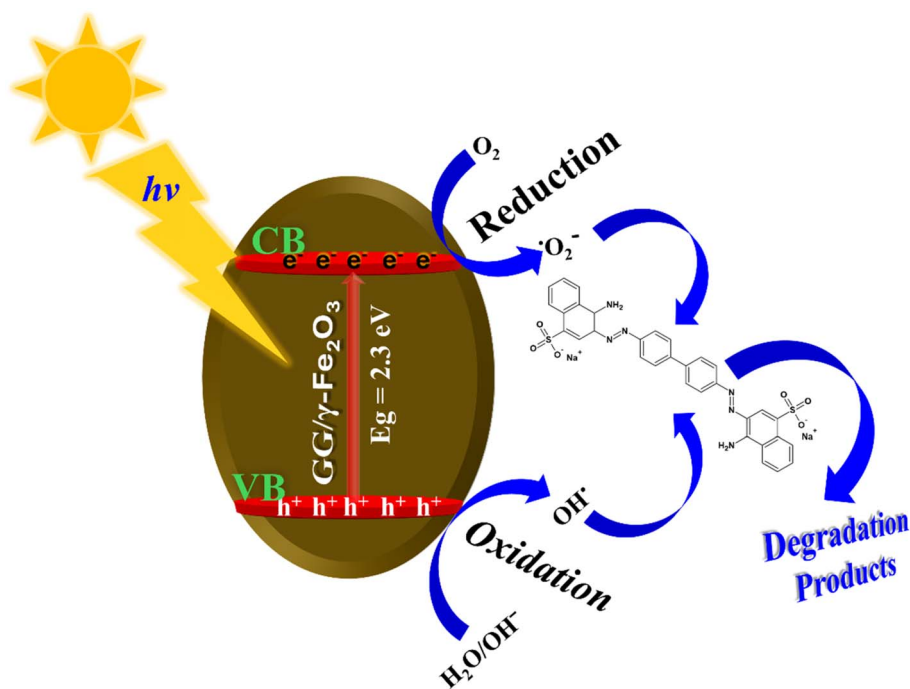


Fig. 8 Proposed mechanism for photodegradation of azo-CR by GG/γ-Fe₂O₃.

3.4.5.2. Liquid film diffusion. The Liquid film diffusion (LFD) model holds good for adsorption systems in which mass diffusion/crossing of the boundary layer by the external liquid film of pollutant from the bulk, formulated around the solid interface and the surface-active sites is established as the RDS. The phenomenon can be justified using Boyd's equation¹¹⁶ [eqn (S5)].

The LFD plots showed linearity for CR and NB sorption but deviated from the origin, yielding a non-zero intercept value, which clarified that the adsorption was not solely governed by the film diffusion kinetics (Fig. S8c and d). The k_{LFD} and R^2 values are given in Table S8.

The foregoing observations suggested a specific chemical interaction of CR and NB with functional sites on the GG/γ-Fe₂O₃, which was found in coincidence with those from the PSO kinetic model. Thereby, it can be concluded that both CR and NB adsorption on GG/γ-Fe₂O₃ surface was governed partially by intraparticle as well as film diffusion steps, supplementing bulk transport and adsorptive attachment.

3.5. Photodegradation of CR dye, kinetics, and degradation mechanism

The photodegradation of azo-group-containing CR using GG/γ-Fe₂O₃ catalyst was performed at 38 °C under sunlight. From the time-dependent UV-visible absorption spectra, the absorbance of the CR solutions decreased over time upon degradation (Fig. S9a). The rate of dye degradation was consistent, and nearly 50% of the CR was degraded within the first 80 min, while up to 92.7% degradation was observed during 160 min of irradiation. This high rate of degradation might be a result of a prominent band gap of the GG/γ-Fe₂O₃. The PFO kinetics plot (Fig. S9b) of $\ln C_t/C_0$ vs. time t (min) produced a straight line

with rate constant 0.014 min^{-1} and $R^2 = 0.877$, indicating obedience to the PFO degradation mechanism. In contrast, the adsorption of CR over the GG/γ-Fe₂O₃ surface followed PSO kinetics. Therefore, the complete removal of CR could be attributed to the simultaneous adsorption in the dark, followed by photocatalytic degradation under sunlight.

