

Evaluation and Optimization of Synthesized Silica Nanocomposite for Degradation of Methylene Blue Dye Using Response Surface Methodology

¹Samina Gull, ²Naeem Abbas, ³Mohsin Raza, ⁴Najma Ameer

⁵Mian Habib-ur-Rehman Mahmood and ⁶Muhammad Hammad Khan

¹Department of Chemistry, Division of Science and Technology, University of Education, Lahore, Pakistan.

^{2,6}Center for Environmental Protection Studies, PCSIR Laboratories Complex, Lahore, Pakistan.

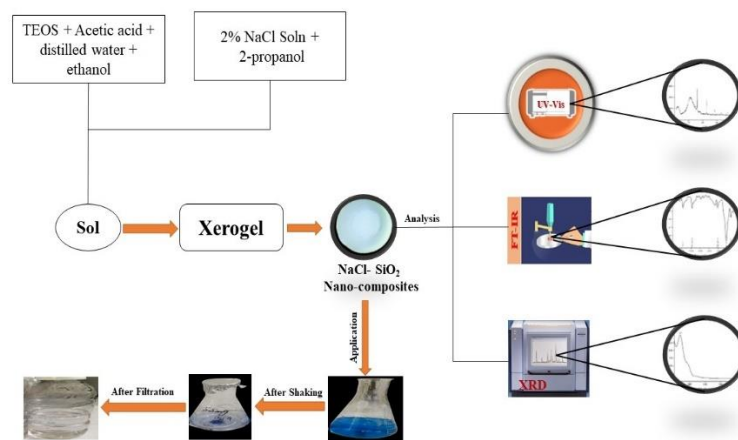
^{3,4,5}Department of Chemistry, Division of Science and Technology, University of Education, Lahore, Pakistan.

saminagull28@gmail.com*

(Received on 25th April 2025, accepted in revised form 18th May 2025)

Summary: Effective wastewater treatment for synthetic dyes is crucial for environmental sustainability attributed to the toxic nature and persistence of these pollutants. Methylene blue (MB), a widely used synthetic dye that can contribute to severe environmental concern if not properly removed from wastewater. Nanomaterials have emerged as highly efficient agents for degrading MB offering a promising solution for wastewater treatment. NaCl-SiO₂ NCs were synthesized through the sol-gel method. The successful formation of the composite was also confirmed by characterization results, with X-ray Diffraction (XRD) patterns showing the presence of a combination of crystalline NaCl and amorphous SiO₂ phases and Fourier Transform Infrared (FTIR) spectroscopy showing the presence of key functional groups, silanols (Si-OH) at 1043 cm⁻¹ and Si-O-Si at 796 cm⁻¹, which are crucial to dye adsorption. The degradation of MB in aqueous solution was used in these nanocomposites. Response Surface Methodology (RSM) was used to optimize processes through a Central Composite Design (CCD) to assess the effect of nanocomposites dose, contact time, and pH. Optimal conditions were considered to be the highest percentage (97.2%) of MB degradation at a nanocomposite dose of 100 mg/50 mL, pH 6, and a contact time of 140 minutes. This suggests that NaCl-SiO₂ nanocomposites are a good, eco-friendly substance that can be used to effectively degrade dye in wastewater treatment and has a high possibility of large-scale applications.

Graphical Abstract



Keywords: Wastewater treatment; Nanocomposites; Sol-gel; Methylene blue; Response surface methodology.

Introduction

Urbanization and industrialization have led to a significant rise in wastewater production containing substantial amounts of heavy metals and synthetic dyes. Industries like distillation plants, leather factories, clothing, and others generate detrimental

effluent that must be cleaned to prevent negative consequences, directly affecting the environment and human well-being. Ensuring the secure and economical disposal of industrial wastes is considered a fundamental goal for both advanced and emerging

*To whom all correspondence should be addressed.

countries [1]. Significant type of industrial waste that is extensively utilized in a variety of sectors, such as those dealing with cotton, timber, food, etc. Releasing colors into water, even in small amounts, will have detrimental effects on all aquatic creatures, including animals and humans [2]. These dyes are toxic, cancer-causing, mutation-inducing, and non-biodegradable compounds that can endure in the environment for long periods. MB, a synthetic cationic dye, has found extensive use in the textile, tannery, plastics, paper, and paint industries. Nevertheless, MB can induce skin irritation, allergic reactions, ocular burns, and carcinogenesis in humans due to its hazardous properties [3]. There has been a significant focus in recent decades on creating appropriate materials and techniques for effectively degrading MB [4]. Different approaches, including adsorption, extracting solvent, combustion, and photocatalytic decomposition have been studied for the cleaning of water contaminated with these harmful compounds [5]. However, these technologies possess several drawbacks, including an inefficient treatment procedure, necessity for costly equipment, heightened labour and supervision demands, reliance on chemical reagents, and the generation of sludge or solid waste that requires separate disposal. These approaches have demonstrated their inefficiency in tackling the significant need for water resources, especially when dealing with considerable quantities [6]. New adsorbent materials that are capable of successfully removing dangerous dyes from wastewater, like MB, have been discovered, according to reports that have been made throughout this year [7]. Cost-effective and naturally occurring siliceous adsorbents include quartz, glass fibres, and perlite. They possess favourable Compatibility with living organisms and exceptional efficiency without poisonousness [8]. These properties make them very suitable for a wide range of applications, including separation processes. SiO₂-nanocomposites (NCs) are widely utilized in the food sector, pharmaceuticals, and in water treatment systems. These potentials are attributed to their low toxicity, ready availability, methods of synthesis that are beneficial for environment, and economic, and biological activity [9]. Several recent studies highlighted significant advancements in the field of silica-based nanocomposites. These studies have demonstrated exceptional ability of synthesized, functionalized, and hybrid SiO₂-NCs to effectively adsorb various dyes, showcasing their impressive adsorption capacities [10]. Presence of surface hydroxyl (-OH) groups attached to the silicon atom on silicon dioxide (SiO₂-NCs) is an essential characteristic and is referred to as silanols [11]. The silanols can selectively interact with dyes and can be enhanced by altering the pH levels. Sodium chloride

(NaCl) is a widely recognized hygroscopic substance that is frequently employed as an adsorbent [12]. The study focused on synthesis of NaCl-SiO₂ NCs, which were subsequently employed for the degradation of MB from aqueous solution. Prior research involved the alteration of silica nanocomposites using discontinuous procedures that involved multiple steps and necessitated the use of costly chemicals. Hence, in our current investigation, NaCl, renowned for its hygroscopic properties and its ability to adsorb, was incorporated into silica nanocomposites using the sol-gel method to produce NaCl-SiO₂ NCs. Subsequently, synthesized NCs were analyzed using UV-visible spectroscopy, FTIR, and XRD techniques to determine their properties. These NCs were then applied for the degradation of MB from aqueous solutions. Prior research has shown that SiO₂ NCs are highly effective as adsorbing a wide range of contaminants from water-based solutions. Nevertheless, the utilization of NaCl-SiO₂ NCs for degradation of pollutants, namely organic dyes such as MB, has not been extensively investigated. The objective of this research is to thoroughly examine the adsorption capabilities of NaCl-SiO₂ NCs.

