

Bio-Assisted Synthesis and Photocatalytic Performance of ZnO–Bentonite Nanocomposite in a Digital Baffle Catalytic Reactor for Organic Pollutant Removal

J. S. Aziz¹, A. H. Rashid², N. J. Jassim¹, A. A. Hassan^{2,3*}, S. A. Abood⁴

¹ Chemical and Petrochemical Technology Engineering Department, Basra Engineering Technical College, Southern Technical University, Basra, Iraq

² Department of Chemical Engineering, University of Muthanna, P.O. Box: 1550, Muthanna, Iraq

³ College of Engineering, Al Ayen University, P.O. Box: 64001, Nasiriyah, Iraq

⁴ Shatt Al-Arab University College, Basrah, Iraq

ARTICLE INFO

Article history:

Received: 14 Jun 2026

Final Revised: 24 Jul 2026

Accepted: 26 Jul 2026

Available online: 25 Oct 2026

Keywords:

Achromatic

Wastewater

Water treatment

Adsorption

Advanced oxidation

Optimization.

ABSTRACT

In this work, a sustainable precipitation method was used to prepare a zinc oxide-bentonite clay (ZnO/BT) composite and to evaluate its catalytic performance in a digitally controlled baffle photocatalytic reactor (DBPCR) for hybrid adsorption and photo-oxidation degradation. The prepared composite was characterized using XRD, FTIR, BET, FE-SEM, and DRS to explain its structure and properties. The working parameters, including pH, process time, temperature, and dose was analyzed using a Box-Behnken design from the response surface methodology to maximize organic removal. The new reactor design provided superior mixing and light distribution, promoting combined physical and chemical treatment. The new composite achieved an excellent removal efficiency of 99.7 % for organic pollutants in refinery wastewater (RWW), compared with 90.5 % for nano clay. The results indicate that photo-oxidation degradation followed pseudo-first-order kinetics, attributed to enhanced interfacial charge transfer, reduced electron-hole recombination during photo-oxidation, and increased free radical formation. The combination of sustainable preparation with a baffled digital oxidation reactor demonstrates a viable, high-performance technique for organic remediation. This nanocomposite displays excellent stability and can be recycled over multiple cycles, more than six times, with organic removal of more than 82.5 %, emphasizing its potential for large-scale industrial applications in adsorption/oxidation processes and ecological catalysis for wastewater treatment. Prog Color Colorants Coat. 20 (2027), 251-269© Institute for Color Science and Technology.

1. Introduction

Wastewater treatment involves collecting waste and making it suitable for discharge back into the environment. The water pollution source is the discharge of raw or partially treated industrial wastewater into ecosystems, a common problem in many republics. Water pollutants can enter the aquatic environment in many ways, either directly from treatment plants that shied away from

their responsibilities or from wastewater [1]. The environmental risk of refinery wastewater stems from the presence of a wide range of organic compounds, including phenols, aromatic compounds, hydrocarbons, and mixtures containing carbon and hydrogen [2]. Crude oil manufacture and refining processes produce huge volumes of wastewater, which need an effective method before release or recycling because of their

*Corresponding author: * ali.alkhafaji@mu.edu.iq
<https://doi.org/10.30509/pccc.2026.167826.1518>

complex composition and potential ecological impacts. As a result, organic pollutants are among the principal wastewater contaminants, and large quantities of these contaminants are toxic even at low concentrations [3]. Classic methods have been developed to be less energetic for removing organic compounds in wastewater owing to their poisonous, non-biodegradable, and stubborn nature. Various wastewater treatment methods are used, such as biological [4], membrane [5], and oxidation [6]. However, these methods are not effective, so they only change from case to case, giving rise to a novel group of contaminants that exhibit additional behavior [7]. These values are finally allowable for release to the sea. An expanded understanding is aimed at environmental provisions of crude oil production, with the essential focus on continuous growth in current treatment services, along with the inspection of new methods for various types of chemical environments [8]. The management of waste from crude oil production is typically based on physical, chemical, and biological methods, with a focus on chemical and physical methods [9].

