Boosted sono-oxidative catalytic degradation of Brilliant green dye by magnetic \( \text{MgFe}_2\text{O}_4 \) catalyst: Degradation mechanism, assessment of bio-toxicity and cost analysis

Saptarshi Bose\textsuperscript{a}, Binay Kumar Tripathy\textsuperscript{b}, Animesh Debnath\textsuperscript{a}, Mathava Kumar\textsuperscript{b, *}

\textsuperscript{a} Department of Civil Engineering, National Institute of Technology Agartala, Tripura 799004, India
\textsuperscript{b} Environmental and Water Resources Engineering Division, Department of Civil Engineering, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India

ARTICLE INFO

Keywords:
Brilliant green dye
\( \text{MgFe}_2\text{O}_4 \) nanoparticles
Sono-catalysis
Persulfate oxidation
Optimization
Toxicity assessment
Cost analysis

ABSTRACT

The magnetic \( \text{MgFe}_2\text{O}_4 \) nanoparticles (NPs) were fabricated via a facile co-precipitation technique and were comprehensively characterized by XRD, FTIR, SEM, EDX and VSM. The prepared NPs were used as catalyst in presence of ultrasound (US) irradiation to activate persulfate (PS) for generation of sulfate radicals (\( \text{SO}_4^{2-} \)) for boosted degradation of toxic Brilliant Green (BG) dye. Preliminary experiments revealed that highest BG dye degradation efficiency of 91.63\% was achieved at \( \text{MgFe}_2\text{O}_4 \) catalyst dose of 1.0 g/L, PS dose of 300 mg/L, and initial dye concentration of 70 ppm within 15 min of US irradiation. However, only US, in presence of PS oxidation and US in presence of \( \text{MgFe}_2\text{O}_4 \) catalyst have shown 20.2\%, 83.6\% and 45.0\% of BG dye removal, respectively. Furthermore, response surface methodology (RSM) based central composite design (CCD) was executed to investigate the effect of interaction between independent variables such as \( \text{MgFe}_2\text{O}_4 \) catalyst dose (0.5–1.5 g/L), PS dose (150–350 mg/L), initial BG dye concentration (50–150 ppm) and US irradiation time (4–12 min). The RSM based quadratic model was used to predict the experimental data, and the prediction accuracy was confirmed by analysis of variance (\( R^2 = 0.98 \)). The established RSM model has predicted the optimum experimental conditions as \( \text{MgFe}_2\text{O}_4 \) catalyst dose of 0.75 g/L, PS dose of 300 mg/L, initial dye concentration of 75 ppm and sonication time of 10 min. Subsequently, the treatment cost analysis was performed for all thirty experimental runs of CCD, and the RSM predicted response was found to be evidently optimum as this has delivered best economic condition (140 $/kg of BG removed) with respect to relative dye removal (%). COD removal and residual sulfate analysis have demonstrated satisfactory reduction of COD (90.31\%) as well as sulfate ions (42.87 ppm) in the dye solution after treatment. Results of degradation pathway analysis portrayed the transformation of BG molecule (M/Z ratio 385) into simpler fractions with M/Z ratio of 193, 161, 73, and 61. Moreover, the toxicity analysis revealed that sono-catalytically activated PS system has efficiently reduced the toxicity level of BG dye from 93.9\% to 5.13\%.

1. Introduction

On account of the lower cost and easy accessibility, synthetic dyes are being used abundantly in various industries including textile, paper production, food technology and leather tanning [1]. Around of 700,000 tons of organic dyes are used every year across the world and dyes are considered to be one of the most significant class of synthetic organic pollutants with severe toxicity causing pollution and carcinogenicity to the receiving water bodies [2]. Brilliant green (BG) is a cationic dye which is extensively used as biological stain, dermatological agent, veterinary medicine, poultry feed to inhibit propagation of mold, intestinal parasites and fungus [3]. Rate of BG dye utilization in paper manufacturing is around 0.8–1.0 kg of dye per tons of paper produced with Lethal Dose 50 value for human being 50–500 mg/kg [4]. BG dye is highly toxic for not only human beings but also for the aquatic system as well as gram positive bacteria. Hence, the degradation of toxic synthetic dyes like BG is imperative before they are disposed into the environment. Numerous physicochemical and microbiological treatment methods like adsorption [5], photo-catalysis [6], electro-coagulation [7], nano-filtration [8], Fenton [9], microwave [10,11], and other biological treatment methods have been studied for effective treatment of wastewater laden with organic dyes.
Ultrasonic (US) assisted treatment methods are considered to be one of the popular advanced oxidation processes and is receiving lots of attention in current times for degradation of organic water pollutants including dye loaded wastewater [12]. The mechanism of US is based on the acoustic cavitation in liquid in an ultrasonic environment [13]. The acoustic cavitation occurs through several steps like the processes of formation (nucleation), rapid growth (expansion) and violent collapse (implosion) of cavitation bubbles in liquid. The sudden collapse of the cavitation bubbles can generate local high temperature (5000 K) and pressure (1800 atm) for very short time which is known as hotspots [14]. Thus US irradiation generates highly reactive radical species due to pyrolysis of water molecules in aqua matrix, through which organic water pollutants are degraded into simpler compounds [15]. However, only US irradiation in macro level wastewater treatment plant is uneconomical due to its high energy-demand and prolong treatment time [16]. To eradicate these shortcomings and to boost the degradation efficiency of organic pollutants, metal oxide and semiconductors are used as catalyst in the ultrasound environment [17]. Sonocatalysts assist as extra nuclei, thus enhance the catalytic activity of the treatment system by increasing the cavitation bubbles generation rate [18,19].

Super-paramagnetic ferrites have gained attention as sonocatalyst due to their narrow band energy gap (∼2 eV) which makes them potential materials to degrade dyes and other organic contaminants [19]. Metal ferrites are expressed as general formula of \( \text{M}_x\text{Fe}_{y}\text{O}_z \), where \( x \) might be \( \text{Mg}^2+, \text{Zn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+} \) or \( \text{Cu}^{2+} \) [20]. The lattice structure of spinel ferrites provides extra catalytic sites which results in the increment of organic pollutant degradation efficiency [21]. Among various ferrites, spinel structured soft magnetic n-type semiconducting material \( \text{MgFe}_2\text{O}_4 \) is being used in water treatment techniques like photocatalysis, adsorption, microwave induced catalysis etc. MgFe\(_2\)O\(_4\) displayed the highest photo-catalytic degradation of acetic acid among all \( \text{MFe}_2\text{O}_4 \) (\( M = \text{Mg, Zn, and Cd} \)) [22] and 2-propanol in the photocatalytic system [23]. It has been reported that the degradation performance of acid orange dye by \( \text{MgFe}_2\text{O}_4 \) in the \( \text{O}_2 \) system reaches beyond 90% which is much higher than other ferrites such as \( \text{NiFe}_2\text{O}_4 \), \( \text{MnFe}_2\text{O}_4 \), and \( \text{CuFe}_2\text{O}_4 \) [24]. Enhancement of MW-Catalytic activity by \( \text{MgFe}_2\text{O}_4 \) in the case of p-nitrophenol (PNP) removal was found due to generation of active species (\( \text{OH} \) and \( \cdot \text{O}_2 \)) by Zhou et al. [25]. In spite of potential application of \( \text{MgFe}_2\text{O}_4 \) nanoparticles in water treatment by the above mentioned processes, the possibility of \( \text{MgFe}_2\text{O}_4 \) to act as a catalyst in ultrasound system to degrade organic pollutants is not yet explored properly. To the best of our knowledge \( \text{MgFe}_2\text{O}_4 \) nanoparticles have not been explored as sonocatalyst to degrade the toxic BG dye from water.

In recent times, addition of in situ chemical oxidants such as peroxodisulfate, persulfate etc. in the sonocatalysis system is becoming popular for complete mineralization of organic pollutants [26]. US irradiation causes breakage of the S-O bond and to generate sulfate radicals (Eq. (1)).

\[
\text{SO}_2\text{O}_4^{--} + \text{US} \rightarrow \text{SO}_4^{2-}
\tag{1}
\]

where the symbol “\( \text{US} \)” represents ultrasonic irradiation [27].