Though some studies had involved the use of pure silica (SiO₂) or other metal-oxide nanocomposites in the removal of dye, this study is the only one that examines synergistic integration of NaCl in a SiO₂ matrix composed through a controlled sol-gel method. In contrast to the traditional approaches which usually require costly dopants or multi-step functionalization, the NaCl structural and ionic modifier is an inexpensive and efficient pathway to increase degradation of cationic dyes. This paper offers a detailed optimization through Response Surface Methodology (RSM), namely closing the material synthesis to industrial applicability since it gives the exact interactions of ionic strength on MB degradation.

Experimental

NaCl (Sodium chloride), C₃H₈O (2-propanol), TEOS (tetraethyl orthosilicate), acetic acid (CH₃COOH) and ethanol (CH₃CH₂OH) were procured from Sigma-Aldrich Germany. All chemicals were of analytical grade and used without further purification.

Synthesis of NaCl- SiO₂ NCs

Two different methods were used to synthesize NaCl-SiO₂ NCs, with minor adjustments [13]. (i) The objective of optimizing the NaCl solution was to decrease the size of the composites, and (ii) by

coating the NaCl with silicon dioxide (NaCl-SiO₂) [12]. The optimization technique involved preparing an aqueous solution of NaCl at a concentration of 2% w/v. Afterward, 20 mL of the NaCl solution was added to 60 mL of 2-propanol while continuously stirred for 2 hours. To synthesize the SiO₂ solution, 18 mL of TEOS was gradually added to 30 mL of acetic acid, then 6.4 mL of distilled water and 20 mL of ethanol were added while vigorously stirring for four hours. Afterward, the previously made NaCl solution, which had been optimized, was added to the SiO₂ solution. Subsequently, the agitation was sustained for an extra two hours at a rate of 250 revolutions per minute (rpm). The pH of the reaction mixture was maintained at 2-3. A sol was prepared and allowed to stand overnight to form a gel through evaporation. Subsequently, the gel was subjected to further drying by heating at 80°C for three hours, resulting in a dry xerogel. This xerogel was then isolated using centrifugation. These were then carefully collected for further analysis. The synthesis was finalized by a calcination step conducted at 600°C for two hours.

Characterization of NaCl- SiO₂ nanocomposites (NaCl-SiO₂ NCs)

To analyze chemically synthesized NCs, FTIR spectroscopy was employed to evaluate their purity, XRD analysis for structural determination (crystal or amorphous) and UV-visible spectroscopy to identify of NaCl- SiO₂ NCs.

UV-Visible Spectroscopy

UV-Vis spectroscopy was employed to investigate influence of particle size on electronic absorption behavior. This technique serves as valuable tool determining desired compounds in sample [14]. The UV-Vis method was proven to be an analytical method. Limit of Detection (LOD) and Limit of Quantitation (LOQ) of MB were determined based on the slope of the calibration curve (S) and standard deviation of response (σ) to determine LOD and Limit of Quantitation, respectively, which were $3.3(\sigma/S)=3.3$ and $10(\sigma/S)=10$. The LOD was calculated as 0.042 mg/L and the LOQ was 0.128 mg/L and this showed the high sensitivity of the method used in the determination of residual dye concentrations.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is used to generate IR spectra, revealing transmission or absorbance various compounds within a sample. Functional groups present in sample can be recognized based on their infrared absorption frequencies within 600-4000 cm⁻¹ range

through automated spectral analysis. Additionally, FTIR aids categorization of synthesized compounds by correlating obtained data with literature references [15].

X-ray Diffraction Analysis (XRD)

XRD analysis helps to identify crystal phase structure of target compound. This technique was applied investigate crystalline structure, crystalline grain size, lattice parameters and amorphous phase structure of silica nanocomposites [16].

Application of synthesized SiO₂-NaCl nanocomposites

The synthesized nanocomposites were evaluated for their ability to degrade color of MB from aqueous solutions. For this purpose, a standardized MB solution was prepared by running 0.1 g of MB in 1 L of distilled water, followed by a preliminary analysis to assess the sample's characteristics and determine suitable treatment strategies. The absorbance was measured using UV-visible spectroscopy (SPECORD 200) at the wavelength of maximum absorption (λ max) of 664 nm, both before and after treatment.

Formation of solutions on the basis of pH

At first 50 mL standard solution was utilized which was categorized into three groups according to different pH levels, contact times, and dosages. The solution was classified based on different pH levels to investigate the pH at which MB degradation was maximized. 10% hydrochloric acid (HCl) and 10% sodium hydroxide (NaOH) solutions were used to regulate the pH.

Batch experiment

Trial reactions were conducted determine the efficacy of NaCl-SiO₂ NCs for degradation of MB from an aqueous solution. Among these batch experiments conducted, it was observed that synthesized NCs showed maximum degradation efficiency at dosage of 100 mg along with contact time of 140 minutes at pH 6.

$$\% \text{ MB degradation} = \frac{\text{Initial}-\text{Final}}{\text{Initial}} \times 100 \quad (1)$$

Following the initial batch experiments, parameters optimization was conducted.

Optimization

The process of optimizing multiple parameters, such as pH, dose of NaCl-SiO₂ NCs, and shaking duration, was conducted using Design Expert software

version 13.0.5.0. To achieve this optimization, the approach of central composite design (CCD) was utilized. The experimental runs were carried out in a total of 20 experimental runs as required by Central Composite Design (CCD). This particular number of runs, which includes 8 factorial points, 6 axial points and 6 center points, had been chosen to have an adequate degree of freedom to estimate only quadratic terms and high statistical power in the ANOVA model. The ranges of the parameters (pH 3 -9, dose 10 -100 mg, time 60 - 140 min) were decided on the basis of preliminary experiments of the one-factor-at-a-time (OFAT) that the highest degradation transition is observed within these parameters. The concentration of the dye 0.1 g/L was chosen because this is similar to the concentration of effluent that is common in the textile finishing and printing industries.

Response Surface Methodology

Conventional optimization techniques usually modify individual variables independently, without effectively accounting for the complex relationships between various factors and their impact on response [17]. In contrast, Response Surface Methodology (RSM) is a powerful statistical tool used to model and analyze process where multiple variables affect a response of interest. It enables the simultaneous optimization of multiple responses by employing mathematical and

statistical techniques such as polynomial equations derived from experimental data. RSM follows a structural approach consisting of four essential stages: experimental design, model fitting, model validation and condition optimization [18]. These steps allow for a systematic investigation of experimental domain while ensuring adequacy of the proposed model. Additionally, RSM provides reliable estimates of experimental variability (pure error), identifies potential lack of fit and predicts response even in experimental regions where direct measurement are not conducted. Among various experimental designs used in RSM, three-level full factorial designs and central composite designs (CCD) are commonly employed to simplify the optimization of complex processes. These approaches facilitate the identification of significant interactions between factors and their relative impact on the response. In this study, RSM was utilized to determine most influential parameters affecting the degradation efficiency of MB using NaCl-SiO₂ NCs. The key variables investigated included contact time, pH of the solution and dosage rate, with objective of optimizing these parameters to achieve maximum degradation efficiency.

