Impregnated chitin biopolymer with magnetic nanoparticles to immobilize dye from aqueous media as a simple, rapid and efficient composite photocatalyst

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Abstract
In the sight of the ever-increasing significance of green-based iron nanoparticles especially in wastewater treatment applications is a compelling reason for their use in a waste prevention opportunity, safer environment and benign precursor materials become the vital considerations. Hence, in the current investigation, an efficient co-precipitation technique was applied to prepare highly active chitosan-coated magnetic iron oxide that is applied for wastewater remediation. In the current investigation, chitosan coupled with magnetite nanoparticles namely CS-M was attained by coupling chitosan (CS) with magnetite nanoparticles via simple co-precipitation in different weight proportions and the attained samples labeled as CS-M-(2:1), CS-M-(3:1) and CS-M-(1:2). The structure, morphology and characteristics of the prepared samples were characterized using X-ray diffraction spectroscopy and transmission electron microscopy (TEM). The catalytic oxidation activity of the prepared samples was investigated to eliminate Basic Blue 9 (BB9) dye from aqueous effluent as simulated textile polluted stream. The experimental data exposed almost BB9 dye emanation. The system parameters revealed the maximal BB9 oxidation (99%) was attained within 2 h of irradiance time. Box–Behnken design factorial design based on response surface methodology was applied to optimize the Fenton’s system (CS-M-(2:1)/H2O2) parameters to maximize the efficiency 2.4 and 767 mg/L of CS-M and H2O2, respectively, at pH 7.0. The experimental data exposed that CS-M-(2:1) is signified as the optimal catalyst mixture. The kinetic data verify the oxidation system follows the second-order reaction kinetic model. Further, thermodynamic variables predicted that the reaction is endothermic and non-spontaneous in nature. Hence, the catalyst could be environmental benign and the evaluation introduces the role of engineers and chemists in a world for a sustainable material use.

Keywords Dye wastewater · Magnetic chitosan · Photocatalyst · Nanotechnology · Kinetics

Introduction
Presently, the most challenge issue that facing our societies is water contamination and pollution, which needs reasonable solution. As an indispensable element for the sustainable modern communities, using environmentally benign materials plays a significant role in global awareness and economics. Noteworthy to mention, water is an exceptionally substance that persist on earth through the ecosystem to preserve the life-quality (Al et al. 2008; Ashour and Tony 2020). Although 71% of water is covered on the earth surface, due to the salty taste, merely 2.5% of freshwater is available. However, only 0.27% is clean water that is ready for use since the residual amounts is scattered in the underground, frozen areas and marshland areas (Thabet et al. 2022b). Recently, in the industrialized modern societies and the quick hike of human population, the result is depletion in water resources. Additionally, the scarce freshwater is not ample to meet up the necessities of massive population (Golka et al. 2004).

Among the various wastewater pollutants types, dyes are signified as key treacherous substances that detected in the industrial sewages since they used in several applications

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such as textile manufacturing, foodstuffs, paper printing, and leather industries (Ioannou and Fatta-Kassinos 2013; Tony and Lin 2020b). Azo dyes between the numerous dye species could only possess an inadequate degradability or may be non-degradable in the atmospheric conditions, besides their water solubility and toxicity (Thabet et al. 2020; Tony and Mansour 2020a). Moreover, some types of these azo dyes may be decomposed in the anaerobic environments into carcinogenic substances. Thus, they might possess the property to resist the oxidant or may be also sunlight. Therefore, the selection of their proper elimination technology is a problematic. From this regard, urgent searching for new technologies for such dyes elimination from aqueous streams is required (Tony and Mansour 2020b; Zubir et al. 2014).

In order to minimize freshwater consumption with the industrialized modern societies, wastewater reclamation and management is suggested to effectively improve water conservation in various ways. Physical, chemical and biological wastewater treatment opportunities are signified a viable wastewater treatment opportunity (Thabet et al. 2022a; Tony and Lin 2021; Yang et al. 2021). Although chemical treatments are a viable option for wastewater treatments among other suggested treatments, it incurs high operational costs due to the large cots of the coagulants, as well as the disposal of massive sludges after treatments which needs further treatments. Under such circumstances, the idea of using environmentally friendly, recoverable, recyclable and reusable material may be favorable. Many possible attempts have been recorded in the literature for using conservative materials in treatments (Laib et al. 2021). Among the possible routes suggested in the literature, using nanocomposite especially environmentally benign material has been gained immense attention in the photo-oxidation ability since of a variety of toxicity caused by the other materials. So, searching for attractive materials is an attractive research technology (Pourali et al. 2021; Thabet et al. 2022b; Tony and Lin 2020a). Choosing the appropriate material that possesses unique and attractive properties such as the catalytic activity, optical activity and also possesses chemical selectivity has a great attention in wastewater treatment applications. Biopolymers are suitable candidates that exhibit extended stability and possess a flexibility of blending or cross-linking with other materials (Ahmadi et al. 2016; Tony 2021a). Thus, they are a superior host compounds to prepare a various composite photocatalytic materials that plays a prominent role in eliminating toxic dyes from aqueous effluents. Moreover, metal augmentation with biopolymers displays a synchronous effect in enhancing the photocatalytic and catalytic oxidation activity (Tony and Eltabey 2022; Yang et al. 2021).