Sonocatalyst containing transition metals (iron, copper, silver, cobalt, zinc, and manganese) can activate persulfate by one electron transfer process [28] (Eq. (2)).

\[
\text{SO}_2\text{O}_4^{--} + \text{M}^{++} \rightarrow \text{M}^{+++} + \text{SO}_4^{2-} + \text{SO}_4^{2-}
\tag{2}
\]

Hybrid application of ultrasonic assisted persulfate degradation can effectively degrade many recalcitrant organic pollutants such as dinitrotoluene [29], methyl tert-butyl ether [30], 1,1,1-trichloroethane [31] and perfluoropolyether carboxylic acids [32].

Thus in this research, \( \text{MgFe}_2\text{O}_4 \) nanoparticles were used as catalyst in sono-oxidative environment for BG dye degradation in order to study the synergistic effect of \( \text{MgFe}_2\text{O}_4 \) catalyst and persulfate as an in situ oxidant. The effects of the \( \text{MgFe}_2\text{O}_4 \) sonocatalyst dose, initial BG dye concentration, US irradiation time, and addition of radical scavengers on the BG degradation performance were explored systematically. The experimental process was optimized by response surface methodology and treatment cost analysis was performed. The plausible degradation pathway of BG dye was also explored and the toxicity was assessed for generated intermediates and end products.

2. Materials and methods

2.1. Chemicals and reagents

The BG dye powder was procured from Loba Chemie Pvt. Ltd (India) and used without further purification. The sodium persulfate and ferric chloride hexahydrate (\( \text{FeCl}_3\cdot6\text{H}_2\text{O} \)) were purchased from Avra Synthesis Pvt. Ltd (India). Other chemicals such as magnesium chloride hexahydrate (\( \text{MgCl}_2\cdot6\text{H}_2\text{O} \)), sulfuric acid (\( \text{H}_2\text{SO}_4 \)), sodium hydroxide (\( \text{NaOH} \)) pellets and potassium dichromate (\( \text{K}_2\text{Cr}_2\text{O}_7 \)) were purchased from Merck (India). The reconstitution solution, diluent and acute reagents for toxicity analysis were obtained from Modern Water (UK). All solutions were prepared using deionized water (resistivity ≥ 18 MΩ cm at 25 °C) from Milli-Q synthesis unit (Millipore®, USA).

2.2. Synthesis and characterisation of \( \text{MgFe}_2\text{O}_4 \) catalyst

The magnesium ferrite nanoparticles were prepared by a simple co-precipitation method [33]. In a typical procedure, \( \text{MgCl}_2\cdot6\text{H}_2\text{O} \) (0.4 M) and \( \text{FeCl}_3\cdot6\text{H}_2\text{O} \) (0.8 M) salts were dissolved into 250 ml deionized water separately. Both the solutions were rigorously stirred on magnetic stirrer to make them homogeneous in nature. Another solution of \( \text{NaOH} \) (0.3 M) was prepared in 250 ml of deionized water. Thereafter, the mixtures of two metal solutions were added drop by drop into the \( \text{NaOH} \) solution through a burette while continuous stirring of the \( \text{NaOH} \) solution was performed. The brown-blackish slurry precipitate was placed in boiling water and digested there for 2 hr. After that the slurry was filtered with Whatman filter paper (Grade: 41) and oven-dried at 80 °C. Next, the dried precipitate was washed several times with deionized water until the pH of supernatant reached near to neutral condition. Then, the precipitate was calcined at 500 °C for 4 hr in muffle furnace. Finally, the calcined material was grounded until the uniform powder form was achieved.

To confirm the spinel structure of \( \text{MgFe}_2\text{O}_4 \) nano-particles, X-ray diffraction (XRD) pattern was recorded by XRD analysis (Bruker, D-8 Advance, Germany) and to identify the available stretching and vibrational bonds Fourier transform infrared (FT-IR) spectroscopy was executed by FT-IR spectrometer (Perkin Elmer, USA). The detailed morphology and elemental composition of \( \text{MgFe}_2\text{O}_4 \) nanoparticles were exhibited by FE-SEM image (FESEM, Hitachi, S-4800, Japan) and energy dispersive x-ray (EDX) (Perkin Elmer, USA) respectively. Vibrating sample magnetometer (Lake Shore VSM, 7404, USA) was used to investigate the room temperature magnetic property of the \( \text{MgFe}_2\text{O}_4 \) nano-catalyst. Total organic carbon (TOC) of raw and treated BG dye samples were determined by TOC analyser (TOC-V-CSV 39208967, Shimadzu).

2.3. Sono-catalytic degradation of BG dye

Persulfate activated sono-catalytic degradation of BG dye was performed by probe sonicator (Frontline Electronics and Machinery Pvt. Ltd., India) possessed with ultrasonic frequency of 20 ± 3 kHz and max power of 250 W. All the experiments were performed in 100 ml beaker in a dark chamber to eradicate the effect of photo-catalysis and photolysis. During the dye degradation experiment, the \( \text{MgFe}_2\text{O}_4 \) dose was varied between 0.5 and 1.25 g/L and the PS dose was varied between 100 and 400 mg/L for 70 ppm (100 ml) BG dye solution and the dye solution was irradiated by probe sonicator for a time period of 15 min. After different time intervals, 5.0 ml sample was taken out and
quenching of dye degradation reaction was performed by adding 1.0 ml of methanol immediately. Thereafter the MgFe₂O₄ nano-catalyst was alienated from BG dye solution using external magnetic field and immediately, the residual BG dye concentration in the solution was determined by UV-spectrophotometer (HACH-DR 5000) at maximum absorbency of BG dye at the wavelength of 624 nm. The degradation efficiency of BG dye was calculated by the following equation (Eq. (3)):

\[
R% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]  

(3)

where, \( C_0 \) and \( C_t \) are the initial BG dye concentration and BG dye concentration after t min of reaction, respectively.

After sono-catalytic treatment of BG dye, the degradation products (DP) formed during the reaction were identified using liquid chromatography-mass spectrometer (LC-MS) consisting of ion trap system (Thermo scientific, USA). A solution mixture of acetonitrile and water (60:40 ratio) was used as mobile phase in this analysis. The flow rate was maintained as 0.5 ml/min with retention time of 10 min and during each run, 10 µL of sample was used for analysis.

2.4. Effect of radical scavenger anions study

Co-existence of various anions in the real wastewater may reduce the performance of persulfate activated sono-catalytic degradation process. Among several anions, chloride and sulfate anions play a pivotal role in the reduction of removal efficiency of pollutants from wastewater by producing less destructive radicals as shown in Eq. (4)-(6) [14,34].

\[
\text{Cl}^- + \text{OH} \rightarrow \text{Cl}^- + \text{OH}^-
\]  

(4)

\[
\text{SO}_4^{2-} + \text{OH} \rightarrow \text{SO}_4^{2-} + \text{OH}^-
\]  

(5)

\[
\text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-}
\]  

(6)

Hence, in this study the effect of chloride and sulfate anions on BG dye removal efficiency was explored.

2.5. Kinetic modeling

Sono-catalytic degradation of BG dye was evaluated as per apparent first order kinetic model as shown in Eq. (7) [35].

\[
\ln \left( \frac{C_t}{C_0} \right) = -kapp \cdot t
\]  

(7)

where, \( t \) is ultrasonic irradiation time and kapp denotes the apparent first order kinetic rate constant.

2.6. Assessment of bio-toxicity of BG dye solution before and after treatment

Microtox analyzer (M500, Modern Water, USA) was used to evaluate the toxicity of treated and untreated BG dye samples to determine the alteration in toxicity after treatment. In this process, 2% screening test (dilution of 2% BG dye) was performed by using luminous bacteria i.e. **Aliivibrio fischeri** (lyophilized bacterial reagent) for the exposure time interval of 30 min (ISO 11348–3:2007 standards). The Microtox analyzer is designed with an array of sample wells to keep sample containing bacterial strain and a photometer to detect reading at 5, 15 and 30 min after mixing with toxic BG dye sample. To estimate EC50, decrement of light emission readings were checked against healthy unaffected control bacteria reading. EC50 can be expressed as the effective concentration of toxicant in percentage with corresponds to original sample which causes 50% light reduction to the bacteria [36,37]. Finally, Microtox data analysis program (Microtox Omni Software (1999)) was applied to analysis the data and evaluates EC50 value. Other procedures such as sample preparation, serial dilution was as per the standard protocol of the supplier (Modern Water, USA).

2.7. Cost analysis for sono-catalytic degradation of BG dye

Treatment cost analysis is a very important step to evaluate the cost effectiveness of any energy extensive treatment processes such as sono-catalytic activated persulfate system. Total cost involved in this process was performed by determining the cost of energy and cost of chemicals required for fabrication of catalyst and treatment process. Following equations (Eq. (8) – (13)) were used to determine the total treatment cost in terms of $/kg of BG dye removed [38].

