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Exploring Clay-Based Catalysts for Wastewater Remediation: Catalytic Degradation of Congo Red Using Montmorillonite and Response Surface Methodology

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ABSTRACT

The growing amount of synthetic dyes, like Congo red (CR), being released into water systems poses a serious risk to the environment and public health because they are toxic, long-lasting, and hard to treat. These colors may obstruct aquatic photosynthesis, disturb biological life cycles, and provide carcinogenic dangers to humans. This research examines the catalytic degradation of CR dye with nanostructured Iraqi bentonite clay (NIBC) as an economical and sustainable catalyst. NIBC underwent purification with glacial acetic acid to enhance its surface activity and catalytic efficacy. The experimental design employed a Box-Behnken Design (BBD) combined with Response Surface Methodology (RSM) to statistically assess and optimize the individual and interactive effects of three chemical agents-hydrogen peroxide (H_2O_2), sodium borohydride ($NaBH_4$), and potassium bromate ($KBrO_3$)-on degradation efficiency. Catalytic degradation tests were performed at neutral pH, using UV-Vis spectroscopy to assess CR content A maximum CR degradation rate of 36.9% was attained under optimum settings. Scavenger trapping studies were used to determine the predominant reactive oxygen species (ROS) involved in the degradation pathway. Results demonstrated that superoxide radicals ($\bullet O_2-$) and hydroxyl radicals (•OH) were the principal reactive oxygen species (ROS) facilitating the degradation of CR molecules, subsequently accompanied by the participation of electrons and holes. Energy-Dispersive X-ray (EDX) and Scanning Electron Microscopy (SEM). These results highlight the promise of chemically modified bentonite clay in the development of effective, environmentally sustainable wastewater treatment methods. The research considerably advances clay-based catalytic systems and offers a viable method for the sustainable elimination of persistent organic contaminants from water.

Keywords: Congo red degradation, Nanostructured bentonite clay, Catalytic advanced oxidation process (AOP), Response Surface Methodology (RSM), Reactive oxygen species (ROS).

INTRODUCTION

Freshwater is Earth's most vital resource, essential for supporting human life and ecosystems. However, modern agricultural and industrial activities are threatening this finite supply through pollution. The increasing demand for food and housing is exacerbating the problem, leading to higher volumes of industrial waste and sewage being dumped into rivers and nearby land-a trend that shows no signs of slowing down[1]. According to the NORMAN Network's findings, water bodies are contaminated with numerous hazardous substances, such as agricultural chemicals, heavy metals, petroleum byproducts, and artificial dyes. Such irresponsible practices will inevitably impose a heavy burden on present and future generations. Experts predict that worldwide pollution levels will keep increasing, resulting in severe consequences[2]. According to the United Nations WWAP, global water demand is expected to exceed 55% by the end of the next twenty years[3]. Recently, several researchers, particularly those associated with ecological science, have emphasized the importance of synthetic dyes as harmful pollutants. The WHO has classified synthetic dyes as one of the ten most prevalent chemical contaminants[4].

Congo red (CR) is a synthetic dye often used in many consumer items, such as fabrics, hair dyes, leather, and ceramics, mostly to augment their aesthetic appeal[5,6]. This dye may be categorized according to its application technique, chemical composition, solubility, and constituent elements[7]. CR has two main parts: the auxochrome, which helps it dissolve better and stick to things, and the chromophore, which gives the dye its color[8]. Despite its extensive use, an increasing amount of research has shown negative health effects associated with exposure to this dye. Exposure to this dye can lead to health issues, such as an elevated heart rate[9], malfunction of the reproductive system[10], and respiratory difficulties[11]. The toxicological effects are mostly ascribed to the aromatic rings and azo functional groups inside the chromophore units of the dye molecule[12,13]. Due to the possible threats to human health and the environment, there is an urgent need to devise and execute sustainable and effective remediation measures to alleviate the effects of this harmful synthetic dye[2].

Synthetic dyes are highly persistent and difficult to fully break down through natural processes like photolysis, biodegradation, or chemical decomposition. To minimize their release into the environment, several treatment methods can be employed, including ion exchange, chemical precipitation, electrochemical treatment, membrane filtration, and adsorption techniques[14–16]. However, these conventional treatment methods have significant drawbacks, such as incomplete dye mineralization, concentrated waste disposal challenges, high energy demands, costly operations, and excessive sludge production, along with other limitations[17–19]. Consequently, there is a pressing need for highly efficient and advanced technology for the thorough elimination of pollutants from aquatic environments[20,21]. One effective way to treat wastewater is through advanced oxidation processes (AOPs), which can change harmful substances into safe minerals. While direct oxidation can effectively degrade pollutants in wastewater, the need for extreme conditions-such as high temperature and pressure-to decompose certain compounds significantly raises the overall treatment costs[22–24]. Catalytic oxidation stands out as a highly efficient advanced oxidation process, leveraging powerful radicals generated through catalytic reactions under mild conditions. This method harnesses the formation of potent oxidizing radicals capable of degrading nearly all wastewater pollutants. Its core objective is converting synthetic dyes into harmless, non-toxic compounds[25]. In catalytic processes, reactions primarily occur on the catalyst's surface, making key characteristics such as porosity, surface area, selectivity for radical generation, structural stability, particle uniformity, and cost critical determinants of overall catalytic efficiency[22–24]. Moreover, Catalytic degradation is an effective technique for decomposing organic contaminants in wastewater using a combination of agents capable of oxidizing, reducing, and accepting electrons. Hydrogen peroxide (H_2O_2) acts as an oxidizing agent, generating hydroxyl radicals that break down complex pollutants into smaller components.[26] Sodium borohydride ($NaBH_4$) functions as a reducing agent, facilitating the elimination of chlorine or organic contaminants such as azo dyes[27]. Potassium bromate ($KBrO_3$) accelerates the process by absorbing electrons, thereby enhancing the stability of intermediate stages and facilitating electron transfer[28]. When combined, these agents work together to improve the effectiveness of catalytic degradation, making it a practical option for cleaning wastewater and restoring the environment[29].

