

Article

RSM-Based Optimization of COD Removal from Synthetic Textile Dye Solutions Using Iron Oxide-Modified Pomegranate Peel Biochar

Mustafa Akgün 

Technical Sciences Vocational School, Ardahan University, Ardahan 75000, Türkiye;
mustafaakgun@ardahan.edu.tr

Abstract

Synthetic textile dye solutions are commonly used as controlled model systems to evaluate adsorbent performance before application to real textile wastewater matrices. In this study, a magnetic adsorbent was developed by functionalizing pomegranate peel-derived biochar with iron oxide (Fe_3O_4) nanoparticles and was applied for chemical oxygen demand (COD) removal from synthetic aqueous solutions containing three individual acid dyes: Buracid Yellow BGL, Buracid Navy Blue RL, and Buracid Red FN. The effects of adsorbent loading, pH, contact time, and dye type on COD removal were systematically evaluated and optimized using Response Surface Methodology (RSM). The experimental results showed that adsorbent loading, pH, and contact time significantly influenced COD removal efficiency. The developed quadratic model showed good explanatory performance, with $R^2 = 83.42\%$ and adjusted $R^2 = 79.28\%$, while the predicted R^2 value of 72.65% indicated moderate predictive capability. Under the identified optimum operating region (pH 7.4, contact time 35 min, and adsorbent loading 80 g/L), COD removal efficiency reached up to 84%, depending on dye type. These findings indicate that Fe_3O_4 -modified pomegranate peel biochar is a promising adsorbent for COD reduction from synthetic textile dye solutions. However, further validation using real textile wastewater is required to evaluate matrix effects caused by salts, surfactants, suspended solids, mixed dyes, and other textile auxiliaries.

Keywords: textile dye; biochar; response surface methodology

1. Introduction

Textile industry wastewater contains complex pollutants, primarily consisting of high levels of organic matter, inorganic matter, and colour parameters, depending on the different types of dyes, surfactants, oils and greases, sulphites, and textile auxiliaries used. Depending on these parameters, the characteristic structures of wastewater arising from the organic and inorganic substances used in the textile industry also differ. The most important parameters to be considered in the treatment of textile wastewater are chemical oxygen demand (COD) and colour. Furthermore, another study reported that dyes, chromium and its derivatives, and sulphur are frequently found in textile wastewater [1,2].

To systematically evaluate the structural origins of these pollutants, the waste-generating processes within the textile sector can be categorized into four main operational stages:

The processes that cause pollution in textile wastewater can be grouped into four main headings.

I. Processes carried out to remove impurities from raw materials;



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- II. Dyeing processes;
- III. Processes applied to impart properties such as resistance to creasing or burning;
- IV. Processes that alter the chemical or physical properties of the fibre without adding any chemical substances or removing any chemicals from the fiber.

The intensive water consumption required across these sequential stages naturally designates the textile industry as a major producer. The textile industry's high-water consumption indicates a sector with intensive wastewater production. A large proportion of this wastewater is generated by textile processes, particularly during washing and dyeing. This wastewater varies in both quantity and in its characteristic properties. The properties of the wastewater depend on the type of fibre used, the type of process applied, and the chemicals involved. For this reason, textile industry wastewater can form aromatic amines in water, especially in dyeing processes where azo dyes are heavily used, and can also lead to carcinogenic products entering the water [3]. In addition, the wastewater produced by the process has pH values ranging from 2 to 12, high suspended solids and high COD concentrations, and low biodegradability [4–9].

To overcome these low biodegradability limitations, the development of advanced adsorption technologies using functionalized biomass has gained significant momentum. For instance, Çatlıoğlu et al. [10] produced iron-modified hydrochar from orange peel waste in their study and treated textile wastewater at a rate of 99 per cent, depending on the parameters of time, temperature and adsorbent quantity. In another study, Çatlıoğlu et al. [11] used iron-modified banana peel for methylene blue removal and achieved a removal rate of 91.89%. In another study, banana peel was used to achieve 94% removal of Mn(II) [12]. Guliyev et al. [13] treated NO₂ from whey water using magnetic nanoparticles (MNP) at a rate of 62.41% and COD at a rate of 48.45%. In another study, MNP coated with Cu²⁺ ions was used as an adsorbent to remove proteins from whey, with protein removal rates of 14–60% depending on the MNP composition [14]. Numerous studies in the literature have examined the treatment of textile wastewater and wastewater from various sources using MNP, and some of these studies are presented in Table 1.

Table 1. Some studies using MNPs for treatment.

Study	Removed Pollution	Treatment Rate	Main Process Conditions	Operational Feasibility/Comment
Çatlıoğlu et al. [10]	Textile dye (Brilliant Black)	99%	26.30 min, 44.79 °C, adsorbent 2.27 g/L	Waste-derived Fe-modified adsorbent; high dye removal; mainly single-dye/color removal
Çatlıoğlu et al. [11]	Textile dye (Methylene Blue)	91.89%	50 min, 45 °C, 2.5 g adsorbent, 5 mg/L	Low-cost biomass-derived adsorbent; RSM-optimized; single-dye system
Ashraf [12]	Mn(II)	94%	Adsorption-based treatment	Demonstrates feasibility of fruit-waste adsorbents; different pollutant class
Guliyev et al. [13]	NO ₂	62.41%	MNP-assisted optimization	Magnetic-particle-assisted COD reduction in a complex wastewater matrix; lower COD removal than the present study
Nicolás et al. [14]	Protein	14–60%	MNP composition-dependent	Magnetic adsorbent approach; different target pollutant/matrix
This study	COD	84%	pH 7.5–8.5, 25–35 min, adsorbent loading 5–6 g	Agricultural waste-derived magnetic biochar; short contact time; magnetic separation potential; real wastewater and reuse tests still required

As shown in Table 1, the COD removal performance obtained in this study is comparable to that of selected adsorbent and MNP-assisted treatment studies. Direct comparison should be done cautiously, as many previous studies have reported dye, color, metal, or protein removal rather than COD reduction. Furthermore, the type of activated carbon used also affects treatment efficiency.

While the structural configurations in Table 1 highlight the clear potential of magnetic adsorbents, selecting an abundant and sustainable carbon precursor remains a fundamental challenge. In this regard, Turkey stands as a global leader in pomegranate cultivation and according to data from the Turkish Statistical Institute (TÜİK), annual pomegranate production is reported as 631,500 tons by 2025 [15]. Considering that approximately 50% of the total weight of the pomegranate fruit consists of the peel [16], hundreds of thousands of tons of pomegranate peel are generated as agricultural waste in our country every year. This high amount makes pomegranate peel a low-cost, abundant, and sustainable biomass source; it offers significant potential for transforming waste into value-added products within the framework of the circular economy approach. In this context, the utilization of pomegranate peel in biochar production stands out as a strategic approach both in terms of reducing the environmental burden and developing innovative adsorbents that can be used in wastewater treatment.