**Power Consumed (kwh)**

\[
\text{Power Consumed (kwh)} = \frac{\text{MW Power} \times \text{Time}}{1000 \times 60}
\]  

(8)

**Energy Cost (Rs/kg of Pollutant Removed)**

\[
\text{Energy Cost (Rs/kg of Pollutant Removed)} = \frac{\text{Power Consumed (kwh) \times Electricity Cost}}{\text{Pollutant Removed (kg/L) \times Volume (L)}} \times 10^6 \left(\frac{\text{Rs}}{\text{kwh}}\right)
\]  

(9)

**MgFe₂O₄ NPs Cost (Rs/kg of Pollutant Removed)**

\[
\text{MgFe₂O₄ NPs Cost (Rs/kg of Pollutant Removed)} = \frac{\text{MgFe₂O₄ NPs required}}{\text{Pollutant Removed (kg/L) \times Volume (L)}} \times \text{Unit Cost} \times 10^6 \left(\frac{\text{Rs}}{\text{kwh}}\right)
\]  

(10)

**Sodium Persulfate Cost (Rs/kg of Pollutant Removed)**

\[
\text{Sodium Persulfate Cost (Rs/kg of Pollutant Removed)} = \frac{\text{N₂S₂O₈ required}}{\text{Pollutant Removed (kg/L) \times Volume (L)}} \times \text{Unit Cost} \times 10^6 \left(\frac{\text{Rs}}{\text{kwh}}\right)
\]  

(11)

**Total Chemical Cost (Rs/kg of Pollutant Removed)**

\[
\text{Total Chemical Cost (Rs/kg of Pollutant Removed)} = \frac{\text{MgFe₂O₄ NPs Cost (Rs/kg of Pollutant Removed)} + \text{N₂S₂O₈ Cost (Rs/kg of Pollutant Removed)}}{\text{Pollutant Removed (kg/L) \times Volume (L)}}
\]  

(12)

**Total Cost ($/kg of Pollutant Removed)**

\[
\text{Total Cost ($/kg of Pollutant Removed)} = \left(\frac{\text{Total Chemical Cost (Rs/kg of Pollutant Removed) + Energy Cost (Rs/kg of Pollutant Removed)}}{\text{Waste to be treated (kg/L) \times Volume (L)}}\right) \times \text{76 (Rs)}
\]  

(13)

2.8. COD, TOC removal and residual sulfate analysis in treated BG dye sample

COD of the treated and untreated BG dye samples by several combinations of methods were determined by standard closed flux titration procedure (5220C. Closed Reflux, Titrimetric Method, APHA, 2017). Total organic carbon (TOC) of raw and treated BG dye samples were determined by TOC analyser (TOC–V–CSN 39208967, Shimadzu).
Considering the toxicity of sulfate ions, the maximum permissible limit of 400 mg/L for inland surface water of sulfate ions was prescribed by Bureau of Indian Standards (BIS) (IS: 2296-1982). As in this research, the sulfate radical based AOP technique was used, the availability of sulfate anions in the treated BG dye sample is very critical for safe disposal of treated BG dye solution. The concentration of sulfate ions in the treated BG dye solutions were measured by Ion chromatography (Thermo fisher scientific; Column from Dionexionpac AS18 4X150mm).

2.9. Response surface methodology (RSM) based optimization

The conventional ‘one factor at a time’ approach of optimization for any experimental process is quite time taking, strenuous and also ineffective for determination of the effect of simultaneous changes of input variables onto the output of the process. Hence, in this research RSM founded optimization method was applied using central composite design (CCD) on accounts of its effectiveness as a mathematical and statistical tool for evaluating interacting variables, prediction modeling and optimization of input parameters [39,40]. Reduction of number of experimental run is another benefit which can be achieved from CCD. In the design of experiment (DOE) fabrication, four factors (initial BG dye concentration (ppm), MgFe$_2$O$_4$ nanoparticles dose (g/L), sodium persulfate dose (mg/L) and irradiation time (min)) and five different levels ($-\alpha, -1, 0, +1, +\alpha$) were utilized. As a result, total 30 runs of experiments (16 factor points, 8 axial points and 6 central replicates) were obtained as shown in Eq. (14)

$$N = 2^k + 2k + 6, \quad (14)$$

where $k$ is number of input variables (here $k = 4$) and $N$ = total number of experimental runs.

To discover the relationship between BG dye degradation (%) and independent input variables, a quadratic equation (Eq. (15)) was used. The predicted response,

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \sum_{i=1}^{k} \beta_{ij} X_j X_i, \quad (15)$$

where $k$ = number of independent variable (parameters), $X_i$= coded value of $i^{th}$ independent variable, $\beta_0$, $\beta_j$ and $\beta_{ij}$ are zero-order, first-order and second-order coefficients of the equation.

The output was examined by analysis of variance (ANOVA) and F-test values and the fitness of polynomial model was checked with the
coefficients of $R^2$ and $R^2_{adj}$. At the end, thorough comparison between the experimental and predicted results was scrutinized to represent statistical significance of the predicted model. The Design Expert software (Version: 11.1.0.1) was used for ANOVA, RSM model plot design, and optimization of the process parameters.

3. Results and discussions

3.1. Characterisation of MgFe$_2$O$_4$ catalyst

The phase examination of crystallographic nature of MgFe$_2$O$_4$ nanoparticles was performed by Cu Kα radiation source X-ray diffraction.
(XRD) method (λ = 1.5438 Å). With a scan rate of 3’ min⁻¹, the well-defined peaks of XRD pattern (Fig. 1(a)) with a scan range of 2θ = 25° to 65° assert the formation of single phase face centered cubic spinel ferromagnetic structure. The observed diffraction peaks at 20 angles such as 30.21°, 35.44°, 42.85°, 52.97°, 57.09°, and 63.14° corresponds to the Miller planes (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0). This results are in well agreement with the previously reported literature for magnesium ferrite [41]. Moreover, broadened width of diffraction peak indicates smaller size of nanoparticles. The SEM morphology displayed the nanostructure of the MgFe₂O₄ powder (Fig. 1(b) and (c)). Although presence of agglomeration due to magnetic property is visible, a more detailed inspection will reveal the cubic structure along with lots of corners and edges which act as active sites [42]. The average particle size can be estimated as 15 nm. The magnetic behavior of MgFe₂O₄ nano-particles was measured by vibrating sample magnetometer (VSM) at room temperature for maximum applied magnetic field of 15 × 10⁴ G (Fig. 1(d)). The perfect S-shaped hysteresis loop confirmed the ferromagnetic property of the nanoparticles (Fig. 1(d)). The obtained saturation magnetization (Mₛ), magnetic remanence (Mᵣ) and coercivity (Hₘ) from the hysteresis loop are found to be 5.531 emu/g, 5.54 × 10⁻⁴ emu/g and 43.78 G, respectively. The magnetic saturation value is comparatively less than the bulk which can be attributed to the lower size of particles [43,44]. In addition, the less magnetic remanence (Mᵣ) and coercivity (Hₘ) than bulk denotes metastable cation distribution and exchange of sites of cations in the ferrite structure. Because of the principle of direct proportional relationship between particle size and coercivity in nano-regime, the nano size of the particles is undeniable [44]. This magnetic property ensures the facile recovery of catalysts during treatment as well as reusability study.

Presence of functional group on MgFe₂O₄ catalyst was investigated by FT-IR spectrum analysis (Fig. 2(a)) in the range of 400 to 4000 cm⁻¹. The two major distinguishable absorption peaks at 437 cm⁻¹ (lower frequency) and 594 cm⁻¹ (higher frequency) corresponding to the stretching vibration bond of octahedral sites (Mg²⁺ - O²⁻ bond) and tetrahedral sites (Fe²⁺ - O²⁻ bond) confirms the generation of spinel magnesium ferrite structure [33]. The peak at 1498 cm⁻¹ refers to the bending of water molecule (H-O-H) while the peak at 3436 cm⁻¹ can be attributed to stretching vibration of hydroxyl group (O-H) from the absorbed water on the surface of the sample [45]. The peak occurred at 1631 cm⁻¹ refers to the bending vibration of adsorbed water molecule (H-O-H) [46]. The insignificant peaks appeared at 1000-1200 cm⁻¹ may be due to the presence of some organic impurities.