Bentonite clay (BC), distinguished by its widespread availability, affordability, and exceptional adsorption capability, has become a very promising material for color removal applications[30,31]. Previous studies have confirmed bentonite clay's efficacy in adsorption and separation processes, underscoring its exceptional cation-exchange capacity, structural stability, and high adsorption affinity for various contaminants[32,33]. To fully harness bentonite clay's adsorption potential, chemical treatments are typically required to expand its surface area and increase active site availability, thereby dramatically improving its dye removal efficiency[34]. Bentonite consists of layers including two tetrahedral sheets of silica interspersed with one octahedral sheet of alumina. Furthermore, Bentonite has a lasting negative charge because some aluminum ions (Al^{3+}) in the tetrahedral layer are replaced by silicon ions (Si^{4+}). In the octahedral layer, magnesium ions (Mg^{2+}) substitute aluminum ions (Al^{3+}). Within the lattice framework, exchangeable cations (Ca^{2+}, Na^{+}, etc.) neutralize the negative charge. This equilibrium facilitates the adherence of cationic pollutants to the structure[35–37]. Bentonite may be readily organo-modified to adsorb nonionic contaminants by the partition method, in addition to cation adsorption[38,39].

The Box-Behnken design is a prevalent and efficient experimental design technique in Response Surface Methodology (RSM) that enhances processes and systems by elucidating the link between many independent variables (factors) and a dependent variable (response)40. The design functions at three tiers: low (-1), middle (0), and high (+1). Each combination of factor values happens with equal frequency[41]. Unlike full factorial designs, Box-Behnken does not assess all possible factor combinations, leading to a lower number of experiments. It thoroughly analyzes the interrelations among components, which is crucial for a complete understanding of the process. This architecture effectively handles several variables, often between three and seven[43].

This work introduces an innovative method using chemically purified nanostructured Iraqi bentonite clay (NIBC) as an economical and eco-friendly catalyst for the breakdown of Congo Red dye. This study uses a three-part system (H_2O_2, $NaBH_4$, $KBrO_3$) for breaking down Congo Red dye, which was improved using Box-Behnken Design (BBD) and evaluated with Response Surface Methodology (RSM), unlike earlier studies that only focused on adsorption or photocatalysis. The addition of scavenger trapping studies helps us understand the main reactive oxygen species at work, showing that superoxide and hydroxyl radicals are the key agents that break down the dye. This detailed study expands the use of natural clays in advanced oxidation processes (AOPs) and develops a scientifically backed model for treating wastewater with locally sourced, modified bentonite, marking a significant improvement in environmental chemistry and sustainable engineering.

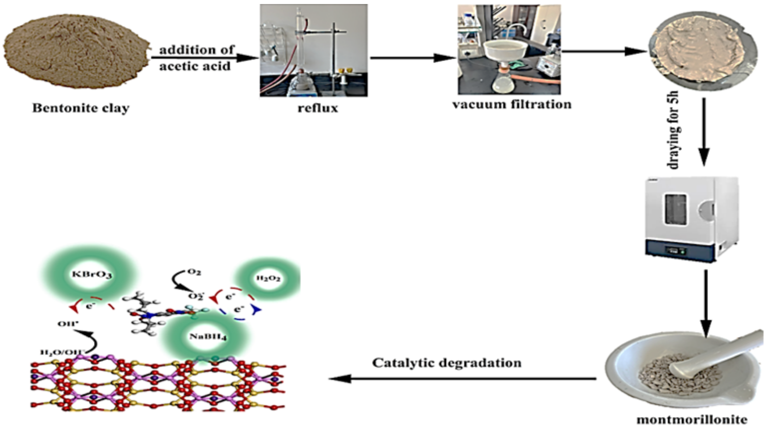


Fig. 1. The diagram indicates the purification of NIBC

EXPERIMENTAL

Instrumentation

A thorough material evaluation was conducted to assess the physicochemical characteristics of the nanostructured Iraqi bentonite clay (NIBC). Field-Emission Scanning Electron Microscopy (FE-SEM, Quanta 4500 FEI, USA) was used to examine the surface morphology and microstructural characteristics of the purified clay. The component composition was determined by energy-dispersive X-ray spectroscopy (EDX), yielding a semi-quantitative assessment of constituent distribution. The crystallinity and phase purity of the clay were evaluated using X-ray Diffraction (XRD) analysis (model to be provided). UV-Visible spectrophotometric examination was performed using a PerkinElmer Lambda 25 UV-Vis spectrophotometer (USA) to observe absorbance variations in Congo red (CR) dye at a maximum wavelength (λ_max) of 498 nm, assessing adsorption and catalytic degradation over time.

Chemicals

All reagents used in this work were of analytical quality and utilized as supplied without additional purification. Raw bentonite clay was sourced from the Al-Anbar/Akashat area of the Western Desert in Iraq. Congo red dye (C.I. 22120) was procured from ROTH GmbH (Germany). Oxidizing and reducing agents-hydrogen peroxide (H_2O_2, 30% w/v), sodium borohydride ($NaBH_4$, 98%), and potassium bromate ($KBrO_3$)-were obtained from Carl Roth GmbH. Glacial acetic acid (CH_3COOH, 70%), sodium hydroxide (NaOH, 99%), and hydrochloric acid (HCl, 37%) were procured from Merck. Isopropyl alcohol (IPA) was provided by Fluka, while ascorbic acid (AA) was supplied by Scharlau Chemicals. Deionized (DI) water was used in all steps for solution preparation, clay washing, and dilution.

Chemical Purification of Bentonite Clay

The raw bentonite was chemically purified to remove inorganic carbonates that might hinder catalytic surface reactions, hence enhancing its catalytic activity. Sixty grams of the clay sample were suspended in 600 mL of 10% (v/v) glacial acetic acid, continuously stirred, and kept at 80–90°C for four hours. The progression of CO_2 gas, signifying the elimination of carbonate, was seen till termination. The successful decarbonation was verified using a turbidity test with lime water. The suspension was left to cool at room temperature for 24 h, thereafter undergoing filtering by vacuum suction. The retained material was repeatedly rinsed with distilled water until the filtrate displayed a neutral pH (~7), so validating the elimination of residual acetic acid. The purified sample was subjected to drying in a hot air oven at 120–130°C for 5 h and thereafter stored in a desiccator. The resulting dry mass of 56.8 g signifies the effective extraction of about 3.2 g of carbonate material. This technique guaranteed the preservation and activation of montmorillonite as the predominant mineral phase in the clay.