Green remediation reduces environmental demand through an attack-and-evade approach, avoiding potential protection and ecological harm. Consequently, using live services for the removal of hazardous compound pollutants is effective through adsorption and oxidation, facilitated by high surface area and high free radical production [10]. The hybrid treatment has been established in recent years to assess the effectiveness of chemical treatments for a diversity of pollutants [11]. Though not all treatment approaches have been experimentally assessed in the work, the actual behavior organization [12]. Furthermore, the catalyst's strong oxide production remains extremely reactive and has high potential, and reacts with all compounds in solution [13]. The photocatalytic process is a valuable treatment for various prepared composites that oxidize organic pollutants using strong oxidants generated by the composite [14]. When exposed to UV or solar light, a sensitizer, or excited catalyst molecule, absorbs energy, primarily to generate strong oxidants (free radicals) for organic compounds and to convert to carbon dioxide and water [15]. In recent years, the authors have focused on improving the performance and sustainability of zinc metal-based composites for ecological remediation and energy-related applications, with particular emphasis on green, sustainable

preparation processes that enhance photo-oxidation and the activities of the nano-catalyst associated with conventional preparation [16]. In a related direction, recent work prepared a presentation on zinc oxide and nano-cellulose-enhanced oxidative desulfurization. Comprehensive wastewater assessments also emphasize the importance of physical modification [17]. In this work, a new composite prepared by precipitation from zinc nitrate hexahydrate and nano-bentonite clay is used as an adsorbent and photocatalyst with unique properties and requirements. The DBPCR was designed to have a greater impact than other reactors. In this new work, we used the DBPCR to facilitate organic removal by photocatalytic oxidation. Next, several trials were conducted under the new design with changed working conditions, and the chemical and reactor performance were assessed. Lastly, the optimization design in Minitab 17 was applied to determine the optimal limits for the adsorption and oxidation treatments.

2. Experimental

2.1 Chemicals and organic measurement

Table 1 presents the properties of wastewater obtained from an oilfield in Muthanna, Iraq. Wastewater from wet oilfields is stored for hybrid wastewater treatment. After the hybrid treatment, a separating funnel was used with 35 mL of wastewater, and 0.15 g of sodium salt was added to break up the pollutant compounds. Then, 4 mL of tetrachloromethane $S(CCl_4)$ was added, and the mixture was shaken for 5 minutes. The lower (organic) layer was used for the absorbance test. After 30 minutes, the wastewater separated into two layers, and the organic compounds were measured using a UV spectrometer and a calibration curve.

Table 1: Refinery wastewater properties

Parameter	Unit	Values
Organic compounds	ppm	132.5
TDS	ppm	423.4
TSS	ppm	15.4
Turbidity	NTU	6.87
pH	---	6.82
Density	g/cm ³	0.995

2.2. The preparation of a nano-composite

The nano bentonite is dried at 105 °C for 240 minutes to remove moisture, then cooled in a desiccator. In addition, disperse 0.2 g of the nanomaterial in 40 mL of DI water in a 200 mL glass beaker, and mix at 300 rpm for 1 hour to swell the bentonite and obtain a uniform solution. Dissolve 0.2 g of zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 30 mL of DI water, agitating for 30 minutes to obtain a uniform solution. Gradually add the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution to the clay slurry dropwise over 0.5 hour while maintaining agitation. This allows zinc to adsorb/disperse on support surfaces. Add a small amount of 0.5 M sodium hydroxide dropwise to the ZnO/BT solution until the pH reaches 10 to precipitate zinc hydroxide on and within the support. Continue agitation for 120 min to stage the slurry and promote intimate contact between zinc hydroxide and nano clay. Optionally, heat to 50 °C for 2 hours to promote better fastening/condensation. Then, wash and calcine to a nanocomposite at 500 °C for 180 minutes, as shown in Figure 1.

2.3. New design digital baffle of adsorption/oxidation reactor

The new catalytic oxidation was designed for hybrid adsorption and oxidation of organic compounds. In this project, we have designed a novel reactor by changing the components of the catalytic reactor. Evaluation of the competence of the photo reactor in the setting of wastewater procedures via physical and chemical processes. The reactor design improved the mass transfer and the distribution of oxidation in the hybrid treatment. The reactor design comprised a digital agitator with an impeller speed up to 3000 rpm, and a three-baffle design for organic treatment. These baffles enhance the transfer of reactants to the reactor (i.e., improving the efficiency of hybrid methods). In addition, three baffles were installed on the reactor wall to minimize still zones and promote a continuous stream of organic compounds. Baffles were distributed across the reactor surface at equal spacing (300 cm between baffles), and a 2 cm woolen solid protrusion was used to seal the oxidation reactor, as shown in Figure 2.