Parameters used

Three process factors were analyzed using the central composite design; Table-1 shows the numerical range of each of these factors.

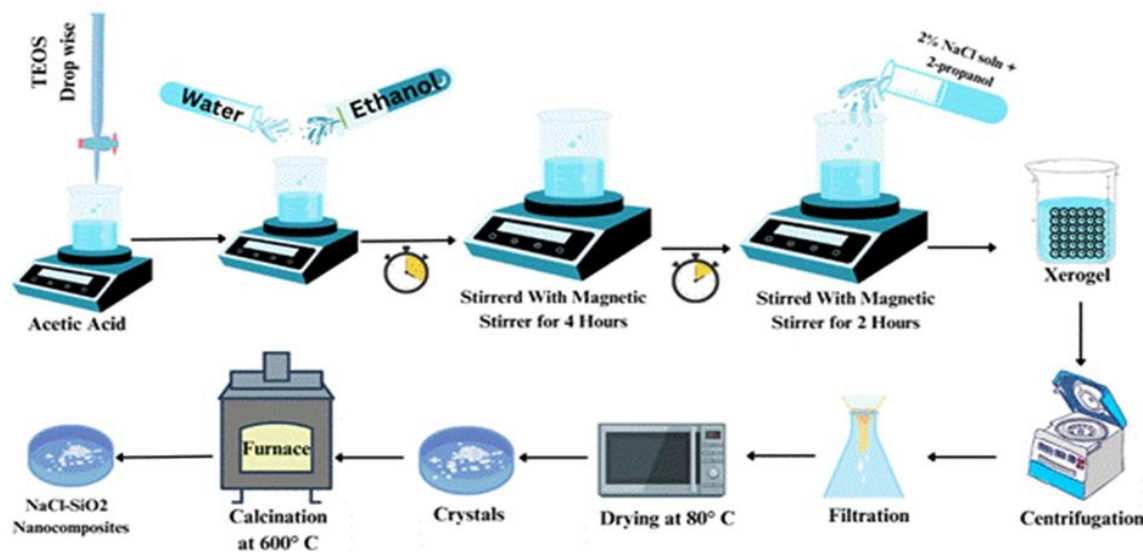


Fig1: Synthesis of NaCl-SiO₂ nanocomposites.

Table-1: Different optimization parameters and their corresponding ranges.

Parameters	Units	-1 level	+1 level	-alpha	+ alpha
Dose	mg	10	100	5	105
pH	-	4	8	3	9
Shaking time	Minutes	60	120	40	140

The impact of these numerical elements was observed on a single answer to optimize conditions. The response was: degradation of MB. It was determined that synthesized NCs showed maximum degradation efficiency.

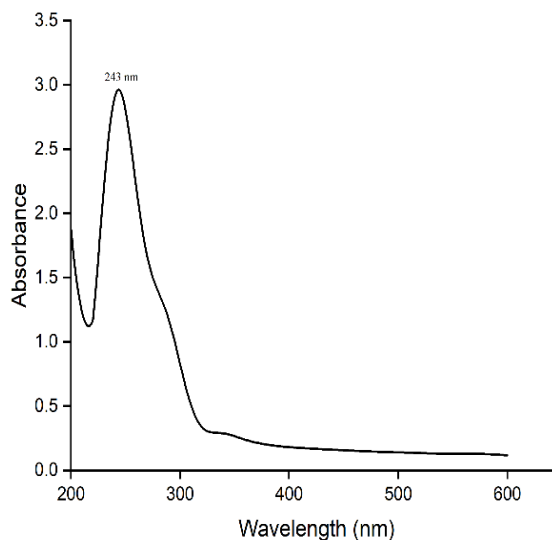
Results and Discussions

Methyl orange (an anionic dye) was tested by using degradation tests to determine the selectivity of the NaCl-SiO₂ NCs. The degradation was determined to be insignificant (<15%). This ascertains that the substance is very selective for cationic species. Since the NC surface is repelled at the neutral to basic pH, anionic dyes such as Methyl Orange are electrostatically repelled whereas the cationic MB is strongly attracted to the NC surface.

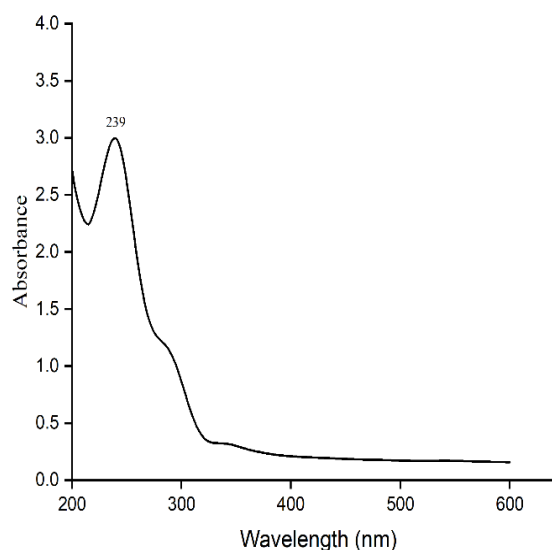
Electrostatic attraction is the main cause of the degradation mechanism. At pH 6 (the optimal pH), the SiO₂-NaCl nanocomposite surface is deprotonated forming a surface of negatively charged species (Si-O⁻). MB molecule, being cationic dye and thus strongly drawn to these sites. This process is improved by the presence of NaCl which increases the ionic strength of the micro-environment which decreases the thickness of the electrical double layer thus enabling the dye molecules to approach the silica surface closer. In addition, the nitrogen atoms of MB hydrogen bond with the silanol groups (Si-OH) on the NC surface before degradation takes place.

UV-Visible spectroscopy

The influence of particle size on electronic absorption behavior of NaCl-SiO₂ nanocomposites was evaluated using UV-visible spectrophotometer. UV-vis absorption spectra of Pure Silica and synthesized NaCl-SiO₂ NCs as shown in Fig 2 (a-b). The absorption spectra of pure silica NCs exhibit peak at 243nm while peak at 239nm demonstrating blue shift of NaCl-SiO₂ NCs, closely aligns with the values reported in the literature [19, 20]. The absorption spectra at 243 nm confirmed successful formation of silica nanocomposites. Na⁺ and Cl⁻ ions might interfere the synthesis of SiO₂ NCs. It was observed that presence of Na⁺ ions resulted in reduced composites size, as they disrupt the Si-O-Si chain network hindering polymerization. Cl⁻ ions may enhance hydrolysis-condensation balance during synthesis process leading to the smaller NCs [21]. The reduction in size of the composite increases adsorption capacity of the MB.