Catalytic Degradation Experiments

The catalytic efficacy of NIBC in the degradation of Congo red dye was examined at different reagent concentrations using a statistically determined methodology. A constant quantity of NIBC (50 mg) was introduced to 50 mL of CR solution (starting concentration: 10 ppm) and underwent catalytic treatment with varying concentrations of H_2O_2, $NaBH_4$, and $KBrO_3$, spanning from 0 to 20 mM. A three-level, three-factor Box-Behnken Design (BBD) inside the Response Surface Methodology (RSM) framework was used to investigate the impacts and interactions of these chemicals on degrading efficiency, improving the process with a limited number of experimental runs (n=16). Before catalytic treatment, the CR solution containing NIBC was subjected to magnetic stirring in darkness for 50 min to attain adsorption-desorption equilibrium. The catalytic process commenced with the introduction of oxidizing and reducing agents, and the system was sustained at ambient conditions (pH = 7, 25±2°C) for 60 minutes. At specified times, 3 mL aliquots were extracted, centrifuged at 10,000 rpm for 1 min to eliminate solid residues, and the supernatant was evaluated using UV-Vis spectroscopy at 498 nm.

To identify dominant ROS, scavengers were introduced:

Isopropanol (IPA) for hydroxyl radicals (•OH)
p-Benzoquinone (p-BQ) for superoxide anions (O_2^{-}•)
Sodium oxalate ($Na_2C_2O_4$) for holes (h^+)
Potassium bromate ($KBrO_3$) for electrons (e^-)[44–48].

Table 1: Parameters' levels examined in the BBD statistical experiment

Independent variable	Unit	Levels		
		-1(low)	0(middle)	+1(high)
H_2O_2	mM	0	10	20
$NaBH_4$	mM	0	10	20
$KBrO_3$	mM	0	10	20

RESULTS AND DISCUSSION

Surface morphology and elemental composition

The surface charge was ascertained using point of zero charge (pHpzc) analysis. The isoelectric point (zero charge point, pHpzc) was found to be about pH 8.4, where montmorillonite has no charge; therefore, all experiments were done at neutral pH levels to ensure a steady pH effect[49–54]. At the point where the pH differential equals zero, one can determine the pHZC[55].

The SEM image of NIBC, shown in Fig. 2(a) and (b), shows a different and very porous structure made of uneven, flat particles. The 15.00 KX zoom shows the clumping of flat and layered particles, which is typical for montmorillonite minerals. The particles have a coarse surface roughness, indicating the existence of many micro- and mesopores, advantageous for adsorption applications. The interconnected porous structure and the existence of gaps within the particles increase the material's surface area, making it appropriate for wastewater treatment and other adsorption-based applications. The observed shape and structure indicate the presence of montmorillonite, the primary constituent of the material.

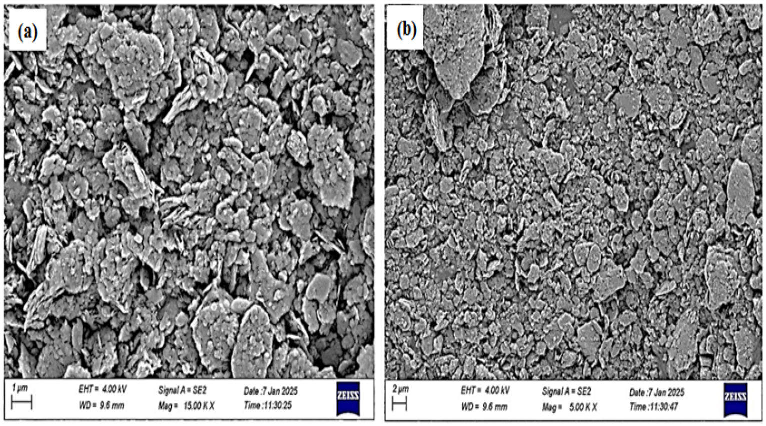
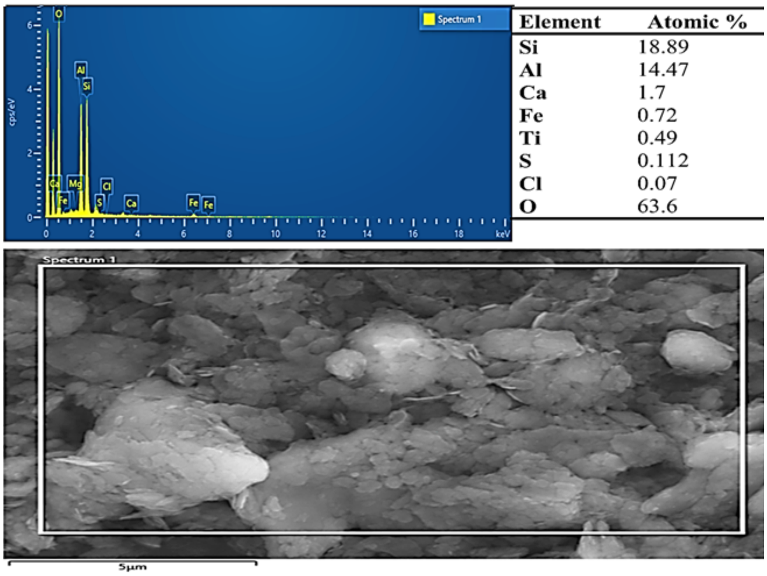


Fig. 2. SEM images of Bentonite clay at (a) 1*μm* and (b) 2 *μm* magnification

Energy-dispersive X-ray (EDX) analysis compared the elemental composition of Iraqi bentonite clay before and after montmorillonite synthesis (Fig. 3), revealing dominant peaks for oxygen (63.6%), silicon (18.89%), and aluminum (14.47%) characteristic of aluminosilicates, along with trace amounts of calcium, iron, titanium, sulfur, and chlorine. While these impurities were present in negligible quantities, they may occupy active surface sites and reduce the material's available surface area, potentially diminishing its adsorption capacity[56].