In addition, an energy dispersive X-ray (EDX) spectrum specifies that synthesized MgFe₂O₄ nanoparticles are composed of mainly Mg, Fe and O (Fig. 2(b)). ‘Mg’ element comprises 18.81%, ‘Fe’ element comprises 42.24% and ‘O’ element comprises 38.77%. Thus it can be asserted that mass ratio of chemical compositions are in line with the EDX results of MgFe₂O₄ nanoparticles.

The photo absorption property of the synthesized MgFe₂O₄ catalyst was examined using UV–Vis diffuse reflectance spectra (DRS) analysis so as to calculate the energy band gap. The absorption versus the wavelength spectrum in the range of 400–800 nm is represented in Fig. 3(a). It is clear from the Fig. 3(a) that the prepared MgFe₂O₄ catalyst manifest a strong absorbance bend in the visible light regions. The (ahu)² versus log plot for calculation of energy band-gap of MgFe₂O₄ catalyst has been shown in Fig. 3(b) and the energy band gap of prepared MgFe₂O₄ catalyst is found to be 2.11 eV [48]. The corresponding energy band diagram with schematics density of states representation for the catalyst is also shown in Fig. 3(c). The room temperature photoluminescence (PL) emission spectrum of MgFe₂O₄ catalyst was studied with excitation wavelength of 310 nm. The PL spectra as obtained in the wavelength range of 320–580 nm for MgFe₂O₄ NPs has been shown in Fig. 3(d). The emission peaks observed at 358 nm and around 550 nm can be ascribed to electronic transitions, which may be due to radiative defects or surface defects [47].

3.2. Studies on degradation of BG dye

3.2.1. Preliminary experiments for BG dye degradation

The effect of MgFe₂O₄ nanoparticles on the performance of sonooxidative catalytic oxidation of BG dye (US + NPs + PS) was examined with reference to other ultrasound based treatment methods such as only ultrasound irradiation (US), ultrasound coupled with persulfate (PS) oxidation (US + PS) and ultrasound coupled with MgFe₂O₄ nanoparticles (US + NPs). Experimental parameters such as initial concentration of BG dye (70 ppm), MgFe₂O₄ nano-particles doses and PS doses were kept constant throughout these comparison experiments (Fig. 4(a)). Nearly 20.2% removal of BG dye was achieved by only ultrasound irradiation within 15 min which is truly inadequate. This less percentage of degradation is surely from the contribution of OH formed during the sonolytic cavitation of bubble in aqueous medium (Eq. (16)) [1,46]. The addition of MgFe₂O₄ nanoparticles in the ultrasound irradiation has been led the BG degradation efficiency up to 45% after 15 min of irradiation as nanoparticles provides heterogeneous nuclei for bubble formations and ‘hotspots’ for pyrolysis of water molecule and subsequently generation of more OH radicals [1,46,49]. Apart from these, ‘sonoluminescence’ mechanism could also be anticipated in this treatment system [22,46].

\[
\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} + \text{H}_2
\]

Moreover, addition of PS coupled with ultrasound manifested better result than pervious system which was almost 83.6% but not satisfactory. Perhaps insufficient SO₄⁻ in the solution was the reason behind this relatively less removal. However, application of both MgFe₂O₄ nanoparticles and PS has enhanced the dye degradation performance due to activation of PS by nano-particles. After 15 min interval removal percentage of BG dye was observed as 91.63%. Thus from the results among all experiments, ultrasound coupled with MgFe₂O₄ nanoparticles as an activator of PS was selected for further studies.

3.2.2. Effect of MgFe₂O₄ catalyst dose onto BG dye removal

The effect of MgFe₂O₄ dose on the removal efficiency of BG was investigated with 70 ppm dye solution at unaltered pH 8.5 in US + NPs + PS system. It can be clearly observed from the Fig. 4(b) that BG removal efficiency was notably increased from 78.02% to 91.63% by the increment of catalyst doses from 0.5 g/L to 1.0 g/L. This amplification of performance is mainly attributed to the boost of ROS (reactive oxygen
species) (SO₄²⁻ and OH⁻) in the presence of large number of catalyst and high active sites for dye molecules degradation [1,34,46]. However, further advancement in catalyst dose to 1.25 g/L resulted to insignificant improvement in dye molecules degradation. This phenomenon indicates aggregation of sono-catalyst provides less active sites and poor diffusion between PS and BG dye on the surface of MgFe₂O₄ catalyst as well as the reduction of utility of MgFe₂O₄ nanoparticles (Eq. (17)) [34]. Hence, optimum dose of catalyst was selected as 1.0 g/L for further studies.

\[ \text{Fe}^{3+} + \text{SO}_4^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \]  
\[ \text{(17)} \]

3.2.3. Effect of oxidant dose onto BG dye removal

In addition to nano-particles, PS has a tremendous role in the dye degradation performance as demonstrated in Fig. 4(a). The surge of removal efficiency from 69.85% to 91.63% has followed the elevation of PS dose from 100 mg/L to 200 mg/L with optimum catalyst dose of 1.0 g/L and initial concentration of dye as 70 ppm (Fig. 4(c)). In one hand, greater PS concentration provides more effective contact of PS molecules on the MgFe₂O₄ surface and on the other hand, high PS concentration also propagates more sulfate radicals. These noteworthy actions assisted this system to achieve such effective removal of dye. Regardless, a negative effect on removal efficiency was noticed when PS dose was raised to 400 mg/L (Fig. 4(d)). This may be due to the fact that, in excess of sulfate radicals, SO₄²⁻ reacts with itself or PS to form ions or radicals with poor or no oxidizing property (Eq. (18), (19)) [34]. Thus, an optimum PS dose of 300 mg/L was adopted for further studies.

\[ \text{SO}_4^{-} + \text{SO}_4^{-} \rightarrow \text{S}_2\text{O}_8^{2-} \]  
\[ \text{(18)} \]

\[ \text{SO}_4^{-} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{S}_2\text{O}_4^{-} + \text{SO}_4^{2-} \]  
\[ \text{(19)} \]

3.2.4. Effect of radical scavenger anions on BG dye removal

Co-existence of various anions in the real wastewater acts as ROS scavenger and eventually affects the degradation performance. To simulate the situation of real wastewater, 70 mg/L of sodium chloride (NaCl) and sodium sulphate (Na₂SO₄) were added separately in two 70 ppm dye solution containing 1.0 g/L of MgFe₂O₄ nano-particles and 300 mg/L of PS. Fig. 5 shows the inhibiting property both sulphate and chloride ion on BG dye removal. But, the presence of sulphate ion has revealed more restraining effect as dye removal efficiency dropped from 91.63% to 82.62% whereas chloride ion has showcased little less restraining effect (91.63% to 85.73%). Mechanism behind this was explained in Eq (5), (6) and (7).

3.2.5. Kinetic analysis of BG dye degradation in US + NPs + PS system

Linear fitting of experimental data with apparent first order kinetic model for (a) MgFe₂O₄ catalyst dose variation, (b) PS dose variation have shown in Fig. 6(a) and (b), respectively. Moreover the variation of apparent first order kinetic rate constant vs. PS dose has been shown in Fig. 6(c) and (d), respectively. Evidently, from the Fig. 6(a) & (c) it is clear that the US + NPs + PS system reactions for MgFe₂O₄ nanoparticles dose variation has followed the apparent first order kinetic model. The kapp value has increased from 0.086 s⁻¹ to 0.163 s⁻¹ with the increase of catalyst dose from 0.50 g/L to 1.25 g/L. Similarly, the influence of PS dose on reactions in US + NPs + PS system has also imitated the same trend i.e. apparent first order kinetic model (Fig. 6(b)). Here, after reaching the kapp value of 0.143 s⁻¹ from 0.076 s⁻¹, a sudden fall was observed at the value of 0.103 s⁻¹ corresponding to the PS dose of 400 mg/L (Fig. 6(d)). Thus from the kinetic analysis results, it can be stated that both catalyst and PS have rate limiting characteristic in US + NPs + PS system.

3.2.6. Possible degradation Pathways

Initially, the M/Z ratio was 385 for untreated BG dye in the aqueous media. Eventually, with the progression of reaction the BG dye degradation occurred and smaller M/Z ratio containing compounds were formed in the solution due to the breaking of larger molecular structure of BG dye (Fig. 7). At first, after breaking of C-N bond and demethylation a compound of M/Z ratio of 348 was formed. Thereafter, two possible degradation pathways were noticed. In the first pathway, due to splitting of two benzene rings and C-N bond cleavage, two consecutive molecules with M/Z ratio of 193 and 161 were formed. Subsequently in the second path, due to splitting of one benzene ring and demethylation, intermediate with M/Z ratio 192 was formed and further benzene ring splitting and C-N cleavage produced intermediate product with M/Z ratio of 161.
Thereafter, from these two compounds with M/Z ratio of 161, another two compounds in the simpler hydrocarbon form with least M/Z ratio (73 & 61) might have formed due to complete breaking down of remaining benzene rings in the solution. This study clearly indicates excellent degradation of BG dye molecules [50,51].