Advanced oxidation processes, AOPs, have been emerged and gained the researchers' attention for their in situ remediation. Thus, AOPs are viable option due to the mineralization of a wide range of pollutants because of the presence of highly selective oxidative hydroxyl radicals, -OH species. Commonly, the attractive use of ultraviolet illumination (UV) through AOPs applications is promising tool since it improves the treatment efficiency capabilities. Fenton-based AOPs are a promising process for their high efficiency. Such system is associated with the initiation of the active reaction intermediates by interacting H₂O₂ and Fe²⁺ that is so-called classical Fenton's or Fenton-Like reaction oxidation (Zhang et al. 2018). Although, some limitations are related to such classical reaction, i.e., working at acidic pH conditions and iron sludge after the catalytic cycle that might be separated still restricts the process practical applications (Shaheen and Emam 2018; Tony 2021b). Hence, searching for an advanced iron source to overcome such limitations is still gaining researchers' interest.

Chitosan, chitin biopolymer is characterized by its high mechanical strength, non-toxic material, cost efficient, high water permeability besides the successful ability to chemical modification through the addition of metal oxides to be a nanocomposites. Chitosan is widely applied in wastewater treatment as adsorbent material since it possesses hydroxyl and amino functional groups. Such groups might protonated in acidic aqueous media, and the result is a massive electrostatic attraction for anionic molecules. However, according to the authors' knowledge it is not applied so far as a photocatalytic material. Moreover, although it is efficient in water remediation, chitosan separation from reclaimed aqueous media is still an obstacle that limiting its real industrial applications.

Recently, with the advanced environmental remediation systems, iron oxides nanoparticles are encouraged due to their small size and high surface area (Tahoun et al. 2022; Thabet et al. 2022a).

However, for their better separation from aqueous media after usage, magnetic iron oxides application with polymers as a support system is preferred. Among iron oxides with magnetic properties, magnetite stands out since it possesses high surface area, chemical and temperature stability, great oxidation ability and superparamagnetic properties. Such composite could be synthesized via simple co-precipitation route to produce high yield and environmentally non-toxic products.

To the best of the authors' knowledge, according to the articles cited, there is a shortage in the research literature cited on modulating chitosan/magnetite composite material as a source of Fenton-Like reaction. Herein, the present investigation is based on altering the source of Fenton reaction and replace iron system with chitosan/magnetite composite (CS-M) as a source of Fenton oxidation to be one of AOPs. The system is investigated for treating Basic Blue 9 (BB9) as a source of azo dye contaminated wastewater that simulated textile effluents polluted water. The influence of...
the operating parameters, i.e., catalyst and H₂O₂ reagents loadings, pH of the aqueous media, dye concentration, and wastewater temperature on the oxidation reaction is assessed.

**Experimental section**

**Synthesis of nanostructures photocatalysts**

Magnetic chitosan, chitosan/magnetite nanoparticles composite (CS-M) were synthesized via simple co-precipitation route followed by hydrothermal treatment (Swayampakula et al. 2009). Initially, one wt% of chitosan is dissolved in drops of CH₃COOH solution prior it is dissolved in 50 mL of distilled water through magnetic stirring for 15 min. Fe²⁺ and Fe³⁺ in 1:2 molar ratio, i.e., FeSO₄·7H₂O (0.829 g) and FeCl₃ (1.607 g) each was dissolved in 50 mL distilled water. Thereafter, the prepared three solutions, i.e., chitosan, Fe²⁺ and Fe³⁺, were mixed together to achieve a mixture of 2:1 of chitosan/magnetite, while a solution of NaOH is added to maintain the pH to 10. Then, the mixture was subjected for heating for 45 min to 90 °C ± 1 °C. The precipitate was then washed with distilled water until pH 7.0 is reached prior to drying in a vacuum oven at 70 °C, and the attained sample is labeled as CS-M (2:1). Furthermore, to obtain chitosan/magnetite nanoparticles composite with different mass ratios different proportions from the precursors were prepared at the same procedure to attain the samples of CS-M (3:1) and CS-M (1:2).

**Wastewater**

Azo dye namely Basic Blue 9, BB9, is supplied by Sigma-Aldrich and is used as a source of synthetic textile dye wastewater aqueous environment. The dye powder was used as received with no further treatment or purification. BB9 dye is dark blue thiazine dye. Primarily, a stock solution of 1000-ppm is prepared at room temperature, and thereafter, a successive dilution is done to attain the desired dye loadings as required.

**Methodology and analytical determination**

100 mL of BB9 dye-containing aqueous effluent is poured into a glass vessel to prepare the dye for catalytic oxidation for dye loading elimination. The initial pH of the effluent is adjusted, when needed, to the required values via diluted H₂SO₄ (1:9) and/or 1 M NaOH solutions using digital pH meter (AD1030, Adwa instrument, Hungary). Afterward, CS-M material is added at a definite amounts and then, the reaction is initiated using hydrogen peroxide (30% 30% w/v). Then, the sample is subjected to UV illumination which irradiated using ultraviolet lamp of 15 W, 230 V/50 Hz, with 253.7 nm wavelength to initiate the oxidation reaction. Consequently, the samples were withdrawn periodically after selected time intervals for spectrophotometric analysis to inspect the remaining concentration after they are filtered, to remove any remaining catalyst, using a micro-filter. The graphical scheme of representation of experimental set-up and reaction steps is displayed in Fig. 1.