From the mechanistic notion, it can be impounded that on absorption of solar radiation of energy $h\nu$, more than the band gap energy, the electrons (e^-) are excited from valence band (VB) to conduction band (CB), with simultaneous accumulation of electrons in CB, and holes (h^+) in VB, respectively.¹²⁵ Fe³⁺ ions have been reported previously to suppress the electro-hole recombination rate, because besides serving as active sites for adsorption and activation, the d-orbitals in Fe³⁺ sites can also enhance the charge transfer efficiency.¹²⁶ The dissolved oxygen (O₂) gets reduced by the photo-induced electrons into superoxide radical anion (O₂^{·-}). Moreover, the positively charged holes oxidize H₂O to OH[·].¹²⁷ Further, to gain complete insight of the photodegradation mechanism, the catalytic effect of active species was investigated through free radical trapping experiment (Fig. S10). The CR degradation involving GG/γ-Fe₂O₃ was considerably inhibited by scavengers in order: EDTA (h^+) < BQ (O₂^{·-}) < IPA (OH[·]). The results revealed that the CR percentage degradation was primarily influenced by OH[·] and O₂^{·-} oxidative species, followed by the holes (h^+). These highly reactive oxygen species (ROS) are powerful oxidants for complete mineralization of CR to simple degradation products, like CO₂, H₂O, NH₄⁺, NO₃⁻, SO₄²⁻, and mineral acids (Fig. 8). Furthermore, Fe₂O₃ and its nanocomposites have been extensively reported as efficient photocatalysts for dye degradation.^{128–130}

In order to determine the possible degradation intermediates, a time-based LC-MS analysis (Fig. S11) of photodegraded



diazo-CR dye solution, at optimum experimental conditions, was examined. The major intermediate species formed during CR degradation, detected by LC-MS, are shown in the Scheme 2. During the initial analysis, partial cleavage of the azo ($-\text{N}=\text{N}-$) bond or modification of side groups in CR might produce large high-mass aromatic fragments. Further, breakdown of large fragments resulted in complete azo bond scission, desulphonation and deamination following $-\text{C}-\text{S}-/-\text{C}-\text{N}-$ bond cleavage, hydroxylation, azo reduction, oxidation, rearrangements, and cleavage of $-\text{C}-\text{C}-$ bonds between the chromophore rings.^{5,131–135} This step produced various intermediates and their derivatives, including 4-aminonaphthalene-1-sulphonic acid (ANSA, $m/z = 246.26$), 4,4'-diaminobiphenyl (benzidine, $m/z = 184.84$), aniline-4-sulphonic acid (sulphanilic acid, $m/z = 172.11$), biphenyl ($m/z = 150.99$), 1-naphthylamine/2-naphthylamine ($m/z = 141.13$), aniline ($m/z = 90.92$), benzene-1-ylum ($m/z = 77.05$), benzene ($m/z = 78$), etc. Later, the oxidative ring opening steps formed low molecular weight aromatics, acid/amine intermediates, polyphenols, and ultimately mineralized into CO_2 , H_2O , NH_4^+ , NO_3^- , and SO_4^{2-} .

3.6. Real water analysis and competitive removal of CR and NB dyes

The adsorption/degradation tendency of the $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ for CR and NB amidst different water environments and co-existing ions is shown in Table S9. The removal efficiency hinders in natural wastewater samples due to the competition between large number of co-existing pollutants (organic, inorganic, and microorganisms) that compete for limited available surface-active sites. The % CR and NB removal decreased in tap water and sewage water, in comparison to RO water or distilled water, due to more competitive effect.

Typically, the solubility of organic contaminants decreases with the addition of salts (ions) owing to self-aggregation, *i.e.*, salting-out or primary kinetic salt effect.¹³⁶ This limits the dye solubility due to fewer available water molecules. However, the CR adsorption remained largely unaffected in the presence of salts. The results showed little effect of co-existing ions on CR adsorption (except that of CO_3^{2-}), indicating excellent resistance of $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ to ion interference, and thus confirming specific CR adsorption by $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$. The interference by CO_3^{2-} might be mainly due its interaction with CR, and not salting.¹³⁶ Moreover, the inhibitory effect of divalent CO_3^{2-} (most) and SO_4^{2-} on CR adsorption/degradation were greater than monovalent Cl^- or NO_3^- , which can be attributed to strong electrostatic attractions between $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ and the higher anions, under similar conditions.¹³⁷ Similar observations were drawn for NB adsorption. Additionally, CO_3^{2-} ions highly and negatively affected percentage CR degradation, due to the hydrolysis of HCO_3^- , an OH^- scavenger.¹³⁸ Moreover, percentage NB adsorption decreased around cations *vis-à-vis* anions, suggesting higher cationic interface potential for cationic NB adsorption surfacing weak electrostatic interactions. Previous studies have shown that both CR and NB undergo stable complexation with metal ions which can affect their adsorption/degradation onto support materials in

presence of different ions.¹³⁹ Furthermore, the competitive influence of other anionic and cationic dyes on the CR and NB removal by $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ from a mixture is shown in Table S10. The results showed the specificity and efficiency of $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ towards CR and NB adsorption, and substantial potential in wastewater treatment.