3.2.7. COD, TOC and residual sulfate analysis

The COD, and TOC analysis of treated and raw BG dye (70 ppm) with various methods (only US, US + PS, US + NPs, and US + NPs + PS systems) were performed to investigate the change in COD and TOC after treatment (Fig. 8(b) and (c)). During the treatment of BG dye solution, the experimental conditions were maintained at MgFe$_2$O$_4$ NPs dose 1.0 g/L, BG dye concentration of 70 ppm, PS dose 300 mg/L and irradiation time of 15 min. It can be observed from Fig. 8(b) and (c) that the highest COD and TOC removal of 90.31% and 73.57%, respectively were obtained with US + NPs + PS system whereas the poorest performance was observed with only US system (64.7%, and 50.02% for COD and TOC, respectively). The highest COD and TOC removal in US + NPs + PS system could be attributed to the effective degradation of large number of BG molecules due to synergistic effect of PS and catalyst. The US + NPs and US + PS systems could exhibit COD removal as 71.02% and 86.75% respectively. However, the same treatment methods have shown TOC removal of 53.71% and 65.33% respectively.

As the sulfate ions present in the wastewater can cause toxicity, a verification check of residual sulfate from the PS ions in the treated BG dye solution was accomplished (Fig. 8(d)). It can be observed that US + NPs + PS system shows edge over the US + PS system under similar experimental conditions (i.e. MgFe$_2$O$_4$ NPs dose 1.0 g/L, BG dye concentration of 70 ppm, PS dose 300 mg/L and irradiation time 15 min). After 5 min of treatment the US + PS and US + NPs + PS system yielded to 2200 ppm, and 1845 ppm of residual sulfate. But, the US + NPs + PS system has reached nearly half of the residual sulfate of US + PS system after 15 min of treatment. This indicates that with time more utilization of sulfate radicals and adsorption of extra residual sulfate ions by MgFe$_2$O$_4$ nanoparticles. Ultimately, US + NPs + PS system produces only 42.87 ppm of residual sulfate at the end of 15 min which can be released safely as effluent. The maximum permissible limit of 400 mg/L for inland surface water of sulfate ions was prescribed by Bureau of Indian Standards (BIS) (IS: 2296–1982).

Fig 7. Intermediates generated during MgFe$_2$O$_4$ catalyst based sono-catalytic activated PS oxidation of BG dye with possible pathway for BG degradation.
3.2.8. Assessment of bio-toxicity for BG dye solution before and after treatment

The toxicity analysis was conducted for untreated BG dye solution (70 ppm) as well as for the BG dye solution treated with US + PS, US + NPs, and US + NPs + PS treatment systems. In all the treatment systems the sampling time was varied at 5, 10 and 15 min and PS dose was maintained at 300 mg/L for US + PS and US + NPs + PS treatment systems. Moreover the NPs (MgFe₂O₄ catalyst) dose was maintained at 1 g/L for the US + NPs, and US + NPs + PS treatment systems. The complete toxicity analysis results are depicted in Fig. 8(a). In case of

![Fig 8. (a) Assessment of bio-toxicity for treated and raw BG dye solution (BG dye treatment conditions: MgFe₂O₄ catalyst dose 1 g/L, PS dose 300 mg/L, initial concentration of dye 70 ppm and sonication time 15 min), (b) COD removal efficiency of MgFe₂O₄ catalyst based sono-catalytic activated PS oxidation system (MgFe₂O₄ catalyst dose 1 g/L, PS dose 300 mg/L, initial concentration of dye 70 ppm and time 15 min), (c) COD removal efficiency of MgFe₂O₄ catalyst based sono-catalytic activated PS oxidation system; (d) residual sulfate ions assessment after treatment with different systems at different time intervals (MgFe₂O₄ catalyst dose 1 g/L, PS dose 300 mg/L, initial concentration of dye 70 ppm and time 15 min).]

Table 1
Input variables used in RSM modeling with experimental and model forecasted BG dye removal (%) and breakup of cost analysis for thirty experimental runs.

| Run | A: MgFe₂O₄ Dose (g/L) | B: BG Dye Conc (ppm) | C: PS Dose (mg/L) | D: Time (min) | BG Removal (%) | BG removed (mg/L) | Catalyst Cost ($/kg) | Oxidant cost ($/kg) | Energy cost ($/kg) | Total Cost ($/kg) |
|-----|------------------------|-----------------------|------------------|---------------|----------------|--------------------|---------------------|-------------------|------------------|-------------------|
| 1   | 0.75                   | 75                    | 200              | 10            | 82.89          | 62.5875           | 71.38               | 33.61            | 26.25            | 131.24           |
| 2   | 1.00                   | 100                   | 250              | 8             | 69.56          | 69.25             | 86.02               | 37.97            | 18.98            | 142.97           |
| 3   | 1.00                   | 100                   | 250              | 8             | 69.16          | 69.25             | 86.02               | 37.97            | 18.98            | 142.97           |
| 4   | 1.25                   | 125                   | 200              | 6             | 67.5           | 68.51             | 86.95               | 24.56            | 11.51            | 123.02           |
| 5   | 1.00                   | 50                    | 250              | 8             | 81.06          | 80.80             | 40.40               | 147.44           | 65.08            | 254.06           |
| 6   | 0.75                   | 75                    | 300              | 6             | 73.25          | 74.00             | 55.50               | 80.50            | 17.76            | 155.11           |
| 7   | 1.00                   | 100                   | 250              | 12            | 88.21          | 87.87             | 67.79               | 29.92            | 22.44            | 120.15           |
| 8   | 1.00                   | 100                   | 250              | 8             | 69.69          | 69.25             | 86.02               | 37.97            | 18.98            | 142.97           |
| 9   | 1.25                   | 125                   | 200              | 10            | 74.04          | 73.08             | 91.35               | 81.51            | 23.02            | 122.52           |
| 10  | 1.00                   | 100                   | 250              | 8             | 68.34          | 69.25             | 86.02               | 37.97            | 18.98            | 142.97           |
| 11  | 0.75                   | 75                    | 300              | 10            | 89.12          | 88.09             | 66.06               | 67.62            | 47.75            | 140.25           |
| 12  | 1.5                    | 75                    | 300              | 10            | 81.58          | 81.84             | 61.38               | 121.31           | 51.4             | 199.48           |
| 13  | 0.75                   | 75                    | 300              | 10            | 71.15          | 71.79             | 89.73               | 49.78            | 35.16            | 183.11           |
| 14  | 1.25                   | 125                   | 300              | 6             | 70.02          | 69.18             | 51.885              | 143.51           | 40.54            | 203.05           |
| 15  | 1.00                   | 100                   | 250              | 10            | 67.8           | 67.07             | 83.83               | 53.29            | 25.09            | 97.98            |
| 16  | 0.75                   | 75                    | 300              | 10            | 75.18          | 75.95             | 56.96               | 130.72           | 36.92            | 196.49           |
| 17  | 1.25                   | 75                    | 200              | 10            | 71.01          | 70.08             | 52.56               | 85.00            | 40.02            | 143.78           |
| 18  | 1.25                   | 125                   | 300              | 6             | 74.52          | 73.76             | 92.20               | 80.76            | 34.22            | 125.67           |
| 19  | 0.75                   | 125                   | 200              | 6             | 56.37          | 55.91             | 69.89               | 63.93            | 30.10            | 108.13           |
| 20  | 0.5                    | 100                   | 250              | 8             | 68.36          | 69.23             | 69.23               | 43.02            | 37.98            | 99.99            |
| 21  | 1.25                   | 125                   | 300              | 10            | 78.14          | 79.05             | 98.81               | 75.35            | 31.93            | 163.91           |
| 22  | 1.00                   | 100                   | 250              | 4             | 68.68          | 69.21             | 69.21               | 86.07            | 37.99            | 133.55           |
| 23  | 1.00                   | 100                   | 350              | 8             | 73.66          | 73.19             | 73.19               | 81.39            | 50.29            | 149.64           |
| 24  | 1.25                   | 75                    | 300              | 6             | 73.63          | 74.34             | 55.75               | 133.55           | 56.59            | 207.82           |
| 25  | 0.75                   | 125                   | 300              | 6             | 60.7           | 59.91             | 74.8875             | 59.66            | 13.17            | 114.95           |
| 26  | 1                    | 150                   | 250              | 8             | 63.39          | 63.84             | 95.76               | 62.2             | 13.73            | 103.39           |
| 27  | 1                    | 100                   | 250              | 8             | 70.46          | 69.25             | 69.25               | 86.02            | 37.97            | 142.97           |
| 28  | 1                    | 100                   | 150              | 8             | 62.63          | 63.30             | 63.3                | 94.1             | 24.92            | 139.79           |
| 29  | 1                    | 100                   | 250              | 8             | 68.33          | 69.25             | 69.25               | 86.02            | 37.97            | 142.97           |
| 30  | 0.75                   | 75                    | 300              | 10            | 88.01          | 88.09             | 66.072              | 73.57            | 97.75            | 140.24           |