**Factorial design**

Box–Behnken design model of experiments based on Response Surface Methodological analysis (RSM) is used to optimize the optimal operating conditions. The most effective operating factors are optimized using such model. Three factors run by the software SAS version (SAS 1990) was used to locate the optimum values of the selected experimental parameters according to preliminary results of experiments. The selected parameters are H₂O₂ and CS-M catalyst concentrations and pH value. Then, the experimental responses were attained from checking the process parameters on the oxidation efficiency. Thus, coded and original values of the process variables used in the matrix designed are displayed in Table 1. The full experimental matrix is designed according to SAS software, and the 15-run experiments are designed according to Table 2. Furthermore, to avoid the experimental errors, the experiments were accomplished in random order and all of them were conducted in duplicates. Then, the second-order polynomial quadratic model for the oxidation system is attained according to Eq. (1). Additionally, to assure the model significance, the statistical analysis using analysis of variance (ANOVA) was performed via SAS software and further, Mathematica software (V 5.2) is applied to locate the numerical values of the optimized variable and responses.

\[ \gamma(\%) = \beta_0 + \sum \beta_i \varepsilon_i + \sum \beta_{ij} \varepsilon_i \varepsilon_j \]  

**Results and discussions**

**Characterization of the prepared nanomaterials**

**XRD analysis**

X-ray diffraction (XRD) pattern using a Bruker–Nonius Kappa CCD diffractometer equipped with CuKα radiation (λ = 1.5406 Å) with 20 ranging from 10 to 80° was used to investigate the XRD pattern of chitosan-magnetite composite materials. The data shown in Fig. 2 exposed the main phases of the chitosan and iron oxide (Fe₃O₄) are attained in the three composite, i.e., CS-M-(2–1), CS-M-(3–1) and CS-M-(1–2). The diffraction peaks of magnetic
nanoparticles which can be indexed to \( \theta \) of 18.30, 30.05, 35.49, 43.22, 53.63, 57.06, 62.48 and 74.24° that correspond to the planes [(111), (220), (311), (400), (422), (511), (440), (533)], respectively, such planes and relative intensities of all diffraction peaks are well corresponding to magnetite. According to the graphs, Fe\(_3\)O\(_4\) phase is of highly crystalline nature. Further, magnetite nanoparticles have been coated by amorphous chitosan, which does not result in phase change of Fe\(_3\)O\(_4\). Also, peak broadening is indicating small size of nanoparticles.

To investigate the morphology of chitosan/magnetite nanoparticles, Transmission Electron Microscope (TEM) analysis has been done (type Tecnai G20, FEI). Figure 3 displays the TEM micrograph of chitosan augmented iron oxide nanoparticles composite materials. The TEM analysis of the products provided information on the size and morphology of the nanoparticles. It can be seen from Fig. 3 that the magnetic particles have a spherical shape with a mean diameter of about 25 nm. The dark dense areas signify the crystalline Fe\(_3\)O\(_4\), while the bright ones surrounding the iron particles are assigned for amorphous chitosan (CS) material. However, some particles are aggregated together due to the iron oxide dipole/dipole attraction force. To add up, the amount of spherical particles of magnetite appeared differs in the three composites Fig. 3A–C according to the ratio of chitosan in the sample.

Furthermore, the particle size distribution was examined using the digital TEM images that were analyzed using the, IMAGEJ 1.48 V program. CS-M composite

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**Table 1**: Boundaries of Box–Behnken design, natural and coded experimental domain with their spacing of levels

| Experimental variable | Symbols | Range and levels |
|-----------------------|---------|------------------|
| \( \varepsilon_1 \) H\(_2\)O\(_2\) (mg/L) | \( \zeta_1 \) | 700 800 900 |
| \( \varepsilon_2 \) CS-M(2:1) (mg/L) | \( \zeta_2 \) | 1.0 2.0 3.0 |
| \( \varepsilon_3 \) pH | \( \zeta_3 \) | 7.0 8.0 9.0 |

\( \varepsilon_i = (\varepsilon_i - 800)/100 \)
\( \zeta_i = (\varepsilon_i - 2.0)/1.0 \)

*Coded levels \( \zeta_1 = (\varepsilon_1 - 0)/100 \), \( \zeta_2 = (\varepsilon_2 - 2.0)/1.0 \)
The particle size distribution of CS-M-(1–2) compos-ite is ranged from 10 to 40 nm, CS-M-(2–1) is in the range of 10–20 nm, and for CS-M-(3–1) is in the range of 10–40 nm. This signifies a reasonable size to offer a high surface area of the CS-M composite materials’ particles to be an efficient photocatalyst for the pollutant elimination through oxidation.