(a)



(b)

Fig2: UV spectra of (a) pure silica NCs and (b) NaCl-SiO₂ NCs

FTIR spectroscopy

The FTIR spectra of pure and synthesized silica composites were recorded within range 500-4000 cm⁻¹. Sharp peaks for pure silica NCs were observed at 3438.57 cm⁻¹, 2932.96 cm⁻¹, 1526.12 cm⁻¹, 1049.24 cm⁻¹, and 798.90 cm⁻¹ as illustrated in Fig 3(a). In contrast, sol-gel synthesized NaCl-SiO₂ NCs exhibited major peaks at 3467 cm⁻¹, 1819 cm⁻¹, 1525 cm⁻¹, 1043 cm⁻¹ and 796 cm⁻¹ as presented in Fig 3(b). Reported values which are closely aligned with our obtained result [12, 22]. The peak at 1043 cm⁻¹ of synthesized nanocomposites assign to the stretching

vibrations of Si-OH. The band 3467 cm^{-1} and 1525 cm^{-1} correspond to Si-OH stretching and bending vibrations respectively. A distinct peak at 3687 cm^{-1} represents Si-OH stretching mode of germinal silanol groups. The peak at 796 cm^{-1} associated to Si-O-Si stretching vibration mode. The peak at 1525 cm^{-1} is likely attributed to water or moisture absorption further indicating the hygroscopic nature of the SiO_2 composite formation. Si-OH and Si-O-Si functional groups confirmed by FTIR spectrum shown in the Fig 3(b), which impart crucial role for the adsorption of dye such as MB. Si-O⁻ group interact with positively charged dye molecule through electrostatic attraction resulting in enhanced adsorption efficiency [23].

XRD analysis

The X-ray diffraction (XRD) pattern in Fig 4 which indicates that the composite is hybrid. The wide peak at around $2\theta = 22^\circ$ is typical of the amorphous silica network, and the sharp and intense peaks at 27.3° , 31.6° and 45.4° are features of the (111), (200) and (220) planes of the crystalline NaCl (FCC structure) [24]. The sharp peaks of NaCl that remain in the SiO_2 matrix indicate NaCl retains its crystalline form, but is physically enclosed or dispersed in the porous amorphous silica shell, giving the required ionic environment to increase the interaction of the dye [25].

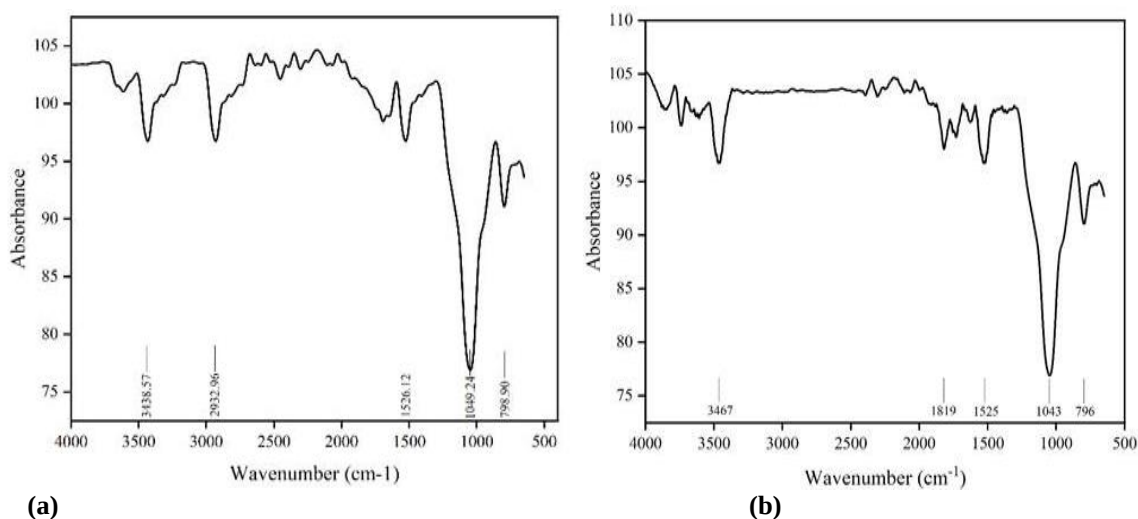


Fig3: FTIR spectra of (a) pure silica NCs and (b) NaCl- SiO_2 NCs.

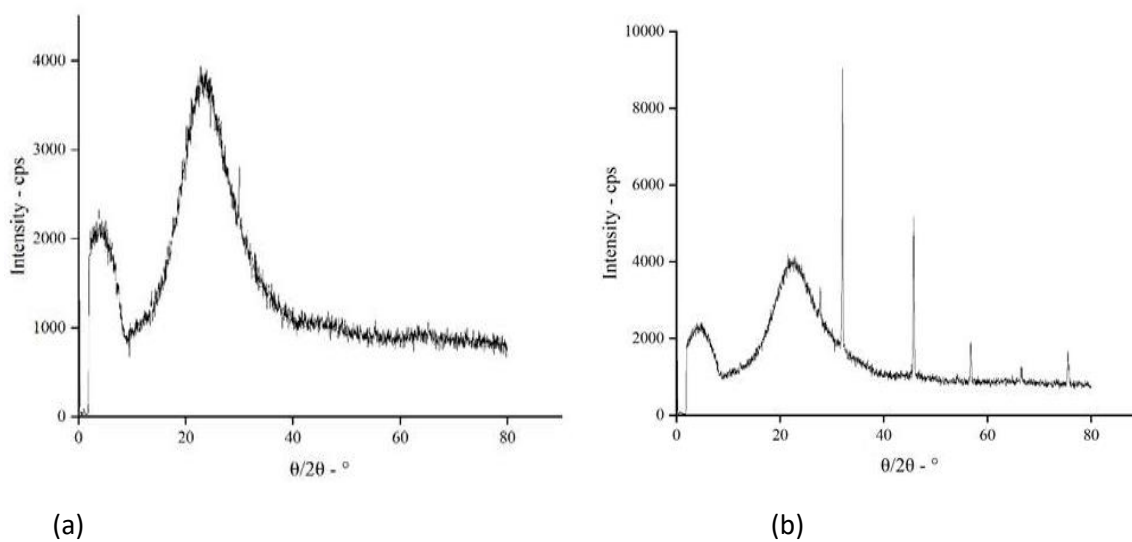


Fig4: XRD graph for (a) pure silica NCs and (b) NaCl- SiO_2 NCs.

Table-2: Reaction scheme and experimentally observed results.