Optimized 0.75  75  300  10  88.01  88.09  66.072  73.57

9
treated and untreated BG solution, overall 30 min exposure time was allowed to *allivibiro fisheri* before measuring toxicity in terms of inhibition (%). At initial condition, the 70 ppm BG solution was highly toxic with inhibition of 93.9%. After 10 min of treatment by sono-catalytic system (US + NPs) the toxicity reduced from 93.9% to 27.42% and after 15 min the toxicity was further reduced to 12.52%. But the US + PS system has displayed much higher toxicity of 54.29% even after prolonged reaction at 15 min. This could be assigned to the sulfate toxicity due to introduction of PS. However, the US + NPs + PS system treated BG dye solution has reported minimum toxicity after 5, 10 and 15 min of reaction. Within 5 min of irradiation the toxicity has reached to 7.32% and after 15 min it was observed as only 5.13%. The miniature toxicity level in US + NPs + PS system may be attributed to the fact that the toxic

extra sulfate adsorption capability of magnesium ferrite nano-particles. This reduction of residual sulfate ions was also confirmed by the residual sulfate study. Hence, this analysis sets forth that sono-catalytic activated persulfate system (US + NPs + PS) was effective to generate less toxic effluent by breaking benzene ring or C-N bond and also adsorbing residual sulfate ions.

BG removal (%) = 133.64 – 52.77A – 0.87B + 0.06C – 3.01D + 0.54AB + 0.02AC – 3.29AD + 1.6 × 10^-5 BC – 0.011BD + 1.8 × 10^-3 CD + 12.61A^2 + 1.2 × 10^-3 B^2 – 1.01 × 10^-4C^2 + 0.58D^2

(20)

Table 2

Results of ANOVA for BG dye degradation by sono-catalytic activated persulfate system based on magnesium ferrite catalyst.

| Source variation | Sum of squares | df | Mean square | F-value | p-value | Status |
|------------------|----------------|----|-------------|---------|---------|--------|
| Model            | 1565.51        | 14 | 111.82      | 106.15  | <0.0001 | Significant |
| A-MgFeO₄ Dose    | 60.55          | 1  | 60.55       | 57.48   | <0.0001 |        |
| B-BG Dye Conc   | 431.8          | 1  | 431.80      | 409.90  | <0.0001 |        |
| C-PS dose        | 146.72         | 1  | 146.72      | 139.28  | <0.0001 |        |
| D-Time           | 522.29         | 1  | 522.29      | 495.80  | <0.0001 |        |
| AB               | 182.52         | 1  | 182.52      | 173.26  | <0.0001 |        |
| AC               | 1.55           | 1  | 1.55        | 1.47    | 0.2439  |        |
| AD               | 43.43          | 1  | 43.43       | 41.23   | <0.0001 |        |
| BC               | 0.0064         | 1  | 0.01        | 0.01    | 0.9389  |        |
| BD               | 4.86           | 1  | 4.86        | 4.62    | 0.0484  |        |
| CD               | 0.5184         | 1  | 0.52        | 0.49    | 0.4937  |        |
| D²               | 17.05          | 1  | 17.05       | 16.18   | 0.0011  |        |
| C²               | 16.14          | 1  | 16.14       | 15.32   | 0.0014  |        |
| B                | 1.75           | 1  | 1.75        | 1.67    | 0.2164  |        |
| A                | 147.9          | 1  | 147.90      | 140.39  | <0.0001 |        |
| Residual         | 15.8           | 15 | 1.05        |         |         |        |
| Lack of Fit      | 12.37          | 10 | 1.24        | 1.8     | 0.2682  | Not significant |
| Pure Error       | 3.44           | 5  | 0.6872      |         |         |        |
| Cor Total        | 1581.32        | 29 | Pred        |         |         |        |
| Quadratic summary statistics (BG removal %) | 0.99 | 0.9807 | 0.9518 | 1.03 | 1.42 | 44.3482 |

3.3. RSM based optimization of US + NPs + PS system for BG dye degradation

RSM was executed for development of model and to investigate the synchronous interface between considered input variables onto the dye degradation in US + NPs + PS system. A total of 30 experimental runs formulated by CCD was carried out and observed responses are represented in the Table 1 along with four experimental parameters (MgFeO₄ dose (g/L), initial BG dye concentration (ppm), PS dose (mg/L) and irradiation time (min)). The developed model predicted and actual experimental responses of BG dye removal are also illustrated in Table 1. The developed model predicted equation for BG dye removal (%) is as follows:

In Eq. (20), the parameter A, B, C and D are MgFeO₄ dose (g/L), initial BG dye concentration (ppm), PS dose (mg/L) and irradiation time (min), respectively.

The significance of the established RSM model on the BG dye removal efficiency was thoroughly checked by performing ANOVA [52,53]. The quadratic model summery statistics and ANOVA results are represented in Table 2. From the Table 2 it is clearly observable that with low F-value (<0.0001), high sum of squares value (1565.51) and F-value of 106.15, the quadratic model is significant and best fitted model. Generally, coefficient of variance (CV) is useful to evaluate results reproducibility and anticipated array for CV is in between 0.5% and 13.5% [54,55]. The detected CV being only 1.42% indicates high chances of reproducibility of this developed RSM model. Moreover, high correlation coefficients (R² = 0.99, Adj R² = 0.98, Pred R² = 0.95) indicate a well fitted model [39]. The Adeq. Precision (i.e. ratio between signal to noise) was obtained as 44.34 indicates that the developed model can be utilized for improved forecast of BG dye removal efficiency [56]. The liner fitting plot of predicted and (actual) experimental dye removal (%) (R² : 0.99) is shown in the Fig. 9(a). Also the variation of residuals vs. 30 experimental runs (Fig. 9(b)) shows all residuals being within ±2%, the developed model can predict more accurate response.

Thereafter, the simultaneous interaction and relationship between various independent variables (MgFeO₄ dose, initial concentration of BG dye, PS dose and irradiation time) on BG dye removal (%) was expressed by developing 3D response surface plots (Fig. 10). Fig. 10(a) shows the relation between MgFeO₄ dose and time with respect to BG dye removal (%). With the increment of MgFeO₄ dose and time the removal percentage increases, as more number of OH and SO₄ radicals were generating in the presence of increased NPs dose. In Fig. 10(b) & (d) it can be clearly visible that the higher PS dose and lower initial BG dye concentration ensures higher removal efficiency with time. This incident is caused by the availability of more quantity of sulfate radicals and less amount of BG dye molecules to degrade. In all cases, surge in sonication time enhances the dye degradation. Though, surge in sonication time will lead to greater operational cost as a result of higher power consumption. Hence, all four parameters were optimized to achieve maximum BG dye degradation efficiency to cope up the challenge regarding cost.

The RSM has predicted the optimized conditions of MgFeO₄ NPs dose of 0.75 g/L, initial concentration of BG dye of 75 ppm, PS dose of 300 mg/L and irradiation time of 10 min to achieve maximum BG dye removal efficiency of 88.01% with a desirability function value of 0.98.
The recorded validation experiment results was 89.29 ± 0.5% with respect to model anticipated response of 88.01% which evidently showcase the significance of RSM based optimization and developed model.