**Application of CS-M composite in BB 9 wastewater oxidation**

Comparison of various oxidation systems

Effect of reaction time on various oxidation systems namely H2O2/UV, CS-M/UV, photo-Fenton (CS-M/H2O2/UV) and dark-Fenton (CS-M/H2O2) is investigated to test the experimental condition for further research. The efficacy of such techniques was assessed in the terms of BB9 dye color removal, and the data are displayed in Fig. 4A. The results compare the BB9 oxidation using different systems at room temperature and pH 3.0. It is clear from the results that in the solo H2O2 oxidation system results in only 50% removal within 80 min of reaction time and the solo catalyst (CS-M/UV) system attains 7% removal (60 min). But, 82% for the photo-Fenton (CS-M/H2O2/UV) system within 170 min and 21% for the dark-Fenton (CS-M/H2O2) system during 60 min of reaction time are achieved. However, it is noteworthy to mention that after 10 min of illumination time the CS-M/H2O2/UV system achieving a higher initial removal compared to the other systems. So, after 10-min of reaction time, 19% dye removal is attained for CS-M/H2O2/UV system in comparison with only 4.8% and 7.5% for CS-M/UV and H2O2/UV, respectively. However, with time prolonging, the BB9 dye removal slowed down and the efficacy became stabilized. Interestingly, such results confirming the role of Fenton’s treatment are related to the ·OH radicals generation that associated with the rapid initial stage of oxidation. The oxidation occurred utilizing the activation of H2O2 with Fe2+/3+ salt (Li et al. 2018a). However, with the
exceeding of reaction time, a decline in the oxidation rate is attained that corresponding to the reduction in the \( \text{H}_2\text{O}_2 \) concentration, which is related to the hydroxyl radicals formation. The result is inhibition in the reaction rate rather than increasing the oxidation rate. Although, hydrogen peroxide is consumed after the initial reaction period, a complex reaction occurred and such reaction producing further radicals that is so-called hydroperoxyl radicals (\( \text{HO}_2 \)). But, such \( \text{HO}_2 \) radical possesses a low oxidation speciation rather than the hydroxyl radical. Thus, BB9 oxidation rate is reduced with
the reaction exceeds. Scattered results (Guan et al. 2005; Li et al. 2018a; Tony 2022a) have displayed the rapid initial reaction time due to the immediate formation of \( \cdot \mathrm{OH} \) radicals. Moreover, the less oxidation tendency of the dark reaction test is related to the absence of the UV illumination, which enhances the oxidation radiation through the production of more \( \cdot \mathrm{OH} \) radicals’ species. It is noteworthy to mention that such catalyst is easily recoverable since it is a magnetic catalyst that possesses the advances of recoverable, recyclable and reusable as a sustainable catalyst.

Figure 4B displays various composite CS-M-(2:1), CS-M-(3:1) and CS-M-(1:2) use in BB9 elimination. The time-profile of BB9 oxidation using various chitosan/magnetite-based Fenton composite mixture was studied at room temperature, and the data displayed in Fig. 4B revealed that the highest oxidation yield is associated with the CS-M-(2:1) system. The majority of the dye is oxidized in the initial 30 min of reaction time 93% using CS-M-(2:1) Fenton system compared to 85 and 88% for CS-M-(1:2) and CS-M-(3:1), respectively. Whereas the final removal rate reached to 95% for CS-M-(2:1) and CS-M-(3:1) Fenton systems and 94% for CS-M-(1:2) Fenton-based system. This could be illustrated by composition ratio of cross-linker that plays a significant role in affecting physical properties and surface morphology of chitosan-Fe\(_3\)O\(_4\) nanoparticles composite materials, thus showing a different behavior in treatment. Also, the composition ratio of chitosan and Fe\(_3\)O\(_4\) influenced the nanoparticles particles characteristic (Clark et al. 2016; Tony and Mansour 2019; Wulandari et al. 2018).

**Effect of pollutant loading**

According the industrial regard and practical point of view, it is essential to analyze and study different aqueous streams concentrations since it is also varied in the industrial discharge (Tony 2020). The initial BB9 dye load in aqueous effect on the dye elimination efficiency by chitosan/magnetite Fenton oxidation is displayed in Fig. 5. The initial H\(_2\)O\(_2\) concentration was adjusted to 800 mg/L, and the CS-M-(2–1) catalyst loading is 2 mg/L at pH 6.0 and the catalytic oxidation in terms of dye removal efficiency undertaken for the dye ranging from 5 to 40 mg/L. Figure 5 illustrates the effect of reaction time on the profile of various BB9 dye concentrations. Whereas, the initial period of reaction is signified with the same rate of rapid oxidation for all BB9 dye concentrations treated. However, examination of Fig. 5 illustrates that the oxidation rate declined with increasing BB9 dye concentration. The removal efficiencies are 99, 99, 90 and 43% for 5, 10, 20 and 40 ppm BB9 dye loading in the aqueous stream, respectively. Moreover, more irradiance time is required to attain such dye elimination with increasing the dye loads, and the reaction time is increased from 110 to 160 min. This could be attributed by at higher

![Fig. 5 Effect of various BB9 dye loading in CS-M-based Fenton system](image)

**Effect of chitosan/magnetite-based Fenton reaction parameters**

**Effect of chitosan/magnetite dosing** \( \cdot \mathrm{OH} \) radical speciation that is well known as the strong oxidative radical is mainly the main responsible of oxidizing pollutant in the Fenton’s reaction, while such radicals’ generation is mainly dependent on various Fenton’s parameters. According to the previous investigations of scattered authors (Hilder et al. 2012; Muthukannan et al. 2015; Saad et al. 2021; Tony 2021a; Tony and Lin 2020a), Fenton’s reaction yield is highly determinate according to the reagent doses and the medium pH. Hence, studying such parameters is crucial.

Metal conversion in the Fenton’s reaction is critically vital for the oxidation system. Therefore, in order to confirm the job of the chitosan and magnetite catalysts in that such CS-M-(2–1) composite in such modified Fenton’s reaction, various doses of CS-M composite ranged from (1 to 40 mg/L) as a catalyst source were checked to investigate its role in the \( \cdot \mathrm{OH} \) radical production. The reaction is conducted, while keeping all other system parameters constant (pH 3.0 and H\(_2\)O\(_2\) 400 mg/L). As depicted in Fig. 6A, BB9 removal is enhanced to reach to 95% with elevating CS-M-(2–1) dose concentration up to 2 g/L and then, the BB9 dye elimination declined with further catalyst elevation.
This could be illustrated by the hydroxyl radicals that are trapped by CS-M catalyst ions in excess (Tony and Mansour 2019). Interestingly, high doses of CS-M catalyst result in adverse effects of excess magnetite and chitosan doses on the solution as the excess catalyst specially iron species in the aqueous media decrees the reactive species of ˙OH radicals’ performance as given in Eq. (2, 3). Therefore, 2 mg/L is the signified as the catalyst concentration required for BB9 dye oxidation. According to the data cited by Cetinkaya et al. (2018), similar trend was recorded in treating wastewater using such Fenton technique.