Element	Atomic %
Si	18.89
Al	14.47
Ca	1.7
Fe	0.72
Ti	0.49
S	0.112
Cl	0.07
O	63.6

Fig. 3. EDX spectrum and comprehensive elemental ratio map of NIBC

Catalytic degradation

The study employed natural Iraqi bentonite clay-derived NIBC in a catalytic degradation process, systematically evaluating the influence of H_2O_2, $NaBH_4$, and $KBrO_3$ through carefully designed experiments and statistical analysis. Key operational parameters and their optimized values are comprehensively outlined in Tables 1 and 2, providing a detailed framework for the reaction conditions.

Response surface methodology

Response Surface Methodology (RSM) is considered as a statistical modeling technique that analyzes experimental data to construct predictive regression equations, enabling systematic optimization of process variables and their interactive effects on degradation efficiency. By integrating designed experiments with empirical results, RSM enhances the understanding of how operational parameters influence reaction dynamics[57,58].

Box-Behnken design (BBD)

The research used the widely used BBD. A notable advantage of the BBD technique is its ability to reduce the overall number of experiments required to determine the yield of catalytic degradation[58–61]. We executed the BBD, concentrating on three specific variables: H_2O_2, $NaBH_3$, and $KBrO_4$. The assessed response variable was the decreasing fraction of CR. Table 2 delineates each independent variable accompanied by three separate levels. Sixteen experimental studies were selected and further examined.

Table 2: Findings of the BBD including fitted and observed values

Run	H_2O_2 (µM)	$NaBH_4$ (µM)	$KBrO_3$ (µM)	% of removal observed CR	% of removal Fitted CR
1	0	20	10	5.62	5.62
2	20	0	10	5.08	5.08
3	20	10	20	7.51	7.51
4	10	10	10	13.83	13.83
5	0	10	0	0.4936	0.4936
6	20	20	10	30.96	32.49
7	10	10	10	9.53	9.53
8	20	10	0	32.22	32.49
9	10	20	20	34.57	32.49
10	0	10	20	12.75	12.75
11	10	20	0	3.33	3.33
12	10	0	20	1.16	1.16
13	0	0	10	1.30	1.30
14	10	10	10	32.22	32.49
15	10	10	10	4.69	4.69
16	10	0	0	4.08	4.08

Note:It is important to note that the pH was maintained at 7, and during the one-hour catalytic degradation, all samples were equilibrated for adsorption and desorption in the dark for one hour

Table 3 shows a clear summary of how well different models explain the breakdown of Congo Red (CR) using montmorillonite as the catalyst. The assessment carefully compares different regression models-linear, two-factor interaction (2FI), quadratic, and cubic-based on important statistics like the sum of squares, degrees of freedom (df), mean square, F-value, and p-value. The quadratic model is the most statistically robust, shown by a high F-value of 32.26 and a low p-value of 0.0004. These measurements demonstrate that the quadratic model substantially improves the fit relative to the 2FI model; hence, it accounts for more variance in the response variable. The model is designated as "suggested," underscoring its statistical validity and appropriateness for characterizing the observed experimental behavior.The linear model has no statistical significance relative to the mean, as shown by an F-value of 0.1112 and a p-value of 0.9519. This indicates that the linear model helps insignificantly elucidate the variation in the data. The 2FI model, with an F-value of 0.0138 and a p-value of 0.9976, inadequately captures the interacting effects and is considered insufficient. The cubic model has a substantial F-value (18.58) and a minimal p-value (0.0193); nevertheless, it is classified as "aliased." This indicates confusion among variables owing to an inadequate number of experimental trials, making the cubic model statistically inaccurate and impracticable for analysis. The leftover error, which is calculated as 6.81 over 3 degrees of freedom, is quite low, supporting that the quadratic model fits well. The overall sum of squares is 4841.23 across 16 degrees of freedom, indicating that the model accounts for a considerable extent of the variability. In general, these results highlight that the quadratic model is the best and most important way to represent how Congo Red breaks down using montmorillonite. This model strikes a good balance between being complicated and being able to make accurate predictions, without issues of overfitting or aliasing, making it a great choice for further improvement and study.

Table 3: Model fit summary for catalytic degradation of CR over montmorillonite

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	2483.41	1	2483.41			
Linear vs Mean	63.77	3	21.26	0.1112	0.9519	
2FI vs Linear	10.54	3	3.51	0.0138	0.9976	
Quadratic vs 2FI	2150.21	3	716.74	32.26	0.0004	Suggested
Cubic vs Quadratic	126.50	3	42.17	18.58	0.0193	Aliased
Residual	6.81	3	2.27			
Total	4841.23	16	302.58			

Table 4 shows the analysis of variance (ANOVA) for breaking down Congo Red (CR), revealing that several factors greatly influence the breakdown process. The main effects of the three chemicals-hydrogen peroxide (H_2O_2), sodium borohydride ($NaBH_3$), and potassium bromate ($KBrO_4$)-are important, with p-values of 0.0373, 0.0279, and 0.0217, showing that each one helps improve the degradation process on its own. The squared terms of the three variables (A^2, B^2, and C^2) are very important, with p-values under 0.0005, showing a strong nonlinear relationship between the amounts of these chemicals and how well degradation happens. Additionally, some interaction terms like A^2C and AB^2 are important, with p-values of 0.0169 and 0.0109, showing that the way some reagents work together, especially in complex ways, is important for the degradation process. Nonetheless, the interaction terms AB, AC, BC, A^2B, and the three-way interaction ABC are not statistically significant, suggesting little interactive impact among these components. The ANOVA model is important, showing an F-value of 86.33 and a p-value of 0.0018, which confirms that it effectively explains the differences in the percent degradation of Congo Red. These results underscore the significance of both the individual and interaction impacts of the reagents, particularly their nonlinear contributions, in optimizing catalytic degradation for efficient wastewater treatment.