3.4. Regeneration of catalyst

The reusability and stability of magnesium ferrite nanoparticles was executed over six cycles under same conditions (i.e. MgFe$_2$O$_4$ NPs dose 1.0 g/L, BG dye concentration of 70 ppm, PS dose 300 mg/L and time 15 min). After each experiment, the magnetically separated catalyst was washed three times with distilled water and once with ethanol in the probe sonicator reactor. The variations of dye removal efficiency of catalyst are illustrated in Fig. 11. After 3rd cycle, the decolorization efficiency was dropped from 91.63% to 83.95%. Finally, after 6th cycle, dye removal efficiency reached 72.11% indicating long-durability and magnificent reusability of magnesium ferrite nanoparticles.

To explore the stability of the crystallite structure of the synthesized MgFe$_2$O$_4$ catalyst during the sonocatalytic degradation of BG dye, the XRD pattern of the five times reused MgFe$_2$O$_4$ catalyst was also executed (Fig. 1(a)). The comparison of the XRD pattern of the fresh and reused MgFe$_2$O$_4$ catalyst suggests that there is no significant change in the diffraction peaks of the catalyst even after dye degradation. Similar phenomenon was reported by Khataee et al. [14]. Therefore it can be
concluded that the catalyst is stable even after sonocatalytic degradation of BG dye, ensuing in high reusability of as prepared MgFe2O4 sonocatalyst. The comparison between the FTIR spectra of fresh MgFe2O4 catalyst and reused MgFe2O4 catalyst after dye degradation (Fig. 2(a)) reveals that after dye degradation there is also no significant change in the bonding configuration of the catalyst. All the significant peaks remain undisturbed, however only the intensity of the peaks have been decreased up to a certain extent. Similar results were also reported by Das et al. [57]. This study also ensures the stability of the catalyst in terms of available active surface bonds after BG dye degradation.

3.5. Treatment cost analysis

The total cost including catalyst cost, oxidant cost and energy cost against per kg of BG dye removed was determined for 30 considered experimental runs of RSM. The details breakup of catalyst cost, oxidant cost and energy cost is depicted in Table 1 which indicates that the total cost is varying between 97.98 and 245.06 $/kg BG dye removed. Among all runs the lowest cost (97.98$/kg BG removed) and highest cost (245.06$/kg BG removed) relates to BG dye removal of 67% and 81% respectively (Table 1). Even though increased sonication time corresponds with better removal performance, on the other hand it also raises the energy cost. However, cost of experimentally optimized conditions is 168.79$/kg BG removed (with respect to removal efficiency of 91%) while the RSM predicted conditions result in removal efficiency of 88.01% with moderate cost of 140.24 $/kg BG removed. Therefore, RSM predicted conditions are preferred over other options as spending 28.55 $ over only 3% increment in removal is not economically feasible (Fig. 12). In comparison with previous studies, US + NPs + PS process shows higher or comparable maximum pollutant removal rate of 6.6 mg/L/min. In a study of BG degradation by MW/ZnO system the observed dye degradation rate was 0.16 mg/L/min for dye concentration of 10 mg/L and NPs dose of 1 g/L [58].

3.6. Possible mechanism for sonocatalytic degradation of BG dye using MgFe2O4 catalyst

Under sonolytic irradiation, cavitation of bubbles generates OH radicals from H2O molecules (Eq. (16)) [1,46]. Similarly, US irradiation causes breakage of the S-O bond of PS and generates sulfate radicals (Eq. (1)) [27]. However, introduction of MgFe2O4 nanoparticles in the aforesaid system has enhanced the dye degradation performance due to activation of PS by nano-particles with a noticeable efficiency of 91.63% (Fig. 3(a)). Hence, the possible mechanism for sonocatalytic degradation of BG dye using MgFe2O4 catalyst can be explained under two different pathways i.e. ‘sonoluminescence’ and ‘hotspot’ site generations [59]. Due to ultrasonic cavitation of bubbles, energy emit in the form of light of wide wavelength range. This phenomenon is called sonoluminescence [1]. As the calculated band gap of MgFe2O4 nano-particles is 2.11 eV, the matching wavelength of emitted light can easily excite the valance electron to jump in the conduction band resulting in electron-hole pair [1; 60]. Thus the generated electron (e−) in the conduction band reacts with dissolved Oxygen (O2) and PS to form super oxide anion (O2−) and sulfate radical (SO4−) (Eq. (21), (22)) [59].
Moreover, reactive hydroxyl radicals (OH⋅) are generated from water molecules and hydroxyl anions by the holes (h+) in the conduction band [1]. In addition, holes can directly attack target pollutants, i.e., BG dye molecules for degradation (Eq. 23–25) [60].

\[
\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{OH}⋅ + \text{H}^+ \tag{23}
\]

\[
\text{h}^+ + \text{OH} \rightarrow \text{OH}⋅ \tag{24}
\]

\[
\text{h}^+ + \text{BG dye} \rightarrow \text{Intermediates + CO}_2 + \text{H}_2\text{O} \tag{25}
\]

Again, following the second pathway, sudden explosion of bubbles can effectively create ‘hotspots’ with temperature around 1000°C on the nano-particles surface. Hence, these sites PS molecules are easily decomposed to reactive sulfate radicals [58]. Simultaneously, transition metal ion present in our nano-catalyst (i.e., Fe²⁺) contributes sulfate radical by reducing the PS molecule (Eq. (26)) [28].

\[
\text{S}_2\text{O}_8^{2−} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2−} + \text{SO}_2\cdot \tag{26}
\]

Therefore, generated reactive species such as SO₄²⁻, O₂⁻, & OH causes rapid degradation to our target BG dye molecules and results in various intermediates and mineralized end products (CO₂ and H₂O) (Eq. 27–29).

\[
\text{SO}_4^{2−} + \text{BG dye} \rightarrow \text{Intermediates + CO}_2 + \text{H}_2\text{O} \tag{27}
\]

\[
\text{O}_2^{−} + \text{BG dye} \rightarrow \text{Intermediates + CO}_2 + \text{H}_2\text{O} \tag{28}
\]

\[
\text{OH}^{+} + \text{BG dye} \rightarrow \text{Intermediates + CO}_2 + \text{H}_2\text{O} \tag{29}
\]

The schematic diagram of possible mechanism for sonocatalytic degradation of BG dye using MgFe₂O₄ catalyst is shown in Fig. 13.

3.7. Comparison with other studies

To judge the overall performance of the proposed US + NPs + PS process, the obtained result was compared with previous studies which is summarized in the Table 3. Based on the BG dye removal (%) and removal rate (mg/L/time), the evaluation of the experiments was accomplished. Although, the BG dye removal efficiency of 91.63% of this study is almost comparable with previous studies, but those studies dealt with a lower initial concentrations of dye and higher irradiation time. Hence, the BG dye removal rate (mg/L/time) reported in this study which is 4.28 mg/L/min is much superior to the previous investigations.

4. Conclusions

In this study, magnesium ferrite nanoparticles have displayed the promising role in activation of persulfate radicals for effective degradation of BG dye molecule in presence of ultrasound irradiation. BG dye removal of 91.63% was achieved within only 15 min for high initial BG dye concentration of 70 ppm. The removal rate of 4.276 mg/L/min was also surpassed other pervious investigation available in the literature. Under CCD, the RSM optimization was performed and the developed quadratic model predicted optimized BG dye removal of 89.29% under conditions: MgFe₂O₄ NPs dose 0.75 g/L, initial concentration of BG dye 75 ppm, PS dose 300 mg/L and irradiation time 10 min. Moreover, COD removal of 90.31% was achieved after treatment. The proposed degradation pathways showed lower M/Z containing intermediates and inhibition toxicity of those has been reached a lower value (5.13%) from a very high value (93.9%). The toxicity of sulfate generated from persulfate has also been nullified which might be attributed to the high adoption affinity of magnesium ferrite nanoparticles towards sulfate ions. Up to six cycles of reusability for magnetically separable nanoparticles indicates overall cost reduction of the proposed process. Further, the RSM optimized reaction conditions revealed optimum cost as 140.24 $/kg BG removed which in turn shows the economic feasibility of this BG dye removal process.
Table 3

| Dye degradation method | Operational conditions | Dye removal (%) | Removal rate (mg/L/min) | Reference |
|------------------------|------------------------|-----------------|--------------------------|-----------|
| Microwave - photo-catalysis | Photo-Catalyst: ZnO, Dose of catalyst: 1.0 g/L | 94.30 | 0.16 [61] |
| Photo-catalysis | Photo-Catalyst: TiO<sub>2</sub>, Catalyst Dose: 0.1 g/L | 95.50 | 0.10 [50] |
| Microwave-Sono-catalysis | Initial Dye Conc: 20 ppm | 93.20 | 0.31 [57] |
| Photo-Catalysis | Photo-Catalyst: CuO, MgO, TiO<sub>2</sub>, Catalyst Dose: 0.75 g/L | 91.30 | 0.04 [62] |
| UV-Oxidation | Oxidants: S<sub>2</sub>O<sub>8</sub>, H<sub>2</sub>O<sub>2</sub>, HSO<sub>4</sub> | 63.10 | 0.50 [6] |
| Photo-Catalysis | Photo-Catalyst: Fe<sub>2</sub>O<sub>3</sub>, CaS, ZnS | 92.93 | 0.31 [63] |
| Sono-Catalytic Activated Persulfate Oxidation | Sono-Catalyst: MgFe<sub>2</sub>O<sub>4</sub>, Catalyst Dose: 1 g/L | 91.63 | 6.28 This Study |

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors thank the Council of Scientific & Industrial Research (CSIR), Government of India (Grant No. 22/0744/17/ EMR-II) to provide funding for this research. The authors also wish to thank IIT Madras (Grant number: CIE/14-15/832/NFG/SMAT) for their funding to purchase biotoxicity analyzer.