\[
\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (2)
\]

\[
\text{Fe}^{2+} + \text{OH}_2 \rightarrow \text{Fe}^{3+} + \text{OH}_2^- \quad (3)
\]

Previous investigators recorded that variation of the hydrogen peroxide doses might affect significantly on the radicals’ generation and thus on the Fenton’s oxidation yield. From this regard, \(\text{H}_2\text{O}_2\) dosage varied from 100 to 1000 mg/L was selected to examine the effect of such reagent on the current studied system (at 10 mg/L of CS-M-(2–1) catalyst and pH of 3.0) and the results are displayed in Fig. 6B. The data in the Fig. 6B revealed that the BB9 oxidation is enhanced from 51 to 93% with the increase in hydrogen peroxide reagent from 100 to 800 mg/L, respectively. Although, the further increase in such reagent is resulting in a decline in oxidation system. Such data are in accordance with phenomena of the high concentration of hydrogen peroxide is predictable to attain a high yield of ˙OH radicals. Thus, an increment in BB9 oxidation is expected. However, in contrary the excess hydrogen peroxide reagent exploits as the ˙OH radicals’ hamper rather than a generator. The result in such case of excess \(\text{H}_2\text{O}_2\) rather than the optimal, \(\text{HO}_2\) radical is produced, which is less active than the highly horsepower ˙OH reactive free species. This results in a negligible contribution in the oxidation reaction. Moreover, \(\text{HO}_2\) radicals react with the remaining ˙OH radicals (according to Eq. (5)) that result in further hindering the reaction rate (Amiri et al. 2017).

\[
\text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (4)
\]

\[
\text{HO}_2^- + \text{HO}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (5)
\]

Not only hydrogen peroxide and CS-M doses affect the Fenton’s system, but also initial aqueous solution pH. Traditionally, Fenton reaction is signified as a strong dependent pH system. To investigate the optimal system pH, the initial pH of the aqueous medium is evaluated by changing the wastewater pH from 2.0 to 6.0 using the same doses of CS-M-(2–1) of 2 mg/L and \(\text{H}_2\text{O}_2\) 800 mg/L. Examination of the data displayed in Fig. 6C revealed that at the initial time period decreasing the pH to the acidic range from the original wastewater’s pH (6.0) consequences to higher BB9 dye elimination. However, with the prolonging time of irradiance, the higher reaction yield is attained to the aqueous media of pH 6.0 (reached to 99% within almost 2 h of reaction time). Although several authors recommended the acidic pH for Fenton’s oxidation, the current new system
CS-M/H$_2$O$_2$/UV could work at various pH range with high yield reached to almost complete dye oxidation. However, it is noteworthy to mention that using pH in acidic range (2.0) shortening the reaction time. This could be illustrated by when pH dropped beyond 3.0, H$_3$O$_2^+$ might be formed; hence, this leads to an enhancement and improvement stability of hydrogen peroxide, whereas the hydroxyl radicals had a strong scavenging effect by H$^+$. In contrary, when the pH exceeded 3.0, iron is hydrolyzed and the hydroxyl radical is formed meanwhile FeOOH is precipitated from the solution. Thus, further experiments are conducted at more than acidic pH (El-Desoky et al. 2010).

**RSM optimization strategy** From the preliminarily investigation data of single-variable tests, the selected most intensive variables effect on the Fenton system, namely, H$_2$O$_2$ concentration, CS-M dose and pH. Their levels were selected and determined. Then, the design of the response values was established. The optimization goal is to maximize BB9 removal efficiency as response values using the constraints explored in Table 1. Box–Behnken design optimization tool was applied for optimization, and the total 15 groups experimental design is tabulated in Table 2. Subsequently, after the experiments were conducted, the detailed test scheme is concluded in Table 2, which reveals the results of the corresponding responses. Then, polynomial model coefficients were processed by the regression equation in terms of coded variables for BB9 oxidation efficacy as stated as the quadratic model Eq. (6).

\[
f(\%) = 69.06 - 0.71\zeta_1 + 0.93875\zeta_2 + 2.18\zeta_3 \\
+ 9.82\zeta_1^2 - 0.43\zeta_1\zeta_2 + 0.76\zeta_1\zeta_3 + 12.31\zeta_2^2 \\
- 0.03\zeta_2\zeta_3 + 14.27\zeta_3^2 \tag{6}
\]

Figure 7A displays the plot that comparing the data of the predicted response attained via the regression model and experimental data accessed experimentally. The regression coefficient value of the residual showed the experimental
data that well presented the quadratic model applied. The plot exposes just few deviations from normal representing well fitness of the subjected model.

Analysis of variance, ANOVA test for BB9 response, is commonly crucial applied to check the model adequacy. In order to investigate, the applied model fitness, ANOVA, is one of the primary numerical techniques to verify the model. ANOVA test is investigated, and the data are listed in Table 3. A t test is used to examine all the model terms, specifically called sum of squares (SS), mean squares (MS), estimated coefficient, standard error, and the corresponding $F$ value and the portability ($p$ values). In such study, the experimental results were suited to polynomial equation. $F$ tests value is applied to check the suitability of the applied model. Also, lack of fit designates the data variation over the suggested model (Adesina et al. 2019; Setyono and Valiyaveettil 2014; Tony 2021a; Yin et al. 2020). Hence, when the model exhibitions lack of fit, it might not be used to evaluate the model response. As given in Table 3, the lack of fit leading to statistical implication as a large value of $F$ value is recorded. $F$ value is much larger than unity, besides a small probability ($p$ value < 0.05) is attained for the regression model. Also, ANOVA revealed a well correlation between the proposed response and the operating parameters. Moreover, $R^2$ (the coefficient of determination) is used to validate the fitness of the model that verifies the model is accepted if it is larger than (80%). The coefficient of determination of the fitted model is recorded 99%.