Although there are studies in the literature on the use of biochar and Fe-modified biochar in wastewater treatment, a large part of these studies focus on single-type dye systems with limited optimization approaches. The originality of this work lies in the functionalization of biochar derived from pomegranate peel with magnetic nanoparticles and the systematic optimization of its removal performance for three distinct textile dyes through separate, individual experimental runs using Response Surface Methodology (RSM). Specifically, this study aims to evaluate how the independent removal efficiencies of Buracid Navy Blue RL (C.I. Acid Blue 193), Buracid Red FN (C.I. Acid Red 151), and Buracid Yellow BGL (C.I. Acid Yellow 42), obtained from the Burboya company, vary depending on critical process parameters such as pH, adsorbent loading and contact time. Furthermore, the quadratic models developed via RSM were utilized to determine the optimum operating conditions and subsequent Chemical Oxygen Demand (COD) reduction for each individual dye system, thereby providing a controlled model-based evaluation of COD removal from synthetic textile dye solutions.

This study presents the synthesis of Fe₃O₄-modified biochar derived from pomegranate peel and evaluates its performance for COD removal from synthetic aqueous solutions containing individual textile dyes. The process was systematically optimized using RSM, providing a controlled model-based assessment of COD reduction in synthetic textile dye solutions.

2. Materials and Methods

2.1. Material

The dyes used to simulate textile wastewater were supplied in solid form by Burboya Bursa Boya Kimya San. ve Tic. A.Ş. For this purpose, Burboya's Buracid Navy Blue RL (C.I. Acid Blue 193), Buracid Red FN (C.I. Acid Red 151) and Buracid Yellow BGL (C.I. Acid Yellow 42) dyes were used. Due to the solid nature of these dyes, 100 mg/L stock solutions were first prepared and then used in accordance with the working conditions specified in the test plan determined by RSM.

The FeCl₂·4H₂O was purchased from Thermo Scientific (Waltham, MA, USA), FeCl₃·6H₂O and NaOH were purchased from ISOLAB (Wertheim, Germany), Hydrochloric acid (HCl) and Phosphoric acid (H₃PO₄) were obtained from Sigma-Aldrich (St.

Louis, MO, USA), Ammonia solutions and COD cell test were obtained from Merck (Darmstadt, Germany).

2.2. Method

2.2.1. COD Analysis

The stock solutions of synthetic textile dyes were diluted at a ratio of 1:3. In total, 3 mL diluted synthetic textile dye solutions were taken and added to Spectroquant brand COD test kits. These mixtures were heated in a thermoreactor (Spectroquant TR320 (Darmstadt, Germany)) at 148 °C for 2 h. After the heating process, the samples were left to cool for 30 min and then analysed using a colorimeter (Spectroquant Move100 (Darmstadt, Germany)).

2.2.2. Biochar Production

In this study, pomegranate peel was utilized as an organic waste precursor for biochar production. To induce a thermal shock dynamic and accelerate the immediate vaporization of volatile fractions, a rapid pyrolysis procedure was adopted. For this purpose, the laboratory-scale chamber furnace (Protherm, PLF 110/10 (Ankara, Türkiye)) was safely pre-heated to the terminal carbonization temperature of 400 °C. A precise mass of 100 g of the dried precursor biomass was then systematically introduced into the stabilized high-temperature zone under a limited-oxygen framework and held for a residence time of 25 min to ensure structural thermal degradation. After cooling to ambient temperature, the resulting biochar matrix was mechanically crushed using a Lavion HC2000 Gr High-Speed Grinder (Hefei, China) and classified according to particle size via sieve separation. In this work, biochar fractions that passed through the 0.125 mm mesh sieve but were retained on the 0.063 mm mesh sieve were collected for subsequent experiments.

2.2.3. Activating the Biochar

The crushed biochar was chemically activated by blending it with a 40% phosphoric acid (H_3PO_4) solution at a strict weight ratio of 1:2 (biochar:acid, *w/w*). The suspension was kept for an impregnation period of 24 h at room temperature, with manual agitation performed every few hours to ensure uniform saturation across the carbonaceous matrix. Following the 24 h chemical soaking, the acid-loaded biochar was filtered from the solution and allowed to dry completely at room temperature. This dried, impregnated matrix was then subjected to thermal activation for 1 h inside the laboratory-scale chamber furnace (Protherm, PLF 110/10 (Ankara, Türkiye)) pre-heated to 600 °C, under a continuous inert nitrogen (N_2) atmosphere fed at a stable flow rate of 0.8 L/min. Finally, the thermally activated biochar was allowed to cool slowly to room temperature, washed thoroughly multiple times with distilled water to remove residual chemical fractions, and dried prior to modification.

Crushed biochar was added to a 40% phosphoric acid solution in a 1:2 ratio (biochar:acid). The biochar was left to stand in this acid solution for 24 h. During this time, it was stirred every few hours to ensure the biochar became uniformly saturated with the acid. After 24 h, the biochar was filtered from the acid solution and left to dry at room temperature. This dried biochar was heated for 1 h in the laboratory-scale chamber furnace (Protherm, PLF 110/10 (Ankara, Türkiye)) preheated to 600 °C with N_2 gas fed into the oven at a flow rate of 0.8 L/min. Finally, the thermally activated biochar was allowed to cool slowly to room temperature, thoroughly washed several times with distilled water to remove any remaining chemical fractions, and dried prior to modification.

2.2.4. Production of Iron (Fe)-Functionalised Biochar

The activated biochar fractions obtained from the previous staging (0.063–0.125 mm) were systematically integrated into the reaction medium during the MNP synthesis phase, allowing the activated biochar surface frameworks to successfully form complexes with iron ions. For this purpose, the chemical co-precipitation framework previously developed by Sadak et al. [17] was carefully modified and implemented. The comprehensive functionalization process workflow is systematically summarized below:

Magnetic nanoparticles (MNPs) were synthesised using a co-precipitation method with Fe^{2+} and Fe^{3+} ions (1:2 molar ratio) in an ammonia solution. Briefly, 25 mL of 2 M HCl, 2.70 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 0.99 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were added to a 100 mL bottle. The solution was sonicated for 15 min. In total, 2 g of the produced biochar were added to this solution and stirred for 15 min at room temperature using nitrogen gas. This homogenised the solution and removed oxygen.

Next, 40 mL of aqueous ammonia solution (28%) was added dropwise to this solution. The resulting black precipitate was collected using a strong permanent magnet and washed several times with deionised (DI) water. The final product of Fe_3O_4 MNPs was obtained by drying the precipitate in a vacuum oven at 60 °C for 12 h.