Run	Factor 1 A: NaCl-SiO ₂ Nanocomposites (mg)	Factor 2B: pH	Factor 3C: shaking time (min)	Response 1: MB degradation %
1	5	6	90	83.82
2	10	4	60	84.70
3	10	4	120	85.30
4	10	8	60	85.70
5	10	8	120	87.60
6	55	3	90	93.98
7	55	6	40	94.20
8	55	6	90	94.40
9	55	6	90	94.50
10	55	6	90	94.50
11	55	6	90	94.64
12	55	6	90	94.70
13	55	6	90	94.82
14	55	9	90	94.99
15	100	8	60	95.60
16	105	4	60	95.60
17	100	4	120	96.01
18	55	6	140	96.10
19	100	8	120	96.60
20	100	6	140	97.20

Table-3: SMSS for MB degradation.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Suggested / Aliased
Mean vs Total	1.720E+05	1	1.720E+05			
Linear vs Mean	296.39	3	98.80	19.34	< 0.0001	
2FI vs Linear	1.27	3	0.4222	0.0682	0.9759	
Quadratic vs 2FI	80.15	3	26.72	793.20	< 0.0001	Suggested
Cubic vs Quadratic	0.2171	5	0.0434	1.81	0.2648	Aliased
Residual	0.1197	5	0.0239			
Total	1.724E+05	20	8621.10			

Experimental

NaCl-SiO₂ NCs were utilized in this experiment for degradation of MB dye from wastewater. Design Expert software was used to generate experimental design based on specific process variables. All experiments were conducted following an approved experimental protocol to ensure accuracy and reproducibility. The recorded responses are accompanied by each set of process parameters, as shown in Table-2.

Degradation of MB

The RSM analysis revealed a quadratic model, demonstrating that MB degradation efficiency improved with increasing concentration of NaCl-SiO₂ NCs and prolonged shaking time. Highest degradation efficiency of 97.20% was achieved at NCs concentration of 100 mg with a shaking time of 120 minutes at pH 6.

Sequential Model Sum of Squares (SMSS)

The experimental response was analyzed using quadratic model which effectively describes the relationship between process parameters and MB degradation efficiency. The results of SMSS analysis depicted in table 3.

The SMSS analysis confirms that the quadratic model is most suitable for predicting degradation of MB. It is statistically significant (F= 793.20, P < 0.0001) and recommended for further analysis. On the other hand, cubic model is aliased (P = 0.2648), indicating redundancy and overfitting. Although linear model is significant (F = 19.34, P < 0.0001) but less accurate than quadratic model. While two factor interaction (2FI) model is not significant (P = 0.9759), suggesting minimal interaction effects. Low residual sum of squares (0.1197) further supports the strong predictive ability of quadratic model. Therefore, quadratic model is most reliable for process optimization whereas cubic model is unsuitable and interaction effects are negligible.

Analysis of Variance (ANOVA) for a Quadratic model

ANOVA identifies significant factors influencing a response by analyzing variance within and between groups. It distinguishes real effects from random variations, aiding hypothesis testing and data analysis. Iravani et al., highlighted that key measures – F-statistics, P-values and effect size- ensure accurate interpretation by assessing variability, significance and effect magnitude [26]. For this study ANOVA was conducted as depicted in Table-4.

Table-4: ANOVA for MB degradation.

Source	Sum of Squares	Df	Mean Square	F-value	p-value	Final Response
Model	377.80	9	41.98	1246.35	< 0.0001	Significant
A-NaCl-SiO ₂ nanocomposites	258.52	1	258.52	7675.71	< 0.0001	Significant
B-pH	2.10	1	2.10	62.25	< 0.0001	Significant
C-shaking time	3.97	1	3.97	117.81	< 0.0001	Significant
AB	1.14	1	1.14	33.97	0.0002	Significant
AC	0.2214	1	0.2214	6.57	0.0282	Significant
BC	0.5887	1	0.5887	17.48	0.0019	Significant
A ²	72.14	1	72.14	2141.93	< 0.0001	Significant
B ²	0.0022	1	0.0022	0.0662	0.8021	Not significant
C ²	0.8420	1	0.8420	25.00	0.0005	Significant
Residual	0.3368	10	0.0337			
Lack of Fit	0.2171	5	0.0434	1.81	0.2648	Not significant
Pure Error	0.1197	5	0.0239			
Cor Total	378.13	19				

The Model F-value of 1246.35 indicates that model is highly significant, with an extremely low probability ($P < 0.0001$) that this result is due to random noise. This confirms that selected factors significantly influence MB degradation. In this analysis, P-values below 0.0500 indicate statistically significant model term. The factors A (NaCl-SiO₂ nanocomposites), B (pH), C (shaking time), AB, AC, BC, A² and C² are significant contributors to the response while B² ($P = 0.8021$) is not, suggesting that quadratic effect of pH is negligible.

The lack of fit F-values of 1.81 is not significant ($P = 0.2648$), indicating that model adequately describe the data. The high P-value suggests that variation observed is likely due to pure error rather than a poor model fit. This confirms that model is suitable for predicting MB degradation under the given experimental conditions.

The Predicted R² value (0.9947) is closely aligned with the Adjusted R² value (0.9983), with a difference of less than 0.2 as shown in Table 5, indicating a strong model fit. Adeq Precision measure signal-to-noise, with a recommended threshold of 4. In this model, a ratio of 100.560 signifies a strong signal, confirming its reliability. Therefore, this model is well-suited for exploring design space effectively.

Table 5: Fit Statistics

Std. Dev.	0.1835	0.1940	R ²	0.9991
Mean	92.75	92.72	Adjusted R ²	0.9983
C.V. %	0.1979	0.2093	Predicted R ²	0.9947
			Adeq Precision	100.5604

The equations that express reduction of color in terms of coded and real components are denoted as Equation 1 and Equation 2, respectively.

Equation expressed in terms of the coded factors

$$\text{Color} = +94.56 + 5.14 * A + 0.4098 * B + 0.5138 * C - 0.3736 * AB - 0.1497 * AC + 0.2715 * BC - 3.89 * A^2 - 0.0156 * B^2 + 0.2424 * C^2 \quad (2)$$

Equation expressed in terms of the actual factors

$$\begin{aligned} \text{Color} = & +82.26368 + +0.360346 * \text{NaCl-SiO}_2\text{nanocomposites} + 0.072737 * \text{pH} - 0.052409 * \\ & \text{shaking time} - 0.004151110 * \text{NaCl-SiO}_2\text{nanocomposites} * \text{pH} - 0.000111 * \text{NaCl-SiO}_2\text{nanocomposites} * \text{shaking time} + 0.004526 * \text{pH} * \text{shaking time} \\ & - 0.001920 * \text{NaCl-SiO}_2\text{nanocomposites}^2 - 0.003903 * \text{pH}^2 + 0.000269 * \text{shaking time}^2 \quad (3) \end{aligned}$$

Actual values refer to the values obtained from experiments conducted under optimum settings as specified in Table 2. Predicted values, on the other hand, are values derived by the RSM based on the actual values provided. Fig 5 displays a graph that compares the projected values with the actual values, as stated in Table-6.

Table-6: Report comparing actual values with expected values.