To evaluate the effects of the parameters and locate the optimal operating variables of BB9 oxidation, the numerical optimization technology provided by Mathematica software (V 5.2) is used. The optimization goal is to maximize the BB9 oxidation rate. The optimal operating condition predicted at 30 min of irradiance time and the point at which the final BB9 oxidation is projected to be in its maximum value that reached to 89% after 30 min. The optimum reagent doses are examined at 767 mg/L and 2.4 mg/L for $H_2O_2$ and CS-M, respectively, and the pH is verified at 7.0. Therefore, in order to validate the quadratic model, experiments were conducted in replicate at the optimal data and the experimental responses were compared to the predicted one. The experimental data revealed a reasonable (65.5%) good settlement to the predicted model value. The result reveals a reasonable (90% after 30 min) good agreement to the predicted value. Also, almost complete BB9 oxidation (99%) is attained at the optimum operating value within 120 min of reaction time. Thus, the determined optimum point through the current proposed empirical model is efficiently verified the maximum dye removal via Box–Behnken design.

Following the model validation, further clarification of the three independent parameters was investigated through 3D surface and 2D contour plots to investigate the correlation between such parameters. The response surface analysis might explore an indication to the type of interactions between the selected variables As displayed in Fig. 7(B–D), the flexure nature of the surface plot explains the interaction between the parameters and response (Tony 2022b). As given in Fig. 7(B, C), BB9 oxidation efficiency is steadily enhanced by the addition of CS-M nanoparticles and $H_2O_2$ reagent. This might be attributed by the formation of hydroxyl radicals in the wastewater media that is related to the reagent doses (see Eq 7–9). This is true till a certain limit the oxidation efficiency is lessened. Such decline is due to the overdosing rate that might act as hydroxyl free radicals’ hinder rather than a generator (Eq. 10). Additionally, as seen in Fig. 7(C and D), BB9 oxidation efficiency is extremely more sensitive to pH change in comparison with the other investigated parameters.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^- \quad (7)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH_2^- + H^+ \quad (8)$$

$$H_2O_2 + HO_2^- \rightarrow +H_2O + O_2 + HO^- \quad (9)$$

$$Fe^{3+} + OH_2^- \rightarrow Fe^{2+} + O_2 + H^+ \quad (10)$$

### Table 3 ANOVA for Box–Behnken design model of BB9 dye oxidation*

| Source        | DF  | SS          | MS          | $F$   | Pr > $F$ |
|---------------|-----|-------------|-------------|-------|----------|
| Linear        | 3   | 49.144725   | 49.144725   | 10.327592 | 0.711868 |
| Interaction   | 3   | 401.036712  | 401.036712  | 84.276457  | 0.315007 |
| Quadratic     | 3   | 394.734925  | 394.734925  | 82.952159  | 0.745234 |
| Regression    | 9   | 1504.397    | 167.1552    | 35.12709  | 0.000542 |
| Model         |     |             |             |        |          |
| Residual error| 5   | 23.79292    | 4.758585    |        |          |
| Total         | 14  | 1528.19     |             |        |          |

* $R^2$ 99%; Adj $R^2$ 96%; DF Degrees of freedom; SS Sum of squares; MS Mean square; $F$ $F$ statistic ($F$ test)

### Thermal effects on kinetics and thermodynamic profile

As previously stated in the literature (Abdou et al. 2018; Oyewo et al. 2020; Rezgui et al. 2021), there is an optimum temperature for conducting the Fenton’s reaction. From this regard, temperature effect on BB9 oxidation reaction on Fenton based CS-M reaction was conducted at four different temperatures, i.e., 26, 40, 50 and 60 °C and the data are displayed in Fig. 8. The purpose of investigating its effects on the oxidation reaction is to determine the overall kinetics and to allow the examination of the Arrhenius-type dependence of the global kinetic constant on temperature. As seen in
Fig. 8, temperature increment had a negative impact on BB9 oxidation rate. Also, it is noted that a shorter oxidation reaction period is required, needed for the BB9 oxidation at low temperature (room temperature). The temperature elevation showed a markedly decline in the BB9 dye oxidation with a subsequently decrease in the reaction yield. This could be due to the significant decomposition of H2O2 reagent into O2 and H2O. Such rapid H2O2 at high temperatures exceeds than 26 °C results in a lessening in the overall reaction efficacy (Ashour and Tony 2017; Guedes et al. 2003; Soliman et al. 2020; Tony and Lin 2020c).

From the theoretical and practical point of view, it is crucial to investigate large-scale treatment capacity. Thus, understanding the oxidation kinetics for eliminating BB9 contaminating wastewater is an essential. Kinetic statistics provides estimation for: the optimal system parameter; reactor design; actual process control and a jointly examination for economic study of capital and operating budget (Al et al. 2008; Ashour et al. 2014; Tony 2021c). Table 4 presented the assessed zero-, first- and second-order kinetic models and their corresponding determination of the kinetic constants and parameters.