2.2.5. Optimization of COD Removal from Synthetic Textile Dye Solutions

The Response Surface Method (RSM) was used to optimize COD removal from synthetic textile dye solutions and experiments were conducted according to the experimental design created with the factors specified for the process (Table 2). For this purpose, 100 ppm stock solutions of textile dyes (Buracid Navy Blue RL (C.I. Acid Blue 193) (Bursa, Türkiye), Buracid Red FN (C.I. Acid Red 151) (Bursa, Türkiye), and Buracid Yellow BGL (C.I. Acid Yellow 42)) (Bursa, Türkiye) were prepared. A total of 50 mL was taken from these solutions to simulate the COD load of textile wastewater related to the dyes, and varying amounts of Fe_3O_4 -modified biochar adsorbent (2–6 g) were added to the mixtures, adjusted to different pH levels (pH 5–9). The mixture was left to stand for different periods of time (15–35 min) to allow the biochar to settle in a magnetic field. After magnetic separation, the treated synthetic dye solution was analysed for COD, and the COD removal efficiency was calculated by comparing the final COD value with the initial COD value.

Table 2. Parameters and levels to be examined for their effect on the optimisation of synthetic textile dye solutions treatment.

Factors	Independent Variables	Levels of Variables		
		−1	0	+1
X1	Duration (min)	15	25	35
X2	pH	5	7	9
X3	Adsorbent loading (g/L)	40	80	120

2.2.6. Characterisation

The dimensions and microstructural characteristics of the synthesized MNPs were determined by Scanning Electron Microscopy (SEM), and the composition of the complex structure was determined by Energy Dispersive X-ray Spectroscopy (EDX) analysis.

SEM imaging was performed on a FEI Quanta FEG 250 (FEI Company, Hillsboro, Ore., USA) under the following conditions: accelerating voltage = 15.00 kV, working distance = 8.0 mm, spot size = 6.0, pressure = 1.26×10^{-3} Pa, using the ETD detector in SE mode at 4000× and 16,000× magnification. EDX analysis was carried out using the

attached EDAX detector (Berwyn, PA., USA) at an accelerating voltage of 15 kV, with a live time of 28.5 s and a take-off angle of 33°.

3. Results and Discussion

Before microscopic characterization, the magnetic separability of the Fe_3O_4 -modified biochar composite was qualitatively evaluated under an external magnetic field. As shown in Figure 1, the dark Fe_3O_4 -modified biochar particles accumulated near the external magnets after treatment of the synthetic dye-containing aqueous solutions, while a clearer supernatant phase remained above the separated solid phase. This visual observation confirms that the synthesized composite responds to an external magnetic field and can be separated from the treated aqueous phase without conventional filtration or centrifugation. Therefore, the magnetic separation behavior observed macroscopically supports the potential recoverability of the Fe_3O_4 -modified biochar after adsorption. Thus, this result can be considered qualitative evidence, but reuse/regeneration tests are still required to fully evaluate its practical wastewater treatment applicability.

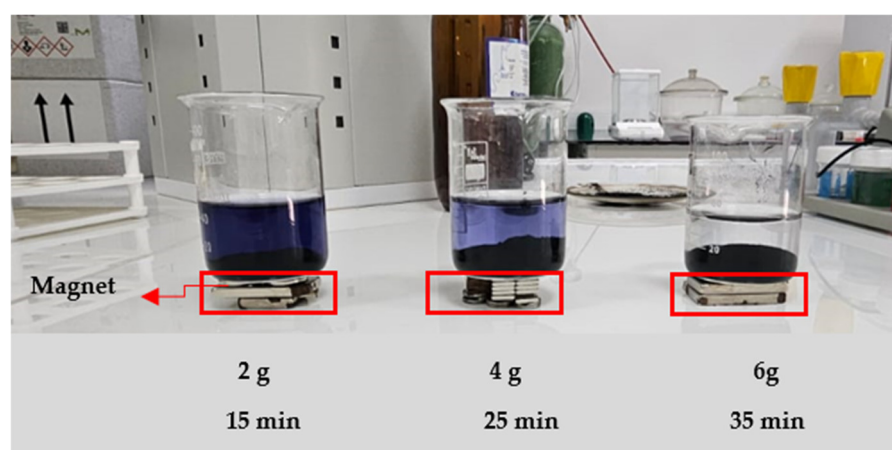


Figure 1. An example of the magnetic separation behavior of pomegranate peel biochar modified with Fe_3O_4 .

3.1. Characterisation of Biochar

The surface morphology of the synthesized Fe_3O_4 -coated biochar composite was investigated using SEM, and the obtained micrographs at different magnifications are presented in Figure 2. The brighter regions observed on the biochar surface in the SEM image are attributed to Fe_3O_4 nanoparticles due to the higher atomic number of iron compared to the carbonaceous biochar matrix, while the darker regions correspond to the porous biochar structure. This contrast difference further confirms the successful deposition of iron oxide nanoparticles onto the biochar surface. The low-magnification SEM image (4000×) reveals that the biochar exhibits an irregular, fractured, and highly porous structure. This rough and heterogeneous surface morphology is characteristic of biochars derived from lignocellulosic biomass after pyrolysis and indicates the formation of an increased specific surface area favorable for adsorption processes. Higher magnification imaging (16,000×) clearly demonstrates the presence of fine particulate structures distributed over the biochar matrix. The granular and rough surface features observed on the biochar surface are attributed to the successful immobilization of Fe_3O_4 nanoparticles. The relatively uniform distribution of these particles suggests effective interaction between iron oxide nanoparticles and the biochar framework, confirming the formation of a stable composite structure. Furthermore, nano- and submicron-scale particle clusters observed on the biochar surface indicate partial aggregation behavior of magnetic nanoparticles, which is

commonly associated with magnetic interactions between Fe_3O_4 particles. Such hierarchical morphology enhances surface roughness and provides additional active adsorption sites, thereby improving pollutant–adsorbent interactions. Overall, the SEM results confirm the successful incorporation of Fe_3O_4 nanoparticles onto the biochar surface and demonstrate that the synthesized composite possesses suitable structural characteristics for efficient COD reduction from aqueous solutions.