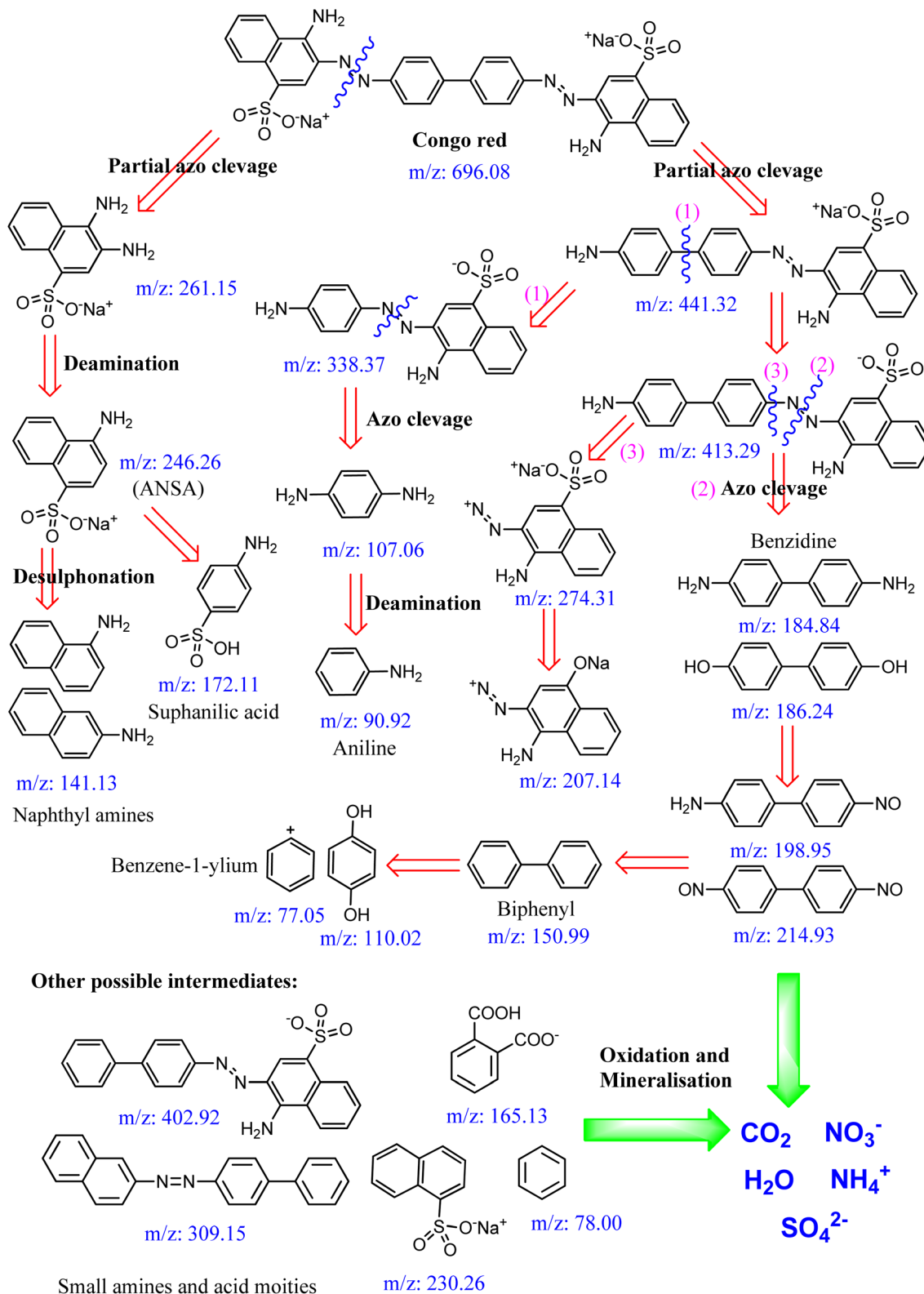
3.7. Regeneration and reusability of $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$

Fig. S12 shows the reusability results of the $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ for CR and NB adsorption up to six cycles. The $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ was found efficient till six consecutive cycles for CR (97.12% to 76.27%), and up to 3 cycles for NB (97.12% to 71.28%). Therefore, the $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ can be more efficiently used for CR, *i.e.*, anionic dye than NB, *i.e.*, cationic dye, sorption for potential practical applications. Further, the FT-IR analysis of the spent $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ after CR adsorption (spent $\text{GG}/\gamma\text{-Fe}_2\text{O}_3@\text{CR}$) and NB adsorption (spent $\text{GG}/\gamma\text{-Fe}_2\text{O}_3@\text{NB}$), Fig. S7, exhibited comparable peak positions to pristine $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$, establishing appreciable structural and functional stability.