Run Order	Actual Value	Predicted Value	Residual	Leverage
1	1	94.50	94.56	-0.0615
2	2	97.20	97.10	0.1027
3	3	94.20	94.38	-0.1784
4	4	95.60	95.44	0.1556
5	5	94.70	94.56	0.1385
6	6	85.70	85.61	0.0939
7	7	87.60	87.48	0.1238
8	8	95.60	95.63	-0.0327
9	9	94.82	94.56	0.2585
10	10	94.99	95.14	-0.1511
11	11	85.30	85.37	-0.0664
12	12	94.50	94.56	-0.0615
13	13	96.60	96.72	-0.1157
14	14	96.10	96.09	0.0088
15	15	96.01	96.10	-0.0902
16	16	83.82	84.05	-0.2276
17	17	94.64	94.56	0.0785
18	18	84.70	84.58	0.1176
19	19	93.98	93.91	0.0684
20	20	94.40	94.56	-0.1615

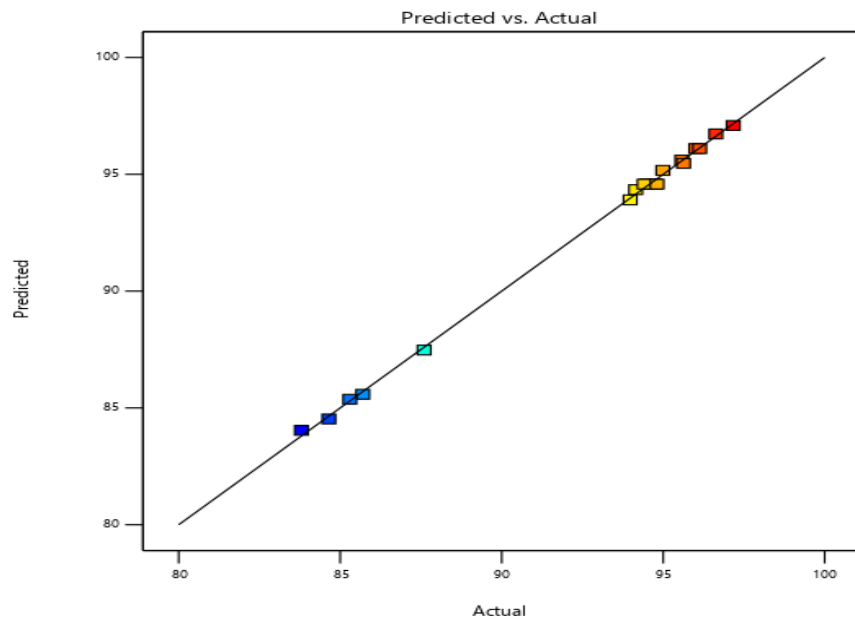


Fig5: Plot showing expected vs. actual MB degradation rate.

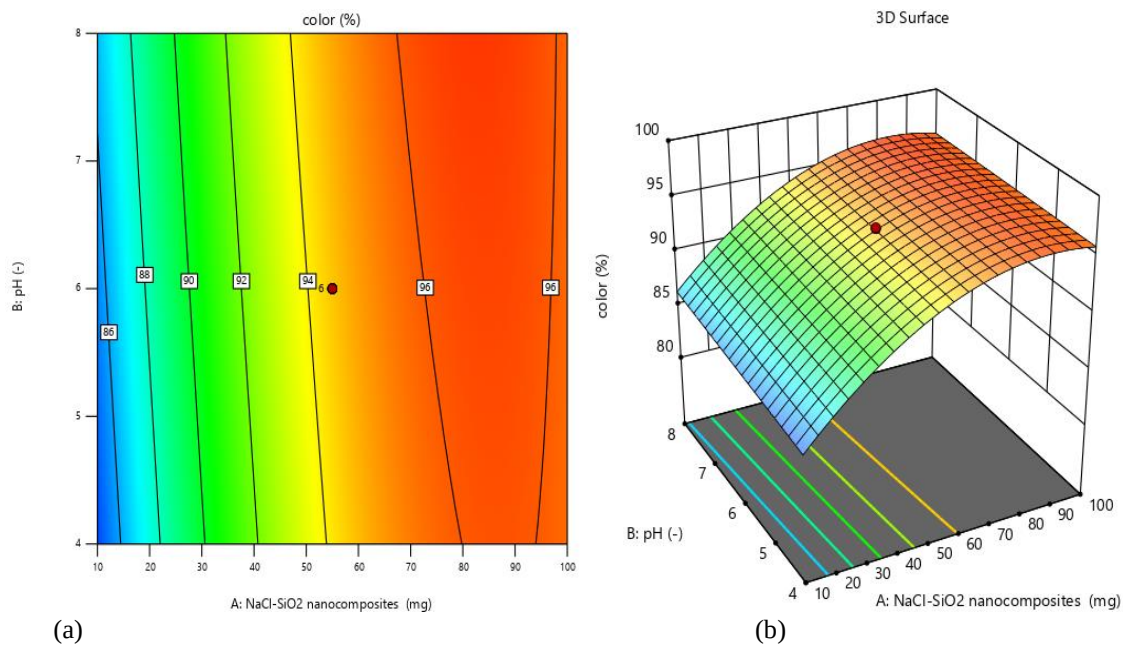


Fig6: (a) Contour graph and (b) 3D surface graph for outcome of NCs and pH on color reduction.

Table-1: Comparison of MB Degradation with Other Methods.

Material	Efficiency (%)	Conditions	Relative Cost	Ref
Pure SiO ₂	72.5%	pH 7, 180 min	Low	[27]
Bio-sorbent (Rice Husk)	84.0%	pH 8, 120 min	Very Low	[28]
TiO ₂ Nanoparticles	95.2%	UV light, 90 min	High	[29]
NaCl-SiO ₂ NCs	97.2%	pH 6, 140 min	Low	This Study

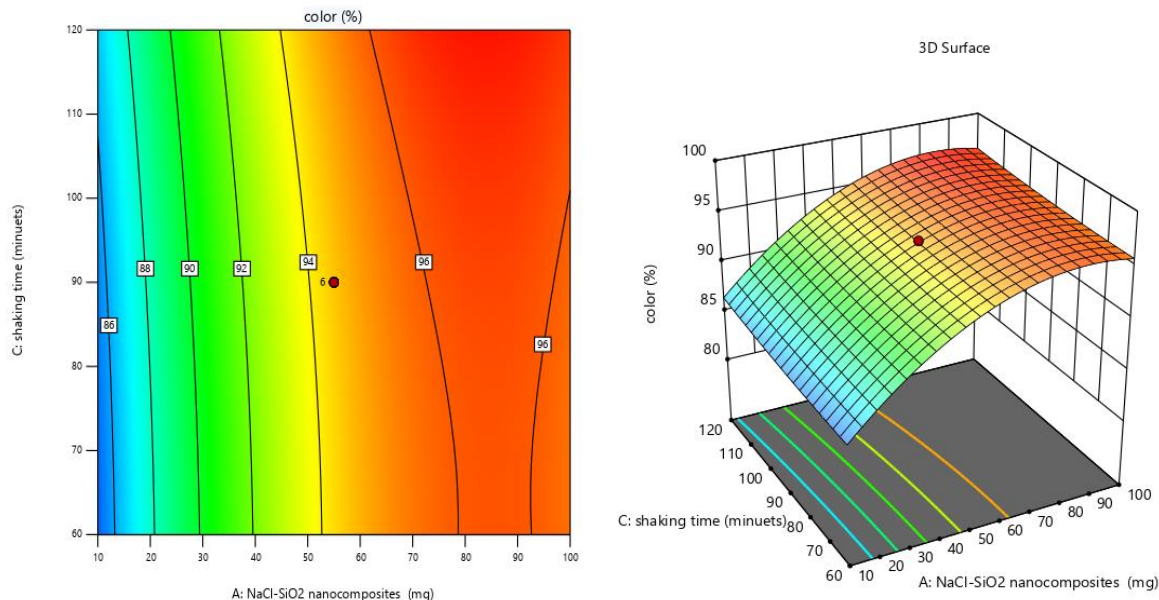


Fig2: The contour and 3D surface graph visually represent the impact of various factors on the percentage of MB degradation. Specifically, it shows how the dosage of nanocomposite (parameter a) and the shaking duration (parameter c) affect the MB degradation percentage.