Table 4: ANOVA for catalytic degradation of CR dye

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2351.02	12	195.92	86.33	0.0018	significant
A-H_2O_2	29.07	1	29.07	12.81	0.0373	significant
B-$NaBH_4$	36.44	1	36.44	16.06	0.0279	significant
C-$KBrO_3$	44.09	1	44.09	19.43	0.0217	significant
AB	0.2083	1	0.2083	0.0918	0.7817	
AC	0.6550	1	0.6550	0.2886	0.6284	
BC	9.68	1	9.68	4.26	0.1309	
A^2	730.51	1	730.51	321.88	0.0004	significant
B^2	593.82	1	593.82	261.66	0.0005	significant
C^2	825.88	1	825.88	363.91	0.0003	significant
ABC	0.0000	0				
A^2B	0.7915	1	0.7915	0.3488	0.5963	
A^2C	52.93	1	52.93	23.32	0.0169	significant
AB^2	72.78	1	72.78	32.07	0.0109	significant
Pure Error	6.81	3	2.27			
Cor Total	2357.83	15				

The effectiveness of breaking down Congo Red (CR) dye was predicted using regression analysis based on three factors: potassium bromate ($KBrO_3$, called C), sodium borohydride ($NaBH_4$, called B), and hydrogen peroxide (H_2O_2, called A). To represent the intricate behavior of the system, the second-order polynomial regression model included linear, interaction, and quadratic factors. The intercept value, which represents the expected deterioration efficiency at the middle values of all variables, was 32.49, as seen in Table 5. The positive number (+2.70) for H_2O_2 in the linear factors shows that it helps improve CR breakdown, probably by increasing the formation of hydroxyl radicals (•OH). $NaBH_4$ and $KBrO_3$ had negative coefficients (−3.02 and −3.32, respectively), meaning that high amounts of these substances can lower degradation efficiency due to competing reactions or scavenging of radicals.Significant impacts were also seen in the interactions between the factors. The positive coefficients of the AC and BC terms (0.4047 and 1.56, respectively) showed that H_2O_2 works well with $KBrO_3$ and $NaBH_4$ works well with $KBrO_3$ together. Interestingly, the BC interaction had the most favorable impact, suggesting that $KBrO_3$ and $NaBH_4$ work together to strongly affect the degradation process. The curvature of the response surface was reflected in the negative values of the three quadratic components (A2, B, and C) (−13.51, −12.18, and −14.37, respectively), which also indicated that the degrading efficiency was decreased by excessively high or low reagent concentrations. The cubic interaction terms also showed that the system was much more intricate. The negative value for A^2C (−6.03) suggests that having a lot of H_2O_2 with $KBrO_2$ has a negative effect, while the positive value for AB^2 (5.14) shows that combining H_2O_2 with a higher amount of $NaBH_4$ greatly improves degradation. In summary, the statistical model showed how important the reagents' individual and combined impacts were on the degrading process. The results, shown in Table 5, suggest that a second-order polynomial model, such as the one from the Box–Behnken Design, is effective for improving the degradation conditions and accurately predicting how well CR can be removed.

Table 5: Regression equation coefficients for CR dye degradation

Parameter	Coefficient value
Intercept	32.49
A-H_2O_2	2.70
B-$NaBH_4$	-3.02
C-$KBrO_3$	-3.32
AB	0.2282
AC	0.4047
BC	1.56
A^2	-13.51
B^2	-12.18
C^2	-14.37
A^2B	0.6291
AB^2	5.14
A^2C	-6.03

Figure 4 shows a detailed evaluation of how well Congo Red breaks down using a nanocomposite catalyst made with $NaBH_4$ (NIBC). Fig. 4(a) presents a contour plot showing the interaction effects of H_2O_2 and $NaBH_4$ concentrations on degradation efficiency. The figure exhibits a symmetrical arrangement of circular contour lines, with the middle red area signifying the peak deterioration efficiency, recorded in experiment[14]. The color gradient transitions from blue, denoting the minimal degradation efficiency of 0.49%, to red, signifying the peak efficiency of 34.57%, demonstrating the vital importance of maintaining an appropriate ratio between the oxidant (H_2O_2) and the electron donor ($NaBH_4$). This nonlinear connection indicates that both excessive and inadequate quantities of either reagent diminish degradation performance, underscoring the need to attain an exact equilibrium for efficient catalysis. Fig. 4(b) illustrates a parity map that contrasts the projected and actual degradation efficiencies of Congo Red. The proximity of data points to the diagonal reference line indicates a robust connection between the experimental outcomes and the model's forecasts. Even though there are small differences at lower degradation levels, the clustering of high efficiency values near the line shows that response surface methodology (RSM) is effective in modeling and predicting how the system degrades. The results from Fig. 4(a) and 4(b) together show that the NIBC catalyst is effective in breaking down Congo Red and suggest that the statistical model provides accurate predictions for improving degradation efficiency.

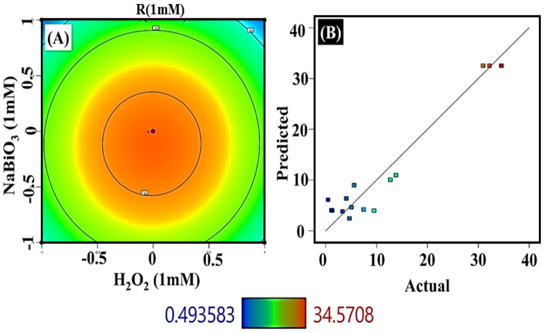


Fig. 4. (a) Contour plot for maximum degradation experiment 14, (b) predicted vs. actual degradation of Congo red over NIBC

Scavenger trapping experiments

Table 6 shows how well Congo Red dye breaks down when different trapping agents are used, pointing out the role of various reactive species in the breakdown process. Without a scavenger, the breakdown efficiency reaches its highest at 36.9%, serving as the control where all reactive species can act freely. Adding $Na_2C_2O_4$, which captures holes, slightly lowers the breakdown to 32.56%, suggesting that holes (h^+) play a significant role in the process. In the absence of a scavenger, the degradation efficiency peaks at 36.9%, functioning as a control in which all reactive species are unrestricted. The addition of $Na_2C_2O_4$, a hole scavenger, results in a small decrease in degradation to 32.56%, indicating a considerable involvement of holes (h^+) in the process. The addition of $KBrO_3$ (an electron scavenger) further reduces the degradation to 25.33%, indicating the involvement of electrons (e^-). A notable reduction is seen with IPA (isopropanol), a hydroxyl radical (•OH) scavenger, where the degradation decreases to 16.67%, indicating the vital role of •OH radicals. The greatest significant reduction is seen with ascorbic acid (A.A.), a superoxide radical ($\bullet O_2^-$) scavenger, leading to just 9.46% breakdown. This big drop shows that superoxide radicals are the most active particles in breaking down Congo Red, followed by hydroxyl radicals, electrons, and then holes.