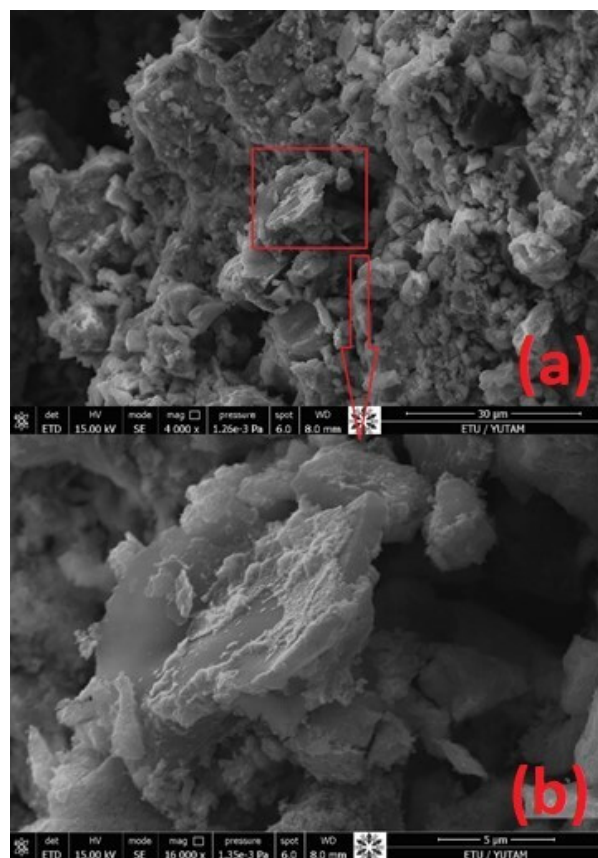


Figure 2. SEM image of Fe_3O_4 -coated biochar composite. SEM micrographs of Fe_3O_4 -coated biochar composite: (a) 4000 $\times$ magnification showing porous biochar morphology; (b) 16,000 $\times$ magnification showing immobilized Fe_3O_4 nanoparticles (bright regions) on the biochar surface.

The elemental composition of the synthesized Fe_3O_4 -modified biochar composite was further analyzed using EDX. The EDX spectrum (Figure 3) clearly confirmed the presence of Fe, C, and O elements in the composite structure. Quantitative elemental analysis obtained from EDX measurements (Table 3) revealed a dominant iron content of 69.70 wt%, confirming the successful loading of Fe_3O_4 nanoparticles onto the biochar surface. A significant carbon content (15.63 wt%) was also detected, representing the carbonaceous structure of the biochar matrix responsible for providing porous adsorption sites. Oxygen (12.39 wt%) originated from both iron oxide phases and oxygen-containing functional groups present on the biochar surface. Minor amounts of phosphorus (0.90 wt%) and chlorine (1.37 wt%) were attributed to inherent biomass minerals or residual synthesis precursors. The coexistence of high iron and carbon contents confirms the formation of a hybrid magnetic biochar composite structure. Furthermore, the iron-rich signals detected in the EDX analysis support the SEM observations, where brighter contrasts correspond to Fe_3O_4 nanoparticles homogeneously distributed over the porous biochar framework.

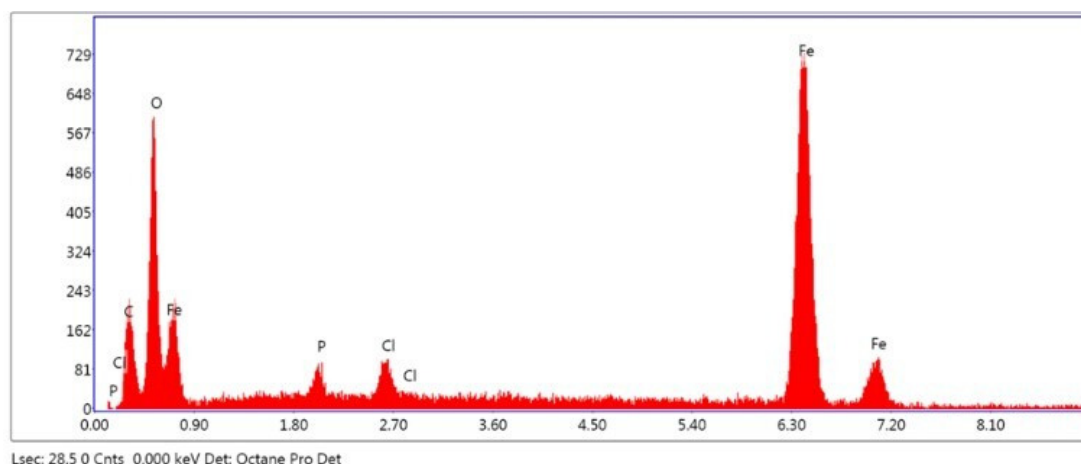


Figure 3. EDX spectrum of Fe_3O_4 -modified biochar composite.

Table 3. Elemental composition of Fe_3O_4 -modified biochar composite obtained from EDX analysis.

Element	Weight %	Atomic %
C	15.63	38.37
O	12.39	22.83
P	0.90	0.86
Cl	1.37	1.14
Fe	69.70	36.79

It is crucial to emphasize that the elevated iron content (69.70 wt%) captured via EDX analysis indicates a highly concentrated surface-localized distribution rather than a representative bulk composition. This high surface density provides direct chemical evidence of the successful complexation achieved between the synthesized magnetic nanoparticles (MNPs) and the functional matrix of the biochar. Since EDX operates as a surface-sensitive diagnostic tool, this prominent peak confirms that the iron fractions are intensely anchored as an active interfacial complex layer precisely where the organic pollutants interact.

The surface of the produced biochar can be iron-functionalized. Furthermore, this material has been used for COD remove the synthetic dye solutions. The efficiency (%) and optimization values of this material in COD removal are presented in Table 4 below.

As shown in Table 4, COD removal efficiency ranged from 38.00% to 84.00%; this indicates that removal performance is largely dependent on the selected operating parameters. The highest COD removal (84.00%) was achieved under conditions of pH 7, a 25 min duration, and an adsorbent loading of 120 g/L for dye 2. Under the same conditions, repeated experiments yielded highly reproducible results with COD removal values ranging from 75.80% to 77.90%, confirming the consistency of the synthesised composite.

Regarding the effect of pH, the data show that neutral pH (7) generally yields higher removal efficiencies compared to acidic (pH 5) or alkaline (pH 9) conditions.

The adsorbent loading also played a critical role. At pH 7 and 25 min, increasing the adsorbent amount from 2 g to 6 g (dye 2) enhanced COD removal from 50.81% to 84.00%, which can be attributed to the greater availability of active adsorption sites.

Furthermore, the duration of adsorption exhibited a positive correlation with removal efficiency up to 25–35 min, beyond which the improvement became marginal (e.g., pH 7, 4 g, dye 2: 61.90% at 15 min vs. 77.10% at 25 min vs. 80.13% at 35 min), indicating that equilibrium is approached within 25–35 min.