3.8. Cost analysis of $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$

The commercial and large-scale implementation of the $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ for dye remediation from industrial effluents widely depends on its cost-effectiveness. The study addresses detailed stepwise consideration of economic feasibility through (a) the cost of synthesis of $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ per batch (on laboratory scale) (Table S11), and (b) their processing cost for use as an adsorbent/catalyst for treating 1000 L of wastewater using $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ (Table S12). The synthetic one-pot coprecipitation approach is comparatively simpler and cost-efficient in comparison to other sophisticated methods.⁴⁴ The *Glycyrrhiza glabra* roots were locally sourced at negligible cost, and were not subjected to any sort of energy-intensive chemical pre-treatment or post synthetic modification through expensive surfactants, toxic solvents, reagents/chemicals or synthetic stabilizers for a greener approach. Additionally, the energy consumption, limited to heating/drying, magnetic stirring, and calcination was moderate, scalable for industrial level production. The lab scale production of the $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ was estimated around \$0.79 to \$0.88, which is significantly lower than the previously reported commercial materials, including silver nanoparticles (\$15.77) and nanopowders (\$20.42) for similar applications.^{140,141} The majority of synthesis expense was due to analytical lab-grade $\gamma\text{-Fe}_2\text{O}_3$ precursors of high purity, which can be drastically reduced by up to 100 times on large scale using industrial-grade reagents. From the perspective of treatment cost, \$158 to \$176 was estimated to treat 1000 L wastewater using optimum dosage 0.2 g L^{-1} of $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$, considering unit synthesis cost of $\text{GG}/\gamma\text{-Fe}_2\text{O}_3$ for adsorption. Solar-photocatalysis was employed for dye degradation, which cuts down the power consumption. Considering practically feasible regeneration up to four cycles, the effective treatment cost reduced by 70–80%, in range \$31.6 to \$52.8 per 1000 L of wastewater.



Scheme 2 Proposed degradation pathways of CR by GG/ γ -Fe₂O₃.

3.9. Comparison study

The comparative evaluation of GG/ γ -Fe₂O₃ adsorbent/photo-catalyst's efficiency in CR and NB dyes remediation was

estimated with reference to the available literature (Tables S13 and S14). The greater effectiveness of the GG/ γ -Fe₂O₃, in comparison to previously studied materials, established its

wider applicability. This validation, supported by cost-effectiveness due to simple synthetic approach, and implementation of highly accessible precursors accounts for potential reliability in realistic and practical scenario.

4 Conclusions and future prospects

In summary, a structurally, thermally, and functionally stable GG/ γ -Fe₂O₃ nanocomposite was synthesized *in situ via* simple co-precipitation method, and employed for subsequent adsorption and photodegradation of CR and NB dyes, with pursuit of superior antimicrobial activity compared to the parent precursor GG. Both CR and NB dyes are extremely hazardous water pollutants that find application in various industries. The GG/ γ -Fe₂O₃ facilitated appreciable sorption capacity (Q_0) of 47.504 mg g⁻¹, and 15.361 mg g⁻¹ for CR and NB at 50 and 30 °C, respectively, achieving 99.78% and 97.23% decolorization of CR and NB, respectively, through adsorption under optimized conditions. The nanocomposite provided 92.7% degradation of CR in 160 min with a pseudo-first order rate constant of 0.014 min⁻¹, dominated by OH[•] and O₂^{•-} active species. The applicability of the GG/ γ -Fe₂O₃ for real wastewater treatment amongst competing ions and dye mixtures, under the same set of optimized experimental conditions illustrate the reliability and transferability of these conditions for large-scale application, while achieving balance between selectivity and efficiency. The comparative economic and evaluative performance of the GG/ γ -Fe₂O₃ with previously synthesized materials, accompanied by regenerative tendency and FT-IR affirmed stability of spent GG/ γ -Fe₂O₃ post treatment indicated significant potential in water treatment. Overall, the study bridges laboratory outcomes with practical applications and contributes to the development of advanced multifunctional materials for decolourising dye-laden industrial wastewater.

However, a proper post-treatment disposal strategy, for the composite, should be designed considering environmental sustainability. Additionally, changes in total organic carbon (TOC) and water quality parameters should be investigated to determine the mineralization efficiency after dye degradation. The future work may address the integration of GG/ γ -Fe₂O₃ for continuous flow or field-scale treatment systems.

Author contributions

Ankita Manchanda: conceptualization, visualisation, formal analysis, investigation, methodology, software, data curation, writing-original draft, funding acquisition. Ahmed Hussain Jawhari: data curation, validation. Ziaul Hasan: conceptualization, investigation. Nazim Hasan: data curation, validation. Sneha Shukla: validation. Adiba Khan: validation. Tabrez Alam Khan: supervision, writing-review & editing. Saif Ali Chaudhry: supervision, project administration, resources, writing-review & editing.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The authors confirm that the data supporting the findings of the study are available within the article and in its supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5ra04982b>.

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