Table 6: Scavengers trapping experiments versus percent of degradation for CR

Trapping agent	Degradation%	Active species
No scavenger	36.9	—
$Na_2C_2O_4$	32.5	Holes (h_2)
$KBrO_3$	25.3	Electrons (e_2)
Isopropanol (IPA)	16.6	Hydroxyl radicals (•OH)
Ascorbic Acid (A.A.)	9.4	Superoxide radicals ($\bullet O_2$–)

CONCLUSION

The study demonstrates that nanostructured Iraqi bentonite clay (NIBC) is a cost-effective and environmentally friendly catalyst for breaking down Congo Red (CR), a harmful synthetic dye. Glacial acetic acid significantly improved the surface activity and porosity of NIBC during chemical purification. The process of breaking down Congo Red (CR) was improved by using a method called Box-Behnken Design, which looked at how hydrogen peroxide, sodium borohydride, and potassium bromate affected how well CR was removed. The optimal degradation conditions achieved a maximum CR elimination effectiveness of 36.9% at neutral pH and ambient temperature. Scavenger trapping tests showed that superoxide and hydroxyl radicals are the main reactive oxygen species (ROS), while electrons and holes play supporting roles. The modified natural clay offers local resources for eco-friendly water treatment and allows for the breakdown of pollutants using radicals in gentle conditions without expensive catalysts or harsh working environments. Future studies should explore NIBC's reuse, stability, effectiveness against other organic pollutants, and its potential for larger or industrial use. Combining this system with other advanced oxidation processes or mixed treatment methods could improve efficiency and support stronger, more eco-friendly water cleaning systems.

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Conflict of 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.

REFERENCES

1. Elgarahy AM.; Elwakeel KZ.; Mohammad SH.; Elshoubaky GA. A critical review of biosorption of dyes, heavy metals and metalloids from wastewater as an efficient and green process., *Clean Eng Technol.*, **2021**, *4*, 100209.
2. Reghioua A.; Atia D.; Hamidi A.; Jawad AH.; Abdulhameed AS.; Mbuvi HM. Production of eco-friendly adsorbent of kaolin clay and cellulose extracted from peanut shells for removal of methylene blue and congo red removal dyes., *Int J Biol Macromol.*, **2024**, *263*, 130304.
3. Eder E.; Preißinger M. Experimental analysis of the humidification of air in bubble columns for thermal water treatment systems., *Exp Therm fluid Sci.*, **2020**, *115*, 110063.
4. Nishikawa E.; da Silva MGC.; Vieira MGA. Cadmium biosorption by alginate extraction waste and process overview in life cycle assessment context., *J Clean Prod.*, **2018**, *178*, 166-175.
5. Jasri K.; Abdulhameed AS.; Jawad AH.; ALOthman ZA.; Yousef TA.; Al Duaij OK. Mesoporous activated carbon produced from mixed wastes of oil palm frond and palm kernel shell using microwave radiation-assisted K_2CO_3 activation for methylene blue dye removal: Optimization by response surface methodology., *Diam Relat Mater.*, **2023**, *131*, 109581.

6. Abdelaziz MA.; Owda ME.; Abouzeid RE.; Alaysuy O.; Mohamed EII. Kinetics, isotherms, and mechanism of removing cationic and anionic dyes from aqueous solutions using chitosan/magnetite/silver nanoparticles., *Int J Biol Macromol.*, **2023**, *225*, 1462-1475.
7. Kausar A.; Zohra ST.; Ijaz S.; Iqbal M.; Iqbal J.; Bibi I.; Nouren S.; El Messaoudi N.; Nazir A. Cellulose-based materials and their adsorptive removal efficiency for dyes: A review., *Int J Biol Macromol.*, **2023**, *224*, 1337-1355.
8. Patel H.; Yadav VK.; Yadav KK.; Choudhary N.; Kalasariya H.; Alam MM.; Gacem A.; Amanullah M, Ibrahium HA, Park JW. A recent and systemic approach towards microbial biodegradation of dyes from textile industries., *Water*, **2022**, *14*(19), 3163.
9. Al-Tohamy R.; Ali SS.; Li F.; Okasha KM.; Mahmoud YAG.; Elsamahy T.; Jiao H.; Fu Y.; Sun J. A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety., *Ecotoxicol Environ Saf.*, **2022**, *231*, 113160.
10. Al Sharabati M.; Abokwiek R.; Al-Othman A.; Tawalbeh M.; Karaman C.; Orooji Y.; Karimi F. Biodegradable polymers and their nano-composites for the removal of endocrine-disrupting chemicals (EDCs) from wastewater: A Review. *Environ Res.*, **2021**, *202*, 111694.
11. Ali H.; Ismail AM. Fabrication of magnetic Fe_3O_4/ Polypyrrole/carbon black nanocomposite for effective uptake of congo red and methylene blue dye: Adsorption investigation and mechanism., *J Polym Environ.*, **2023**, *31*(3), 976-998.
12. Mukkera VK.; Katuri S. Decolorization of azo dye-contaminated water using microbes: a review. Innov Trends Hydrol Environ Syst Sel Proc ITHES 2021. Published online **2022**, 821-835.
13. Pandey S.; Makhado E.; Kim S.; Kang M. Recent developments of polysaccharide based superabsorbent nanocomposite for organic dye contamination removal from wastewater-A Review. *Environ Res.*, **2023**, *217*, 114909.
14. Madrakian T.; Afkhami A.; Ahmadi M. Simple in situ functionalizing magnetite nanoparticles by reactive blue-19 and their application to the effective removal of Pb^{2+} ions from water samples., *Chemosphere.*, **2013**, *90*(2), 542-547.
15. Ganzenko O.; Huguenot D.; Van Hullebusch ED.; Esposito G.; Oturan MA. Electrochemical advanced oxidation and biological processes for wastewater treatment: A Review of the Combined Approaches., *Environ Sci Pollut Res.*, **2014**, *21*, 8493-8524.
16. Ganzenko O.; Trellu C.; Papirio S.; Oturan N.; Huguenot D.; Van Hullebusch ED.; Esposito G.; Oturan MA. Bioelectro-Fenton: evaluation of a combined biological-advanced oxidation treatment for pharmaceutical wastewater., *Environ Sci Pollut Res.*, **2018**, *25*, 20283-20292.
17. Luo Y.; Guo W.; Ngo HH.; Nghiem LD.; Hai FI.; Zhang J.; Liang S.; Wang XC. A Review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment., *Sci Total Environ.*, **2014**, *473*, 619-641.
18. Shah PD.; Dave SR.; Rao MS. Enzymatic degradation of textile dye Reactive Orange 13 by newly isolated bacterial strain Alcaligenes faecalis PMS-1., *Int Biodeterior Biodegradation.*, **2012**, *69*, 41-50.
19. da Silva MER.; Firmino PIM.; dos Santos AB. Impact of the redox mediator sodium anthraquinone-2, 6-disulphonate (AQDS) on the reductive decolourisation of the azo dye Reactive Red 2 (RR2) in one-and two-stage anaerobic systems., *Bioresour Technol.*, **2012**, *121*, 1-7.
20. de Oliveira DM.; Cavalcante RP.; da Silva L de M.; Sans C.; Esplugas S.; de Oliveira SC.; Junior AM. Identification of intermediates, acute toxicity removal, and kinetics investigation to the Ametryn treatment by direct photolysis (UV254), UV254/H_2O_2, Fenton, and photo-Fenton processes., *Environ Sci Pollut Res.*, **2019**, *26*, 4348-4366.
21. Richardson SD.; Kimura SY. Emerging environmental contaminants: Challenges facing our next generation and potential engineering solutions., *Environ Technol Innov.*, **2017**, *8*, 40-56.