Table 4. COD removal rates under different experimental conditions.

pH	Duration (min)	Adsorbent Loading (g/L)	Dye *	COD Removal %	Initial COD (mg/L)	Final COD (mg/L)
7	15	80	2	61.90	234	89.15
9	35	120	3	72.51	213	58.55
5	35	40	1	41.21	108	63.49
9	15	40	3	54.54	213	96.83
5	15	40	3	50.71	213	104.99
9	15	120	1	59.86	108	43.35
7	25	80	2	77.10	234	53.59
5	35	120	1	58.76	108	44.54
7	25	80	2	76.80	234	54.29
7	25	80	2	77.90	234	51.71
5	15	40	1	38.00	108	66.96
7	25	80	3	74.29	213	54.76
7	25	120	2	84.00	234	37.44
9	15	40	1	52.00	108	51.84
5	35	40	3	53.01	213	100.09
9	35	40	3	64.40	213	75.83
5	35	120	1	71.80	108	30.46
7	25	40	2	50.81	234	115.11
9	15	120	3	71.23	213	61.28
7	25	80	1	55.62	108	47.93
9	25	80	2	65.00	234	81.90
5	35	120	3	75.95	213	51.23
9	35	40	1	59.00	108	44.28
7	25	80	2	76.00	234	56.16
7	25	80	2	76.50	234	55
7	25	80	2	75.80	234	56.63
7	25	80	2	76.05	234	56.04
5	15	120	3	65.88	213	72.68
7	35	80	2	80.13	234	46.50
9	35	120	1	67.50	108	35.10
5	25	80	2	60.00	234	93.60

* Dye 1: Buracid Yellow BGL (C.I. Acid Yellow 42), Dye 2: Buracid Navy Blue RL (C.I. Acid Blue 193), Dye 3: Buracid Red FN (C.I. Acid Red 151).

Overall, the data in Table 4 demonstrate that the Fe₃O₄-coated biochar composite is most effective for COD reduction from synthetic dye solutions under near-neutral pH (7), an adsorbent loading of 120 g/L, and a contact time of 25–35 min.

The performance of the present Fe₃O₄-modified pomegranate peel biochar was further compared with selected literature reports in Table 1 in terms of removal efficiency, process conditions, and operational feasibility.

3.2. Optimization of COD

In this study, the effects of pH, time, adsorbent loading and dye type on COD removal from synthetic textile dye solutions were investigated using RSM. According to the results

of the analysis of variance (ANOVA), the F-value of the established model was 13.18 and the p -value was less than 0.001, indicating that the model was statistically highly significant (Table 5).

Table 5. Analysis of variance (ANOVA) for COD removal efficiency based of pH, duration, adsorbent loading, and dye type.

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	p -Value
Model	6	3531.01	83.42%	3531.01	588.50	20.13	0.000
Linear	5	3282.22	77.54%	2359.89	471.98	16.14	0.000
pH	1	142.89	3.38%	188.38	188.38	6.44	0.018
Duration (min)	1	240.80	5.69%	266.26	266.26	9.11	0.006
Adsorbent loading (g/L)	1	1376.61	32.52%	1333.18	1333.18	45.59	0.000
Dye type	2	1521.91	35.96%	535.96	267.98	9.16	0.001
Square	1	248.79	5.88%	248.79	248.79	8.51	0.008
pH * pH	1	248.79	5.88%	248.79	248.79	8.51	0.008
Error	24	701.77	16.58%	701.77	29.24		
Lack-of-Fit	17	613.45	14.49%	613.45	36.09	2.86	0.081
Pure Error	7	88.31	2.09%	88.31	12.62		
Total	30	4232.78	100.00%				

Note: pH * pH represents the quadratic (interaction) term of pH to account for non-linear effects in the model.

The ANOVA results indicate that the refined quadratic model is highly significant for COD removal efficiency ($F = 20.13$). The Lack-of-Fit test result is $p = 0.081$, which is statistically non-significant ($p > 0.05$), thereby confirming that the model adequately represents the experimental data within the investigated factor ranges.

The linear terms account for the largest portion of the total variation, with a contribution of 77.54%, and are statistically highly significant ($p < 0.001$). Among these terms, dye type shows the highest contribution to the model (35.96%, $p = 0.001$), followed by adsorbent loading (32.52%, $p < 0.001$), duration (5.69%, $p = 0.006$), and pH (3.38%, $p = 0.018$). Since dye type was treated as a categorical factor, its major contribution indicates that the three dye systems produced distinct COD removal responses depending on their molecular characteristics. However, among the controllable continuous process variables, adsorbent loading is the dominant factor affecting COD removal efficiency ($F = 45.59$, $p < 0.001$). Contact time also exerts a statistically significant positive linear effect ($F = 9.11$, $p = 0.006$). Notably, after the statistical elimination of non-significant parameters, the linear effect of pH was also confirmed to be statistically significant ($F = 6.44$, $p = 0.018$).

The square terms account for 5.88% of the total variation and show a highly significant statistical effect ($p = 0.008$). Among the quadratic terms, only the pH^2 interaction remained in the system and is statistically significant ($F = 8.51$, $p = 0.008$), confirming the presence of a nonlinear pH effect and a distinct optimum pH region. In contrast, the quadratic effects of duration and adsorbent loading were systematically eliminated during the backward regression as they were not statistically significant ($p > 0.05$). This indicates that COD removal changes in a strictly linear manner with increasing contact time and adsorbent loading within the tested boundaries, while pH defines the main parabolic curvature of the response surface. All two-way interaction terms were excluded from the final model due to their statistical insignificance ($p > 0.05$), demonstrating that COD removal is predominantly governed by the main individual effects rather than synergistic or antagonistic interactions.

Because dye type is a categorical factor, response surface and 3D contour plots were generated separately for each matrix. The dominant effect of adsorbent loading among the controllable continuous variables can be mechanistically explained by the increase in the total number of available active binding sites, accessible surface area, and surface sites associated with the deposited Fe_3O_4 particles. Increasing the adsorbent loading from 40 to 120 g/L (corresponding to 2–6 g adsorbent in 50 mL solution) expanded the solid phase available for interaction with dye-derived oxidizable organic compounds, thereby enhancing COD removal efficiency. This interpretation is consistent with previous adsorption studies reporting that higher adsorbent dosage generally improves removal performance by providing more active binding sites and greater surface availability [18,19].

In contrast, the investigated contact time range of 15–35 min likely covered a period in which a substantial fraction of adsorption had already occurred, resulting in a positive but less dominant time effect compared with adsorbent loading. The categorical effect of dye type can be attributed to differences in molecular structure, size, charge distribution, and affinity toward the Fe_3O_4 -modified biochar surface. However, COD removal represents the reduction in total oxidizable organic load rather than direct dye removal or decolorization. Therefore, differences among dye systems should be interpreted in terms of COD reduction from synthetic dye-containing aqueous solutions.

The significant quadratic effect of pH ($p = 0.008$) indicates that pH mainly controls the optimum electrostatic environment through protonation/deprotonation of surface functional groups and changes in surface charge, rather than directly increasing the number of adsorption sites. Such pH-dependent behaviour is commonly reported in iron-based nanoparticle and dye-containing adsorption systems, where surface charge, electrostatic attraction/repulsion, and functional group ionization strongly affect adsorption performance [19–21]. Consequently, adsorbent loading enhanced the overall COD removal capacity, while pH determined the optimum operating region.