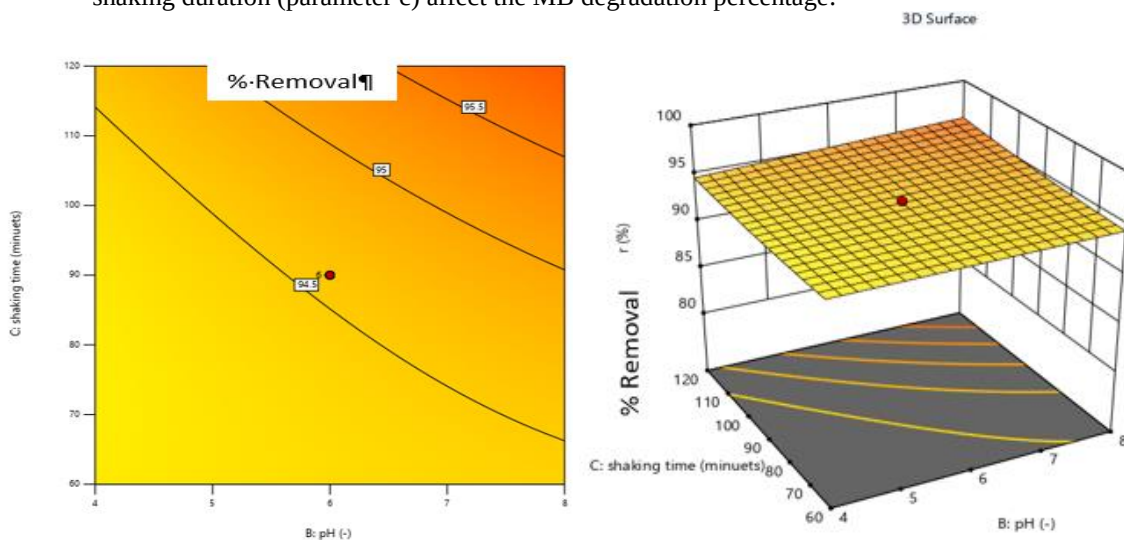


Fig8 The contour and 3D surface graph visually represent the impact of several factors on the percentage of MB degradation, specifically the influence of shaking time (b) and pH (c) on the MB degradation percentage.

Comparison with other methods

Model Graphs

The provided graphs indicate the combined impact of the process variables on the analyzed response, using both 2D contour and 3D surface representations. The visual illustrations summarized

the information in a clear and readily understandable way.

Fig 6. illustrated the impact of NaCl-SiO₂ NCs and pH on MB degradation. It was observed that increasing NCs dosage at a pH of approximately 6 significantly enhanced MB degradation. Conversely, at the minimal nanocomposite dosages and higher pH values, the reduction in MB was least pronounced.

Furthermore, increasing dosage beyond a certain point had little impact on MB degradation at elevated pH levels.

Fig 7. Examined the impacts of nanocomposite dosage and shaking duration on MB degradation. Extending the shaking time from 80 to 100 minutes resulted in a notable enhancement in MB degradation from 86% to 96%. Furthermore, increasing the dosage of NCs led to an improvement in MB degradation efficacy.

Fig 8. illustrate the effects of pH and shaking duration on MB degradation. There was a positive correlation between an increase in pH and an improvement in degradation of MB effectively. In addition, increasing the shaking time from 60 to 120 minutes led to a slight improvement in MB degradation, with the percentage increasing from 94.5% to 95.5%.

Effect of Reaction parameters on MB adsorption

The adsorption process of MB utilizing NaCl-SiO₂ NCs is highly influenced by pH, contact duration, and dose. These characteristics are critical for optimizing MB degradation [30]. Changing the pH of the solution can significantly influence the rate of MB adsorption. The absorption efficiency of MB increases proportionally as the pH level rises; MB's absorption efficiency increases proportionally. At pH 6, the NCs achieved a maximum degradation efficiency of 97.2% for MB. Sodium chloride (NaCl) enhances the ionic strength of the solution. Increased ionic strength reduces the electrostatic repulsion between entities with the same charge in a solution, such as dye molecules. The negatively charged surface areas of the SiO₂ NCs may interact more strongly with the positively charged MB molecules because they have a higher ionic strength. At pH values over 8, the presence of OH anions from NaOH likely reduced the degradation effectively [31]. Due to the presence of these anions, they have the potential to hinder the electrical adhesion between the NaCl-SiO₂ NCs and MB molecules, by neutralizing the positive charges present on the surfaces of the MB molecules.

Despite the increase in contact duration from 60 to 140 minutes, the observed decrease in MB was not as significant as expected. During prolonged contact periods, the active sites on the NCs can reach their maximum capacity, thereby limiting their ability to adsorb additional MB molecules.

The dose of NaCl-SiO₂ NCs is a crucial factor in MB degrading, along with pH and contact

duration. Enhancement of the NCs dose led to a significant reduction in color. Raising the dosage from 10 to 55mg led to the highest reduction of MB [32]. Increasing the adsorbent dosage increases the surface area and the number of active adsorbed sites. Yet, increasing the dose from 50 to 100 mg did not lead to a corresponding decrease in MB attributed to the saturation of adsorption sites on the NCs surface.

Conclusion

The sol-gel synthesis method was used to synthesize NaCl-SiO₂ NCs. Synthesized NCs were characterized by UV spectroscopy, FTIR, and XRD. Response surface methodology was utilized to optimize the parameters. The maximum degradation efficiency of 97.20 % was achieved under following conditions: NCs dosage of 100 mg/50 mL, pH 6 and with a contact time of 140 minutes. Increasing contact duration from 60 to 140 minutes resulted in less significant degradation in MB as expected. During prolonged contact periods, the active sites on the NCs can reach their maximum capacity, thereby limiting their ability to adsorb additional MB molecules. It was concluded that NaCl-SiO₂ NCs have the potential to be a viable and environmentally friendly solution for treating wastewater polluted with dyes.

Acknowledgments

The authors express their gratitude to all individuals who contributed to the execution of this study.