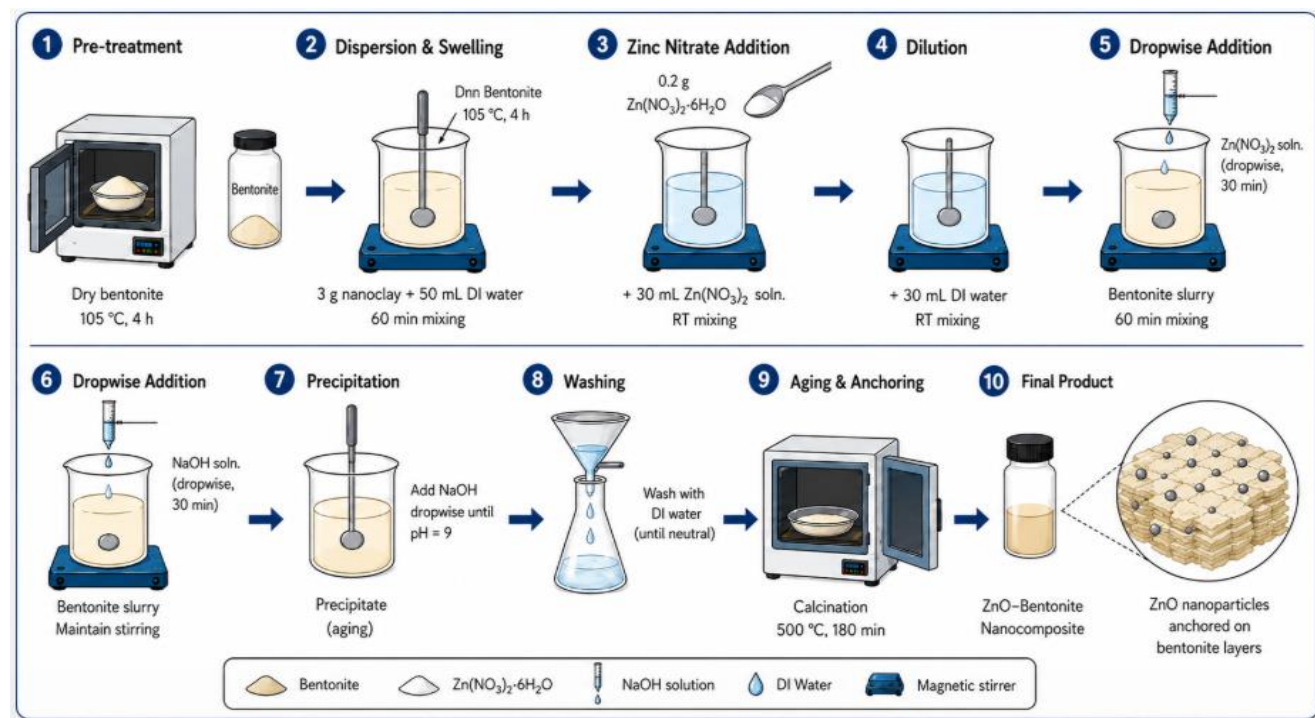


Figure 1: The preparation of ZnO/BT.