The generated 3D surface and 2D contour plots (Figures 4–6) perfectly support the ANOVA results. In all dye systems, COD removal increases linearly with increasing adsorbent loading and contact time, confirming the dominant role of adsorbent availability and kinetic advancement. Concurrently, the smooth parabolic curvature observed exclusively along the pH axis visually confirms the significant pH^2 term, establishing a clear universal maximum COD removal plateau under neutral-to-moderately alkaline conditions (pH around 7.4), while lower removal efficiencies are observed at the acidic and strongly alkaline edges of the tested pH range.

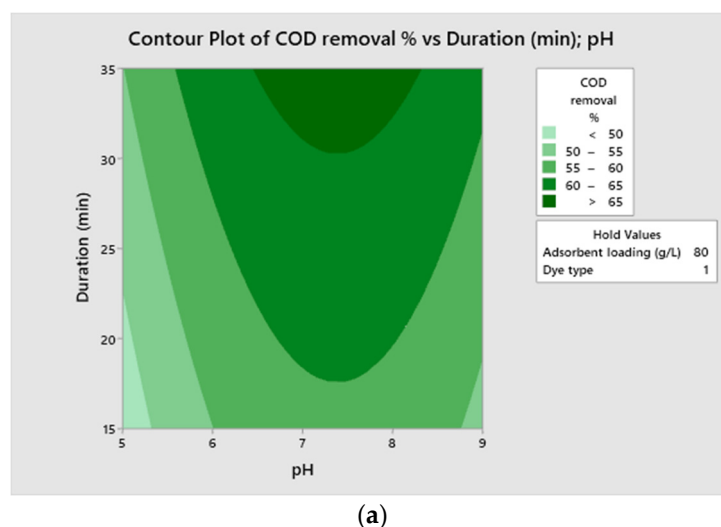


Figure 4. Cont.

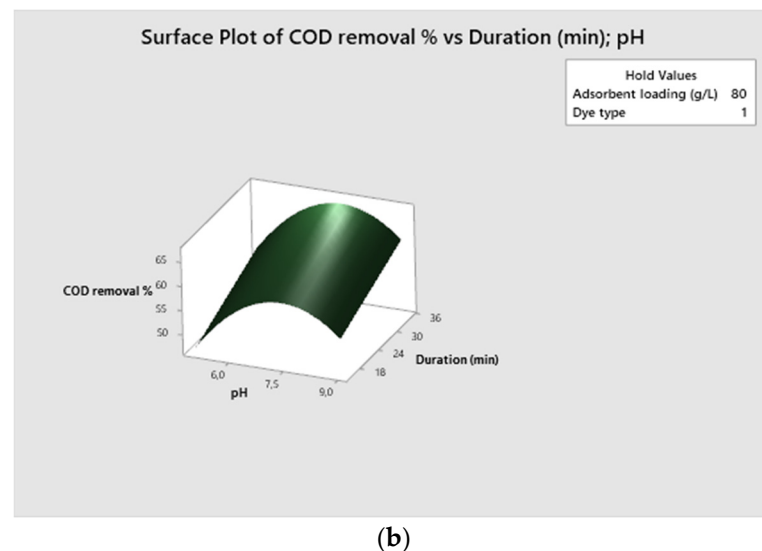


Figure 4. (a) Effect of reaction time and pH on COD removal (Dye 1, Contour Plot). (b) Effect of reaction time and pH on COD removal (Dye 1, 3D).

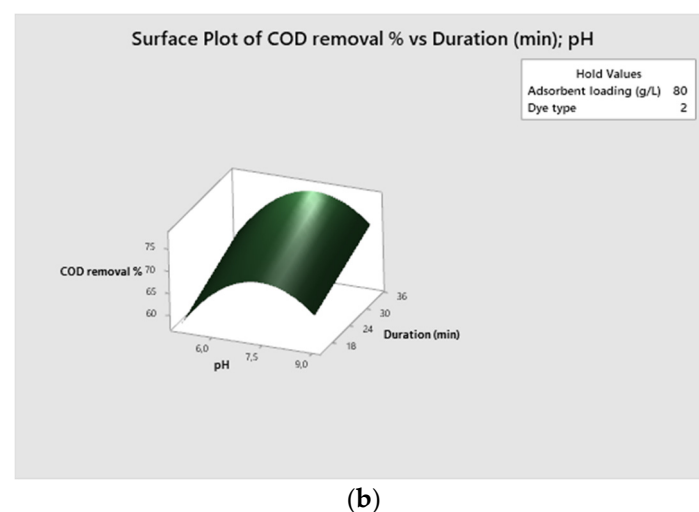
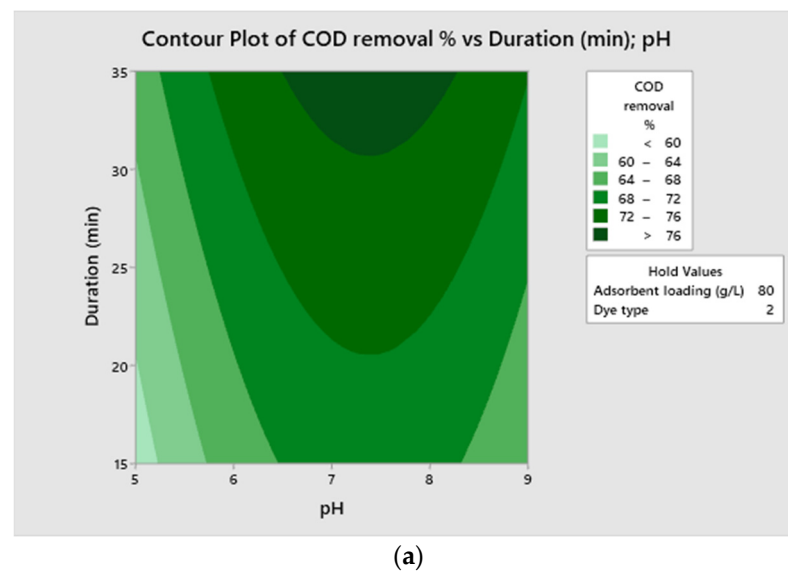


Figure 5. (a) Effect of reaction time and pH on COD removal (Dye 2, Contour Plot). (b) Effect of reaction time and pH on COD removal (Dye 2, 3D).