22. Sun Y.; Yang Z.; Tian P.; Sheng Y.; Xu J.; Han YF. Oxidative degradation of nitrobenzene by a Fenton-like reaction with Fe-Cu bimetallic catalysts., *Appl Catal B Environ.*, **2019**, *244*, 1-10.
23. Lyu L.; Han M.; Cao W.; Gao Y.; Zeng Q.; Yu G.; Huang X.; Hu C. Efficient Fenton-like process for organic pollutant degradation on Cu-doped mesoporous polyimide nanocomposites., *Environ Sci Nano.*, **2019**, *6*(3), 798-808.
24. Zhang Y.; Zhang N.; Wang T.; Huang H.; Chen Y.; Li Z.; Zou Z. Heterogeneous degradation of organic contaminants in the photo-Fenton reaction employing pure cubic β-Fe_2O_3., *Appl Catal B Environ.*, **2019**, *245*, 410-419.
25. Matavos-Aramyan S.; Moussavi M. Advances in Fenton and Fenton based oxidation processes for industrial effluent contaminants control-a review., *Int J Environ Sci Nat Resour.*, **2017**, *2*(4), 1-18.
26. Zhou L.; Song W.; Chen Z.; Yin G. Degradation of organic pollutants in wastewater by bicarbonate-activated hydrogen peroxide with a supported cobalt catalyst., *Environ Sci Technol.*, **2013**, *47*(8), 3833-3839.
27. Santos FL.; Giroto AS.; Torres JA.; Oliveira AVPS, e Santos VMF, Nogueira AE. Hydrogen generation via $NaBH_4$ hydrolysis over cobalt-modified niobium oxide catalysts., *Int J Hydrogen Energy.*, **2024**, *92*, 113-123.
28. Almulhem NK.; Awada C.; Shaalan NM. Study of phenol red photocatalytic decomposition on $KBrO_3$-supported TiO_2 nanoparticles for wastewater treatment., *Separations.*, **2023**, *10*(3), 162.
29. Javaid R.; Qazi UY. Catalytic oxidation process for the degradation of synthetic dyes: an overview., *Int J Environ Res Public Health.*, **2019**, *16*(11), 2066.
30. Amin MT.; Alazba AA.; Shafiq M. Adsorptive removal of reactive black 5 from wastewater using bentonite clay: isotherms, kinetics and thermodynamics., *Sustainability.*, **2015**, *7*(11), 15302-15318.
31. Esan OS.; Kolawole AO.; Olumuyiwa AC. The removal of single and binary basic dyes from synthetic wastewater using bentonite clay adsorbent., *Am J Polym Sci Technol.*, **2019**, *5*(1), 16-28.
32. Rouhani H.; Farhadi F.; Kenari MA.; Eskandari E.; Ramakrishna S. Selection of suitable bentonite and the influence of various acids on the preparation of a special clay for the removal of trace olefins from aromatics., *Clay Miner.*, **2021**, *56*(3), 185-196.
33. Wan D.; Li W.; Wang G.; Chen K.; Lu L.; Hu Q. Adsorption and heterogeneous degradation of rhodamine B on the surface of magnetic bentonite material., *Appl Surf Sci.*, **2015**, *349*, 988-996.
34. Sanagi MM. Recent advances in the preparation of oil palm waste-based adsorbents for removal of environmental pollutants-A Review. Malaysian *J Anal Sci.*, **2018**, *22*(2), 175-184.
35. Hu QH.; Qiao SZ.; Haghseresht F.; Wilson MA.; Lu GQ. Adsorption study for removal of basic red dye using bentonite., *Ind Eng Chem Res.*, **2006**, *45*(2), 733-738.
36. Tahir SS.; Rauf N. Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay., *Chemosphere.* **2006**, *63*(11), 1842-1848.
37. Wang CC.; Juang LC.; Hsu TC.; Lee CK.; Lee JF.; Huang FC. Adsorption of basic dyes onto montmorillonite., *J Colloid Interface Sci.*, **2004**, *273*(1), 80-86.
38. Chen B.; Zhu L.; Zhu J.; Xing B. Configurations of the bentonite-sorbed myristylpyridinium cation and their influences on the uptake of organic compounds., *Environ Sci Technol.*, **2005**, *39*(16), 6093-6100.
39. Zhu L.; Zhu R. Surface structure of CTMA+ modified bentonite and their sorptive characteristics towards organic compounds., *Colloids Surfaces A Physicochem Eng Asp.*, **2008**, *320*(1-3), 19-24.
40. Ankita B.; Rakshitha R.; Pallavi N. Degradation of cefixime by photocatalysis via Ba-doped $BiFeO_3$ nanomaterial using RSM analysis under LED light source., *Environ Monit Assess.*, **2024**, *196*(7), 625.
41. Zulfiqar M.; Chowdhury S.; Omar AA.; Siyal AA.; Sufian S. Response surface methodology and artificial neural network for remediation of acid orange 7 using TiO_2-P25: optimization and modeling approach., *Environ Sci Pollut Res.*, **2020**, *27*, 34018-34036.