References

1. Sharma, P., et al., *Industrial wastewater purification through metal pollution reduction employing microbes and magnetic nanocomposites*. Journal of Environmental Chemical Engineering, 2021. **9**(6): p. 106673.
2. Aiguoarueghian, I., et al., *Waste management and circular economy: A review of sustainable practices and economic benefits*. World Journal of Advanced Research and Reviews, 2024. **22**(2): p. 1708-1719.
3. Bahrami, M., et al., *The removal of methylene blue from aqueous solutions by polyethylene microplastics: Modeling batch adsorption using random forest regression*. Alexandria Engineering Journal, 2024. **95**: p. 101-113.
4. Radoor, S., et al., *Low-cost and eco-friendly PVA/carrageenan membrane to efficiently remove cationic dyes from water: Isotherms, kinetics, thermodynamics, and regeneration study*. Chemosphere, 2024. **350**: p. 140990.

5. Afzal, S., et al., *Recent advances of MXene@MOF composites for catalytic water splitting and wastewater treatment approaches*. Chemosphere, 2024. **364**: p. 143194.
6. Dwivedi, P., et al., *A sustainable approach for the simultaneous removal of cationic and anionic dyes from waste water using multilayer MWCNT, UMCNO, and PVA coated cotton fabrics*. Cellulose, 2024: p. 1-17.
7. Blaga, A.C., et al., *Biosorbents based on biopolymers from natural sources and food waste to retain the methylene blue dye from the aqueous medium*. Polymers, 2022. **14**(13): p. 2728.
8. Venkatesan, R., et al., *Morphological, mechanical, and antimicrobial properties of PBAT/poly (methyl methacrylate-co-maleic anhydride)-SiO₂ composite films for food packaging applications*. Polymers, 2022. **15**(1): p. 101.
9. Hamza, M., et al., *Evaluation and Optimization of Synthesized Poly (acrylamide-co-acrylic acid) for Tannery Wastewater Treatment via RSM*. Arabian Journal for Science and Engineering, 2024. **49**(1): p. 231-259.
10. Khabra, A., et al., *Synthesis of a SiO₂/Co (OH) 2 Nanocomposite Catalyst for SOX/NOX Oxidation in Flue Gas*. Catalysts, 2022. **13**(1): p. 29.
11. Gharbi, A.H., et al., *Novel CuO-SiO₂ nanocomposites: synthesis, kinetics, recyclability, high stability and photocatalytic efficiency for Rose Bengal dye removal*. Transition Metal Chemistry, 2024. **49**(3): p. 195-213.
12. Bermeo, M., et al., *Adsorption capacities of hygroscopic materials based on NaCl-TiO₂ and NaCl-SiO₂ core/shell particles*. Journal of Nanotechnology, 2020. **2020**(1): p. 3683629.
13. Azlina, H., et al., *Synthesis of SiO₂ nanostructures using Sol-Gel method*. Acta Physica Polonica A, 2016. **129**(4): p. 842-844.
14. Rovani, S., et al., *Highly pure silica nanoparticles with high adsorption capacity obtained from sugarcane waste ash*. ACS omega, 2018. **3**(3): p. 2618-2627.
15. Mohammadi, M., M.K. Khorrami, and H. Ghasemzadeh, *ATR-FTIR spectroscopy and chemometric techniques for determination of polymer solution viscosity in the presence of SiO₂ nanoparticle and salinity*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2019. **220**: p. 117049.
16. Mourdikoudis, S., R.M. Pallares, and N.T. Thanh, *Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties*. Nanoscale, 2018. **10**(27): p. 12871-12934.
17. Xu, H.-Y., et al., *Heterogeneous Fenton-like discoloration of Rhodamine B using natural schorl as catalyst: optimization by response surface methodology*. Environmental Science and Pollution Research, 2013. **20**: p. 5764-5772.
18. Baş, D. and İ.H. Boyacı, *Modeling and optimization I: Usability of response surface methodology*. Journal of food engineering, 2007. **78**(3): p. 836-845.
19. Balakrishnan, V., et al., *In vitro evaluation of cytotoxicity of colloidal amorphous silica nanoparticles designed for drug delivery on human cell lines*. Journal of Nanomaterials, 2013. **2013**(1): p. 729306.
20. Manikandan, R. and J. Thomas, *Sustainable approaches in green synthesis of silica nanoparticles using extracts of chlorella and its application*. Applied Biochemistry and Biotechnology, 2024. **196**(11): p. 7928-7939.
21. Saha, A., et al., *A facile cost-effective electrolyte-assisted approach and comparative study towards the Greener synthesis of silica nanoparticles*. Nanoscale Advances, 2023. **5**(5): p. 1386-1396.
22. Prasad, T., S. Halder, and S. Dhar, *Process parameter effects on particle size reduction of sol-gel synthesized silica nanoparticles*. Materials Today: Proceedings, 2020. **22**: p. 1669-1675.
23. Sharma, P., J. Prakash, and R. Kaushal, *Eco-friendly synthesis of amino and carboxyl-functionalized silica nanoparticles for enhanced adsorption of water pollutants*. Hybrid Advances, 2024. **6**: p. 100209.
24. Ali, S.A.K., et al., *Synthesis of nano-silica particles using Eucalyptus globulus leaf extract and their innovative application as an adsorbent for malachite green dye*. Russian Journal of Applied Chemistry, 2024. **97**(1): p. 75-87.
25. He, L., et al., *Preparation and characterization of NaCl/SiO₂ composites as anti-icing materials for asphalt pavement*. Materials Today Communications, 2025: p. 111988.
26. Irvani, M., et al., *Experimental insights into the stability of graphene oxide nanosheet and polymer hybrid coupled by ANOVA statistical analysis*. Scientific Reports, 2024. **14**(1): p. 18448.
27. Almethen, A.A., et al., *Highly efficient and rapid removal of methylene blue from aqueous solution using folic acid-conjugated dendritic mesoporous silica nanoparticles*. Processes, 2022. **10**(4): p. 705.
28. Hummadi, K.K., S. Luo, and S. He, *Adsorption of methylene blue dye from the aqueous solution via bio-adsorption in the inverse fluidized-bed adsorption column using the torrefied rice husk*. Chemosphere, 2022. **287**: p. 131907.

29. Dariani, R., et al., *Photocatalytic reaction and degradation of methylene blue on TiO₂ nano-sized particles*. Optik, 2016. **127**(18): p. 7143-7154.
30. Nayl, A.A., et al., *A novel P@ SiO₂ nano-composite as effective adsorbent to remove methylene blue dye from aqueous media*. Materials, 2023. **16**(2): p. 514.
31. Jaber, H.A. and M.F.A. Jabbar, *Adsorption of cationic and anionic dyes from aqueous solution using sunflower husk*. Chemistry, 2021. **4**: p. 567-574.
32. Liu, T., et al., *Adsorption of methylene blue from aqueous solution by graphene*. Colloids and Surfaces B: Biointerfaces, 2012. **90**: p. 197-203.