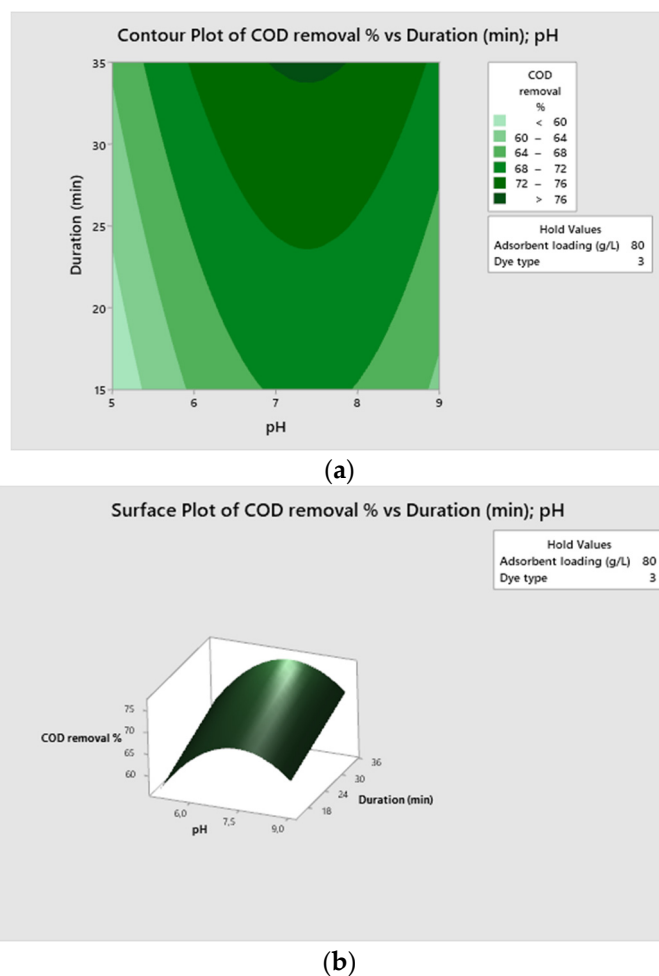


Figure 6. (a) Effect of reaction time and pH on COD removal (Dye 3, Contour Plot). (b) Effect of reaction time and pH on COD removal (Dye 3, 3D).

Model Performance

Model F-value = 20.13 and $p = 0.000$, the model was found to be statistically significant overall. The parameters related to the model are given in Table 6. The model explains 83.42% of the total variation in COD removal with an adjusted R^2 of 79.28%. Remarkably, yielding a robust predicted R^2 of 72.65%. The close convergence between the adjusted and predicted R^2 values (<7%) verifies the strong predictive ability of the final model.

Table 6. Model summary statistics for COD removal efficiency.

S	R-sq	R-sq(adj)	PRESS	R-sq(pred)	AICc	BIC
5.40743	83.42%	79.28%	1157.75	72.65%	207.23	212.15

Figure 4a is a contour curve showing the combined effect of pH and reaction time on COD removal efficiency (%) for Dye type 1 under fixed adsorbent dose conditions of 80 g/L. As clearly shown in the graph, both operating parameters exert a significant influence on the COD removal performance. The maximum COD removal efficiency (above 65%) was obtained within a well-defined parabolic region in the pH range of 6.5–8, near the neutral boundary and at contact times of 30–35 min. It was determined that the COD removal efficiency decreased rapidly to 50–55% when the pH dropped toward the acidic region ($pH < 6.0$) or shifted toward the strongly alkaline region ($pH > 8.5$). This decrease in efficiency at extreme pH values can be attributed to the weakening of electrostatic interactions between the organic matrix, causing COD and the active sites, or

to competitive ion effects, due to changes in the surface charge of the modified biochar. Furthermore, increasing the reaction time from 15 to 35 min allowed for a steady kinetic advancement, reflecting a linear performance improvement as the organic matter gradually occupied the active centers on the adsorbent surface. Consequently, the optimum process conditions for Dye Type 1 are distinctly concentrated around high contact times and neutral pH levels.

Figure 4b presents the 3D response surface plot showing the combined effects of pH and reaction time on COD removal efficiency (%) for Dye Type 1. The 3D topography visually confirms the optimization framework, where the highest COD removal efficiency forms a smooth parabolic crest around pH 6.5–8.0 and extended reaction times up to 35 min. Deviations from the neutral pH limits result in a sharp decrease in performance due to electrostatic instability, while a linear increase along the time axis reflects stable kinetic progression.

Figure 5a presents the 2D contour plot illustrating the interactive effects of pH and reaction time on the COD removal efficiency (%) for Dye Type 2. Consistent with the quadratic model outcomes, the contour lines display a symmetric parabolic curvature along the pH axis, where the maximum COD removal plateau (exceeding 76%) is securely localized in the neutral-to-slightly alkaline region of pH 7.0–8.0 and at maximum contact times of 30–35 min. Moving toward highly acidic (pH < 5.5) or strongly basic (pH > 8.5) boundaries triggers a noticeable drop in performance down to below 60% due to electrostatic destabilization. Concurrently, the steady vertical shift across the duration axis reflects a strictly linear kinetic advancement, confirming that longer operational intervals maximize the saturation of active sites on the modified biochar surface.

Figure 5b presents the 3D response surface plot showing the combined effects of pH and reaction time on the COD removal efficiency (%) for Dye Type 2. The 3D surface topography visually confirms the optimized model framework, where the highest COD removal efficiency forms a smooth, symmetrical parabolic crest tightly constrained around a neutral-to-slightly alkaline pH range of 7.0–8.0 and extended reaction times up to 35 min. Deviations into highly acidic (pH < 5.5) or strongly basic (pH > 8.5) regions induce a sharp decline in performance due to the electrostatic destabilization of the adsorbent surface. Concurrently, the smooth, uncurved ascent along the duration axis reflects a strictly linear kinetic advancement, confirming that longer operational intervals maximize the saturation of active sites on the modified biochar surface without reaching early equilibrium.

Figure 6a presents the 2D contour plot illustrating the interactive effects of pH and reaction time on the COD removal efficiency (%) for Dye Type 3. Consistent with the refined quadratic model outcomes, the contour lines display a highly symmetrical parabolic curvature along the pH axis, where the maximum COD removal plateau (exceeding 76%) is securely localized in the neutral-to-slightly alkaline zone of pH 7–8 and at maximum contact times of 35 min. Deviations into highly acidic (pH < 5.5) or strongly basic (pH > 8.5) boundaries induce a sharp, predictable decline in performance down to below 60% due to the electrostatic destabilization of the functional groups on the biochar surface. Concurrently, the steady vertical shift across the duration axis reflects a strictly linear kinetic advancement, confirming that longer operational intervals maximize the target organic load reduction without encountering early saturation barriers.

Figure 6b presents the 3D response surface plot showing the combined effects of pH and reaction time on the COD removal efficiency (%) for Dye Type 3. Consistent with the 2D contour trends, the 3D surface topography visually confirms the optimized model architecture, where the highest COD removal efficiency forms a smooth, tunnel-like parabolic crest peaking above 75% around a neutral pH range of 7.0–8.0 and extended reaction times up to 35 min. Deviations into extreme acidic or basic conditions induce a

sharp decline in performance due to the electrostatic destabilization of the biochar surface, while the steady, uncurved ascent along the duration axis reflects a strictly linear kinetic progression. Consequently, the 3D topology demonstrates that maximizing the reduction in total oxidizable organic load requires a precise synchronization of high contact times and neutral pH levels.