42. Rakshitha R.; Sinchana HC.; Pallavi N. Assessing the Effectiveness of Coprecipitation -Assisted ZnS/C Nanoclusters in the Photocatalytic Decomposition of 2, 4-dichlorophenoxyacetic Acid Herbicide., *World J Environ Biosci.*, **2025**, *14*(1-2025), 1-9.
43. Rezaei M.; Mengelizadeh N.; Berizi Z.; Salehnia S.; Asgari M.; Balarak D. Synthesis of MMT– $CuFe_2O_4$ composite as a peroxymonosulfate activator for the degradation of reactive black 5., *Chemistry Select.*, **2023**, *8*(2), e202201729.
44. Idrees SA.; Salih RN.; Bashir K.; Hamasaeed AA. Kinetic Study of Congo-Red Photo-Catalytic Degradation in Aqueous Media Using Zinc Oxide as Photo Catalyst Under Led Light., *Sci J Univ Zakho.*, **2021**, *9*(1), 20-24.
45. Xie K.; Zhang H.; Sun S.; Gao Y. Functions of boric acid in fabricating TiO_2 for photocatalytic degradation of organic contaminants and hydrogen evolution., *Mol Catal.*, **2019**, *479*, 110614.
46. Idrees SA.; Jamil LA.; Omer KM. Silver-loaded carbon and phosphorous co-doped boron nitride quantum dots (Ag@CP-BNQDs) for efficient organic waste removal: theoretical and experimental investigations., *ACS omega.*, **2022**, *7*(42), 37620-37628.
47. Idrees SA.; Jamil LA.; Omer KM. Fabrication of novel metal-free phosphorous doped boron nitride as UV. active photo-catalyst., *Iran J Catal.*, **2021**, *11*(4).
48. Ju P.; Wang P.; Li B.; Fan H.; Ai S.; Zhang D.; Wang Y. A novel calcined Bi2WO6/BiVO4 heterojunction photocatalyst with highly enhanced photocatalytic activity., *Chem Eng J.*, **2014**, *236*, 430-437.
49. Ahile UJ.; Wuana RA.; Itodo AU.; Sha'Ato R.; Dantas RF. Stability of iron chelates during photo-Fenton process: The role of pH, hydroxyl radical attack and temperature., *J Water Process Eng.*, **2020**, *36*(October 2019): 101320. doi:10.1016/j.jwpe.2020.101320
50. Tang WZ.; Zhang Z.; An H.; Quintana MO.; Torres DF. TiO_2/UV photodegradation of azo dyes in aqueous solutions., *Environ Technol* (United Kingdom)., **1997**, *18*(1), 1-12. doi:10.1080/09593330.1997.9618466
51. Konstantinou IK.; Albanis TA. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A Review. *Appl Catal B Environ.*, **2004**, *49*(1), 1-14.doi:10.1016/j.apcatb.2003.11.010
52. Ghattavi S.; Nezamzadeh-Ejhieh A. A brief study on the boosted photocatalytic activity of AgI/WO3/ZnO in the degradation of methylene blue under visible light irradiation., *Desalin Water Treat.*, **2019**, *166*, 92-104. doi:10.5004/dwt.2019.24638
53. Nadjia L.; Abdelkader E.; Ahmed B. Photodegradation study of Congo Red in Aqueous Solution using ZnO/UV-A: Effect of pH And Band Gap of other Semiconductor Groups., *J Chem Eng Process Technol.*, 2011, *02*(02), 1-7. doi:10.4172/2157-7048.1000108
54. Simonsen ME. Heterogeneous Photocatalysis. Chem Adv Environ Purif Process Water Fundam Appl., Published online., **2014**, 135-170.doi:10.1016/B978-0-444-53178-0.00004-3
55. Jamil T.; Yasin S.; Ramzan N.; Aslam HMZ.; Ikhlaq A.; Zafar AM.; Aly Hassan A. Bentonite-Clay/CNT-based nano adsorbent for textile wastewater treatment: optimization of process parameters., *Water.*, **2023**, *15*(18), 3197.
56. Sarran MA.; AbdulRazak AA.; Abid MF.; Jawad AD. Oily wastewater treatment using low-cost and highly efficient natural and activated Iraqi bentonite., *Desalin Water Treat.*, **2024**, *319*, 100412.
57. Debnath S.; Ballav N.; Nyoni H.; Maity A.; Pillay K. Optimization and mechanism elucidation of the catalytic photo-degradation of the dyes Eosin Yellow (EY) and Naphthol blue black (NBB) by a polyaniline-coated titanium dioxide nanocomposite., *Appl Catal B Environ.*, **2015**, *163*, 330-342.doi:10.1016/j.apcatb.2014.08.011
58. Idrees SA.; Ibrahim MK. Optimization of Congo-Red Photo-Catalytic Degradation by Central Composite Design. In: 2018 International Conference on Advanced Science and Engineering (ICOASE)., **2018**, 389-393. doi:10.1109/ICOASE.2018.8548919

59. Molla-Babaker MM.; Idreesb SA. Degradation of Congo Red Dye Using Homogeneous Photo Fenton Catalyst Coupled with Oxygen Kinetics and Statistical Analysis., *Asian J Appl Chem Res*., **2020**, *6*(1), 1-9.doi:10.9734/ajacr/2020/v6i130147

60. Berkani M.; Kadmi Y.; Bouchareb MK.; Bouhelassa M, Bouzaza A. Combinatıon of a Box-Behnken design technique with response surface methodology for optimization of the photocatalytic mineralization of C.I. Basic Red 46 dye from aqueous solution., *Arab J Chem*., **2020**, *13*(11), 8338-8346.doi:10.1016/j.arabjc. 2020.05.013

61. Chaker H.; Ameur N.; Saidi-Bendahou K.; Djennas M.; Fourmentin S. Modeling and Box-Behnken design optimization of photocatalytic parameters for efficient removal of dye by lanthanum-doped mesoporous TiO_2., *J Environ Chem Eng*., **2021**, *9*(1), 104584. doi:10.1016/j.jece.2020.104584