In light of R² values (regression coefficient), the highest was chosen to select their corresponding model to be the most adequate one. By examining the data in Table 4, second-order reaction kinetics model was chosen to be the appropriate model that represents the data. k₂, the second-order model rate constants are elevated from 0.0157 to 0.0028 L/mg.min with temperature increase. Further, t₁/₂, the half-life time increases with the temperature elevation. The lowest t₁/₂ for the BB9 oxidation is estimated at the temperature 26 °C. Hence, the second-order model proposed the oxidation yield is precise by the reaction temperature up to 26 °C. Scattered authors previously reported the Fenton’s reaction is controlled by the second-order model kinetics (Ahmadi et al. 2016; Al et al. 2008; Ashour et al. 2014; Tony et al. 2016).

To further understanding the oxidation of CS-M-based Fenton system, thermodynamic parameters were tested and the data are tabulated in Table 5. Based on the second-order kinetic rate constant, Arrhenius principle Eq. (11) might be written in the linearized form taking the natural logarithm yielding Eq. (12):

\[
k_2 = Ae^{-\frac{E_a}{RT}}
\]

\[
\ln k_2 = \ln A - \frac{E_a}{RT} 
\]

where A is the constant corresponding to pre-exponential factor; Eₐ is the energy of activation (kJ/mol); R is the gas constant (8.314 J/mol.K) and T is temperature (K). Further, the linear fit of lnk₂ and −1/T (Fig. 9) could leading to the calculation of energy of activation. Consequently, the energy of activation (Eₐ) for the system is 43.49 kJ/mol.

### Table 4 Kinetic parameters for different reaction order models for BB9 treatment in aqueous media*

| Kinetic model | Parameters | \(T\) | \(299\) | \(313\) | \(323\) | \(333\) |
|---------------|-----------|------|------|------|------|------|
| Zero-order \(C_t = C_o - k_o t\) | \(k_o\) (min⁻¹) | 0.0691 | 0.0808 | 0.0996 | 0.1255 |
| | \(t_{1/2}\) | 66.21 | 57.09 | 47.25 | 34.74 |
| | \(R^2\) | 0.85 | 0.75 | 0.67 | 0.61 |
| First-order \(C_t = C_o - e^{-k_1 t}\) | \(k_1\) (min⁻¹) | 0.0377 | 0.0215 | 0.0151 | 0.0134 |
| | \(t_{1/2}\) | 51.72 | 45.89 | 32.23 | 18.38 |
| | \(R^2\) | 0.99 | 0.86 | 0.8 | 0.73 |
| Second-order \(\frac{1}{C_t} = \left(\frac{1}{C_o}\right) - k_2 t\) | \(k_2\) (L/gm.min⁻¹) | 0.0157 | 0.0053 | 0.0031 | 0.0028 |
| | \(t_{1/2}\) | 6.96 | 20.45 | 34.28 | 40.96 |
| | \(R^2\) | 0.94 | 0.93 | 0.92 | 0.84 |

*C, o and C₀: initial and at time t BB9 concentration (mg/L); t time (min); k₀, k₁, k₂ kinetic rate constants of zero-, first- and second-orders kinetic models
Such minimal energy of activation significance confirms that the BB9 oxidation conducted at low energy barrier through CS–M-based Fenton system. Previous investigators Ahmadi et al. (2016) and Sun et al. (2007) recorded low energy barrier (53.96 and 45.84 kJ/mol, respectively) in treating dyes and p-nitroaniline from wastewater using such Fenton reaction. Eyring’s relation (Bounab et al. 2015) (Eq. (13)), Gibbs free energy of activation ($\Delta G^*$) was calculated to estimate the viability of the oxidation.

$$k_2 = \frac{k_B T}{h} e^{\left(\frac{-E_a}{RT}\right)}$$  \hspace{1cm} (13)

where $k_B$ and $h$ are constants of Boltzmann and Planck’s. Also, the enthalpy of activation ($\Delta H^*$) (Eq. (14)) and the entropy of activation ($\Delta S^*$) (Eq. (15)) were estimated (Wahab and Hussain, 2016).

$$\Delta H^* = E_a - RT$$  \hspace{1cm} (14)

$$\Delta S^* = \frac{(\Delta H^* - \Delta G^*)}{T}$$  \hspace{1cm} (15)

As exhibited in Table 5, $\Delta G^*$ (Gibbs free energy) showed positive values and its values increased with the temperature elevation and the minimum Gibbs free energy value is corresponding to the temperature of 26 °C, this reveals that the reaction is non-spontaneous in nature. Besides, $\Delta H^*$ values (enthalpy of activation) that is attained also positive values indicating the reaction is endothermic. But, $\Delta S^*$ (entropy of activation) is negative sign that is confirming the non-spontaneity nature of such oxidation system. This illustrates a decline in the degree of freedom of the BB9 molecules and supported a high hydroxyl radicals that maximizing the oxidation yield. Such results in accordance with previously stated in the literature (Argun and Karatas 2011; Tony 2022c).