Consequently, a comparative analysis of the three contour plots and three surface plots confirms that, although there were differences in the absolute removal percentages for each dye, a neutral to slightly alkaline environment and a long contact time (up to 35 min) are effective in the treatment of synthetic textile dye solutions using modified biochar.

Based on the RSM optimization topography, the optimum conditions for maximizing COD removal across all three dye matrices are given below. Optimal conditions:

- pH: 7.4;
- Time: 35 min;
- Adsorbent loading: 80 g/L (4 g in 50 mL) under which COD removal efficiency reached up to 77.72%, depending on dye type.

Figure 7 shows the response optimization graph plotted for the predicted COD removal efficiency. Based on the model equations, the selected optimum operating conditions were determined as pH 7.40, contact time of 35.0 min, and adsorbent load of 80.0 g/L for Dye type 2. Under these conditions, the predicted maximum COD removal efficiency was determined to be 77.72%.

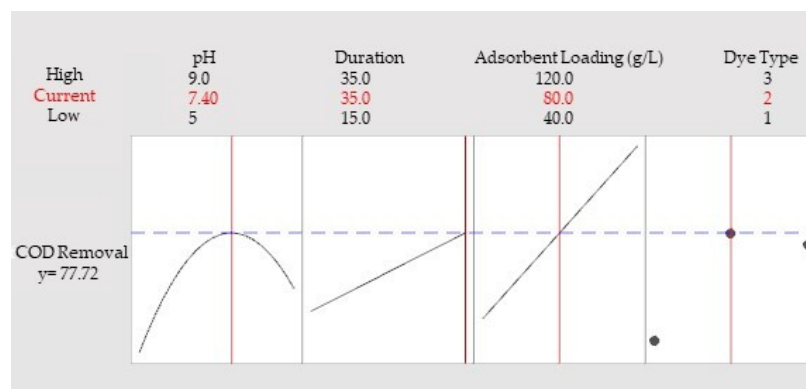


Figure 7. Minitab (version 19.1) response optimizer plot.

This study demonstrated that optimizing pH, adsorbent loading, and contact time can significantly improve the efficiency of COD removal from synthetic textile dye solutions and that systematic optimization using the RSM approach yielded efficient results.

It should be noted that the present study was conducted using synthetic dye-containing aqueous solutions under controlled experimental conditions. In real textile wastewater matrices, which can contain competing ions, salts, suspended solids, surfactants, dyeing auxiliaries, and mixed organic matter, these constituents may affect adsorption by altering ionic strength and surface charge interactions, competing with dye-derived oxidizable organic compounds for active adsorption sites, blocking pores, or increasing the background COD of the wastewater. Therefore, further studies using real textile wastewater are required to evaluate the effects of competing ions, suspended solids, mixed organic matter, and wastewater matrix complexity on COD removal performance.

RSM optimization validation and confirmation matrix for different synthetic textile dye solutions.

To verify the reliability and practical applicability of the optimization process, the results of independent validation experiments were evaluated comparatively with the comprehensive RSM design results previously compiled in Table 4 and are presented in

Table 7. In actual laboratory trials, COD removal efficiencies of 77.14% for red dye, 77.78% for blue dye, and 52.38% for yellow dye solutions were achieved. When these validation profiles are cross-examined with the experimental design combinations presented in Table 4, a clear operational consistency is observed. The experimental removal efficiencies achieved at the optimized coordinates match the highest treatability runs recorded in the initial design matrix. The fact that the Red and Blue dye setups consistently reached high-efficiency zones (~77%), while the Yellow dye stabilized at a lower but model-consistent plateau (52.38%), demonstrates that the system dynamics are highly reproducible. This agreement between the validation studies and the experimental records in Table 4 confirms that the developed optimization framework reflects the true physical and chemical limits of the treatment process.

Table 7. Validation of the Optimization Model and Comparison with the Design Matrix.

Synthetic Dye Matrix	Experimental COD Removal (%)
Yellow Dye Solution	52.38%
Blue Dye Solution	77.78%
Red Dye Solution	77.14%

4. Conclusions

In this study, COD removal from synthetic textile dye solutions was investigated using MNP-functionalized biochar and systematic optimization was performed via RSM. ANOVA results and model performance indicators ($F = 20.13$; $p < 0.001$; $R^2 = 0.8342$; $\text{Adj-}R^2 = 0.7928$; $\text{Pred-}R^2 = 0.7265$) indicate that the developed model is statistically significant and provides a reliable representation of the experimental data. The insignificant lack-of-fit ($p = 0.081$) further confirms the adequacy of the model. Although the model exhibits good explanatory power, its predictive capability is moderate. The results indicate that biochar treated with MNP is an effective adsorbent for the three different textile dyes used in the study.

In the study, adsorbent loading was identified as the most influential parameter affecting COD removal efficiency, followed by dye type and contact time, while pH showed a comparatively lower but statistically significant effect. Response surface and contour plots revealed that removal efficiency increased with higher adsorbent dosage and at moderately alkaline conditions, suggesting an optimal pH range. Contact time contributed positively and statistically significantly, enhancing removal efficiency, though its effect was less pronounced than that of adsorbent loading. The removal efficiencies obtained under optimal conditions ranged from 75 to 84%.

The novelty of this study is that it is the first to report the functionalization of pomegranate peel-derived biochar with Fe_3O_4 magnetic nanoparticles for COD removal from textile wastewater, coupled with a systematic RSM-based optimization. Unlike previous studies that focused on the removal of a single dye or used non-magnetic biochars, this study demonstrates an optimization process for COD removal and a magnetically separable adsorbent through separate experimental studies using multiple synthetic textile dye solutions.

Future studies should focus on (i) evaluating the adsorbent's performance using real synthetic textile dye solutions matrices containing mixed pollutants; (ii) investigating the reusability and magnetic recovery efficiency of the Fe_3O_4 -coated biochar over multiple adsorption–desorption cycles; (iii) testing the adsorbent against different dye classes (e.g., reactive, disperse, acid dyes); and (iv) optimizing the composite structure to lower the required adsorbent dosage, and conducting a techno-economic analysis to assess the scalability and cost-effectiveness of the synthesis process.

Overall, the results demonstrate that the RSM approach is an effective tool for process optimization, and the developed Fe₃O₄-coated pomegranate peel biochar shows promising potential for the removal of COD from synthetic textile dye solutions.

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Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The author declares no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

RSM	Response Surface Methodology
COD	Chemical Oxygen Demand
MNP	Magnetic nanoparticle

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