References

[1] A. Khataee, S. Saadi, M. Safapour, S.W. Joo, Sonocatalytic performance of Er-doped ZnO for degradation of a textile dye, Ultrason. Sonochem. 27 (2015) 379–388.
[2] V. Katharinas, J. Kamedo, S.Y. Lau, Efficiency of various recent wastewater dye removal methods: a review, J. Environ. Chem. Eng. 6 (4) (2018) 4676–4677.
[3] B.K. Nandi, A. Govimani, M.K. Pursuit, Adsorption characteristics of brilliant green dye on kaolin, J. Hazard. Mater. 1 (2009) 387–395.
[4] L. Zhang, X. Liu, X. Guo, M. Su, T. Xu, X. Song, Investigation on the degradation of brilliant green induced oxidation by NFeO<sub>4</sub> under microwave irradiation, Chem. Eng. J. 3 (2011) 737–742.
[5] N.H. Singh, K. Kero, A. Debnath, B. Saha, Enhanced adsorption performance of a novel Fe-Mn-Zr metal oxide nanocomposite adsorbent for anionic dyes from binary dye mix: Response surface optimization and neural network modeling, Appl. Organomet. Chem. 32 (3) (2018) e4165, https://doi.org/10.1002/aoc.v32.310.1002/aoc:4165.
[6] F. Rehman, M. Sayed, J.A. Khan, N.S. Shah, H.M. Khan, D.D. Dionsioyi, Oxidative removal of brilliant green by UV/S<sub>2</sub>O<sub>8</sub>, UV/H<sub>2</sub>O<sub>2</sub>, and UV/H<sub>2</sub>O<sub>2</sub> processes in aqueous media: a comparative study, J. Hazard. Mater. 357 (2018) 506–514.
[7] B.K. Nandi, S. Patel, Removal of brilliant green from aqueous solution by electrocoagulation using aluminum electrodes: experimental, kinetics, and modeling, Sep. Sci. Technol. 49 (4) (2014) 601–612.
[8] Y. Zheng, G. Yao, Q. Cheng, S. Yu, M. Liu, C. Gao, Positively charged thin-film composite hollow fiber nanofiltration membrane for the removal of cationic dyes through submerged filtration, Desalination. 328 (2013) 42–50.
[9] C.V. Rao, A.S. Giri, V.V. Goud, A.K. Golder, Studies on pH-dependent color variation and decomposition mechanism of Brilliant Green dye in Fenton reaction, Int. J. Ind. Chem. 7 (1) (2016) 71–80.
[10] B.K. Tripathy, S. Kumar, M. Kumar, A. Debnath, Microwave induced catalytic treatment of brilliant green dye with carbon doped zinc oxide nanomaterials: Central composite design, toxicity assessment and cost analysis, Environ. Nanotechnol. Monit. Manag. (2020) 1–15.
[11] B.K. Tripathy, M. Kumar, Suitability of microwave and microwave-coupled systems for landfill leachate treatment: An overview, J. Environ. Eng. 5 (6) (2017) 6165–6178, https://doi.org/10.1061/jjee.2017.11.039.
[12] M. Antonopoulou, E. Evgenidou, D. Lambropoulou, I. Konstantinou, A review on advanced oxidation processes for the removal of taste and odor compounds from aqueous media, Water Res. 53 (2014) 215–234.
[13] N. Shimizu, C. Ogino, M.P. Dadidjour, T. Murata, Sonocatalytic degradation of methylene blue with TiO<sub>2</sub> pellets in water, Ultrason. Sonochem. 2 (2007) 184–190.
[14] A. Khataee, S.A. Osokou, L. Samaei, ZnFe-Cl nanolayered double hydroxide as a novel catalyst for sonocatalytic degradation of an organic dye, Ultrason. Sonochem. 40 (2018) 703–713.
[15] A. Hamadani, Y. AJ, G. Lee, S. Kim, C.M. Park, M. Jang, N. Her, J. Han, D. Kim, Y. Yoon, Sonocatalytic degradation of carbamazepine and diclofenac in the presence of graphene oxides in aqueous solution, Chemosphere. 205 (2018) 719–727.
[16] Y.L. Pang, A.Z. Abdullah, S. Bhata, Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater, Desalination. 3 (2011) 1–14.
[17] A. Khataee, R. Kayan, P. Gholami, D. Kalders, S. Akay, Sonocatalytic degradation of an anthraquinone dye using TiO<sub>2</sub>biochar nanocomposite, Ultrason. Sonochem. 39 (2017) 120–128.
[18] K.H. Chu, Y.A.A. Hamadani, C.M. Park, G. Lee, M. Jang, A. Jang, N. Her, A. Son, Y. Yoon, Ultrasonic treatment of endocrine disrupting compounds, pharmaceuticals, and personal care products in water: a review, Chem. Eng. J. 327 (2017) 629–647.
[19] X. Liu, S. An, W. Shi, Q. Yang, L. Zhang, Microwave-induced catalytic oxidation of malachite green under magnetic Cu-ferrites: new insight into the degradation mechanism and pathway, J. Mol. Catal. A: Chem. 395 (2014) 243–250.
[20] D.H.K. Reddy, Y.S. Yun, Spinel ferrite magnetic adsorbents: alternative future materials for water purification? Coord. Chem. Rev. 315 (2016) 90–111.
[21] R. Dom, R. Subbari, K. Radha, P.H. Bone, Synthesis of solar active nanocrystalline ferrite, MFeO<sub>4</sub> (M = Ca, Zn, Mg) photocatalyst by microwave irradiation, Solid State Commun. 6 (2011) 470–473.
[22] K. Tendka, M. Kogure, Y.J. Shan, Photocatalytic degradation of acetic acid on spinel ferrites MFeO<sub>4</sub> (M = Mn, Zn, and Cd), Catal. Commun. 48 (2014) 11–14.
[23] S.Y. Oh, H.W. Kim, J.M. Park, H.S. Park, C. Yoon, Oxidation of polynvinyl alcohol by persulfate activated with heat, Fe<sup>2+</sup>, and zero-valent iron, J. Hazard. Mater. 168 (1) (2009) 346–351.
[24] J. Lu, X. Wei, Y. Chang, S. Tian, Y. Xiong, Role of Mg in mesoporous MgFe<sub>2</sub>O<sub>4</sub> for degradation of a textile dye, Ultrason. Sonochem. 27 (2015) 395–403.
[25] H. Zhou, L. Hu, J. Han, R. Yang, X. Yu, H. Li, J. Chen, L. Wang, X. Lu, Microwave-enhanced catalytic degradation of p-nitrophenol in soil using MgFeO<sub>4</sub>, Chem. Eng. J. 284 (2016) 54–60.
[26] L. Hou, H. Zhang, X. Xue, Ultrasound enhanced heterogenous activation of peroxysulfate by magnetic catalyst for the degradation of tetracycline in water, Sep. Purif. Technol. 84 (2012) 147–152.
[27] X. Wang, L. Wang, J. Li, J. Qiu, C. Cai, H. Zhang, Degradation of Acid Orange 7 by persulfate activated with zero valent iron in the presence of ultrasound irradiation, Sep. Purif. Technol. 122 (2014) 41–46.
[28] M. Zhang, X. Chen, H. Zhou, M. Muruganathan, Y. Zhang, Degradation of p-nitrophenol by heat and metal ions co-activated persulfate, Chem. Eng. J. 264 (2015) 39–47.