It is essential to compare the current study with the other investigated articles cited in the literature to demonstrate the importance of the current composite material application. Table 6 displays a comparison of various combinations composite materials in the last decades for the elimination of different types of wastewater polluted effluents. The Table are comparing Fenton-based catalyst which compromises of iron composed with other materials or Fenton-Like-based system such as Cu-based system. Tony and Mansour (2020a) applied Cu/Cu$_2$O/CuO as a Fenton-Like active system, whereas Thabet et al. (2021b), Wang et al. (2019), Thabet et al. (2021a) and Guan et al. (2020) applied magnetite-based composite as a source of Fenton’s catalyst which possess the merit of recoverable, recyclable and the principle of reusable catalyst. Furthermore, Tony (2022a) and Thabet et al. (2022c, d) applied alum sludge waste as a source of catalyst combined with other materials to be a source of Fenton’s reaction. Generally, the use of waste materials is superior due to their advantages for industrial ecology aspects. Such regard appeals the contribution of reducing cost disposal and sustains the environment. From this regard, the current study satisfies such view since CS-M catalyst compromising of chitosan which is attained from waste materials and magnetite that is a recyclable catalyst. It is noteworthy to mention that almost a complete pollutant elimination is attained through the current investigation. Moreover, the catalyst used is a minimum amount compared to the other amounts of catalysts used. Thus, such advantages make the current system more environmentally green and economically efficient compared to other systems.

Table 5  Thermodynamic data of BB9 oxidation via CS-M(2–1)-based Fenton system

| Temperature, K | Ln $k_1$ | $E_a$, kJ/mol | $\Delta G^*$, kJ/mol | $\Delta H^*$, kJ/mol $^\circ$ | $\Delta S^*$, J/molK |
|---------------|----------|---------------|----------------------|-----------------------------|----------------------|
| 299           | −4.15    | 43.49         | 83.56                | 41.01                       | −142.31              |
| 313           | −5.24    | 90.42         | 40.89                | 80.89                       | −158.23              |
| 323           | −5.78    | 94.83         | 40.81                | 80.81                       | −167.25              |
| 333           | −5.89    | 98.14         | 40.72                | 80.72                       | −172.39              |

Fig. 9  Arrhenius plot of the pseudo-second-order kinetic constants
Conclusion

The co-precipitation of magnetite with chitosan is a promising treatment method when augmented with H2O2 as a Fenton method for the elimination of BB9 dye from aqueous stream. Crystalline magnetite nanoparticles embedded in the chitosan polymer showed a superior oxidation efficiency. The oxidation parameters demonstrated that the CS-M dosing and H2O2 concentration limiting the oxidation reaction. However, the reaction might work in a wide pH values that introduces the advantage of such system. The photo-catalytic oxidation efficiency increased with lessening the initial dye concentration in aqueous effluent. Further, elevating the temperature from ambient temperature declines the pollutant oxidation. The kinetic data showed the reaction following the second-order kinetics with global activation energy of 43.49 kJ/mol. Hence, it might be signified that the system is a promising technology for treating aqueous effluent in a green efficient way.

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| Table 6 | Comparison of the current study with the various treatment systems from the literature through composite-based Fenton systems |
|---|---|---|---|---|---|---|
| Catalyst based composite | Catalyst preparation method | Pollutant/initial concentration | Induction source | Operating conditions | Removal, % | Refs. |
| CS-M | Co-precipitation | BB9/10 ppm | UV | PH (7), CS-M (2.4 mg/L), H2O2 (767 mg/L) | 99.5 | Current study |
| AS/magnetite | Co-precipitation and hydrothermal | Levafix Blue/50 ppm | UV | pH (2), catalyst (2 g/L), H2O2 (800 mg/L) | 100 | Thabet et al. 2022b |
| AS/Fe2O3 nanocrystals | Co-precipitation | Methomyl/50 ppm | UV | PH (6.0), H2O2 (150 mg/L), AS/Fe2O3 (50 mg/l) | 100 | Thabet et al. 2022c |
| Silica-supported iron | Selective precipitation | Lannate/100 ppm | Solar | pH (2.8), iron-sand (45 mg/L), H2O2 (103, mg/l) | 98 | Tony, 2022a |
| Cu/Cu2O/CuO | thermal decomposition | Methomyl pesticide/50 ppm | MW | pH (6.5), catalyst (3.0 g/L), H2O2 (5000 mg/L) | 91 | Tony & Mansour 2020a, b |
| LaFeO3/BiOBr | NA | RhB/5 ppm | UV | Catalyst (0.1 gm), H2O2 (0.5 ml) t (30 min) | 98.2 | Guan et al. 2020 |
| Sawdust/magnetite | Co-precipitation/ hydrolysis/mixing with heating | Red K-HL dye/50 ppm | – | pH (3.0), catalyst (1 g/L) | 99 | Tony, 2022b |
| Fe3O4/Co3O4/g-C3N4 | Wet impregnation | TCH/50 mg/L | Visible-light | pH (2.7), catalyst (50 mg/L), H2O2 (10 mM), T (35 °C), t (180 min) | 96.63 | (Wang et al. 2021) |
| Ag2S/BiFeO3 | Co-precipitation | MO/40 ppm | Visible-light | Catalyst (0.6 g/L), H2O2 (2 mmol/l), t (4 h) | ~97 | (Di et al. 2019) |
| TiO2/FeOOH | Deposition–precipitation | MO/80 ppm | UV | PH(4.5), Catalyst (200 mg/L), H2O2 (300 mg/L) | 97.2 | (Xu et al. 2013) |
| TiO2@NH2-MIL-88B(Fe) | Solvothermal method | MB/100 ppm | LED lamp | PH (7), Catalyst (200 mg/L), H2O2 (20 mM), T (Ambient temp.), t (2.5 h) | 100 | (Li et al. 2018b) |

*NA not available; CS-M chitosan-magnetite; BB9 Basic Blue 9; MB methylene blue; AS alum sludge; UV ultraviolet; MW microwave; RhB Rhodamine B dye; MO Methyl Orange; TCH tetracycline hydrochloride
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**Declarations**

**Conflict of interest** The authors confirm that there is no conflict of interest to declare.

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