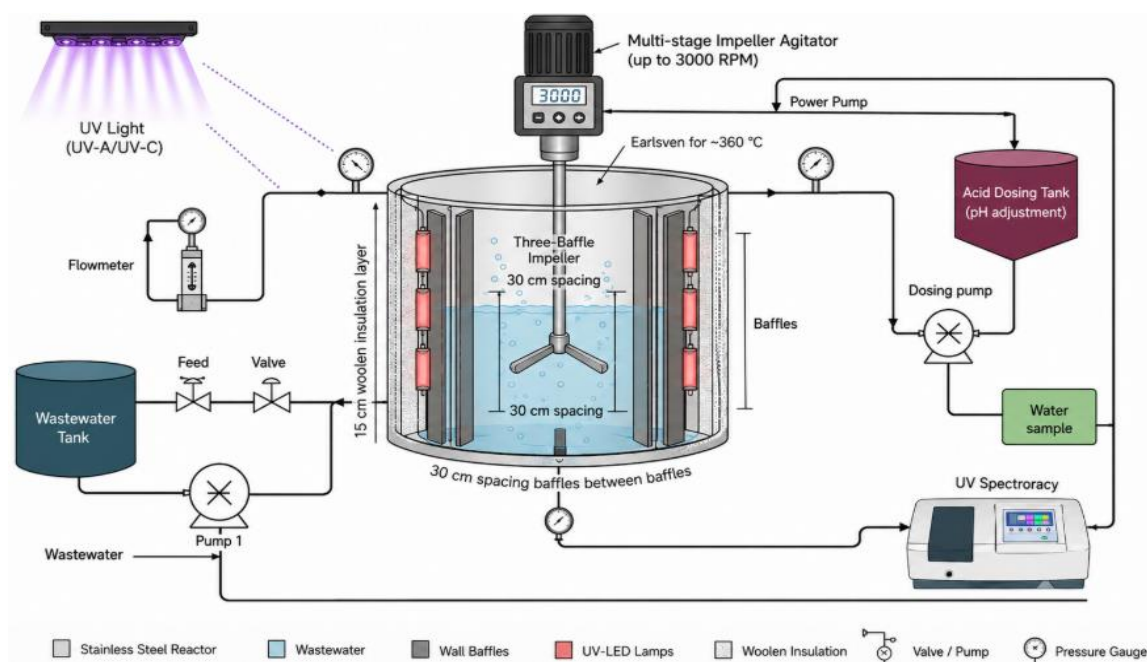


Figure 2: The design of the adsorption/oxidation batch reactor.

2.4. Experimental design

A statistical method, a procedure for response surface design, and the Minitab-17 program were used to independently and collaboratively anticipate the consequences of parameter issues. The main variables, pH (X_1), time (X_2), dose (X_3), and temperature (X_4), were varied from low value to high value in the range (3-9), (30-120 min), (0.25-1.5 g), and (25-60 °C), respectively.

3. Results and Discussion

3.1. The characterization of the composite

The nano bentonite was analyzed for functional groups using FTIR measurement. The peak size in the range is a direct indication of the number of groups present. The FTIR results confirmed the presence of many typical functional groups in the Nano support. Figure 3 shows the complete band at 3355.88 cm^{-1} for nano clay, and the new composite from bentonite and zinc oxide is attributed to amine or hydroxyl stretching or flaring of polymeric mixes. This band appeared in the medium region, $2922.44\text{--}2896.11\text{ cm}^{-1}$, in the spectral analysis of ZnO/BT, which is attributed to the presence of the bond. Previously, the bands below 795 cm^{-1} are in the fingerprint region of phosphate and sulfur functional groups [18].

The peak location values of nano bentonite and nano composite samples used as adsorbents and for oxidation were examined relative to the standard peak, as shown in Figure 4. The sharp peak typical of nano bentonite appears at the diffraction angles of 21° and 37° . The broadened peak is an unusual characteristic of Nano clay, indicating the presence of anions in the current between the Nano clay support surface and crops, with the distance between cells at the sharpest peak ($20.77.7^\circ$). The XRD pattern of the nanocomposite clearly shows the characteristic peaks (100 and 002), confirming the successful formation of the nano-composite [19].

The examination by FE-SEM of the nano-bentonite section showed homogeneous surfaces at low magnifications, as presented in Figure 5 for nano-bentonite and nanocomposite. The BT clay exhibits a nearly spherical, agglomerated morphology [20]. These new composites were prepared with particle sizes in the range (20-110 nm), with a mean diameter of 90 nm [21]. The new catalyst distribution analysis of the ZnO/BT provides vital insights into the material's characterization, which is directly related to its photo-oxidation performance, confirming that the nanomaterial has been effectively combined in the nanoparticle regime, which is vital for maximizing the surface-to-volume ratio and enhancing quantum properties for photo-catalysis, as shown in Figure 6 [22].

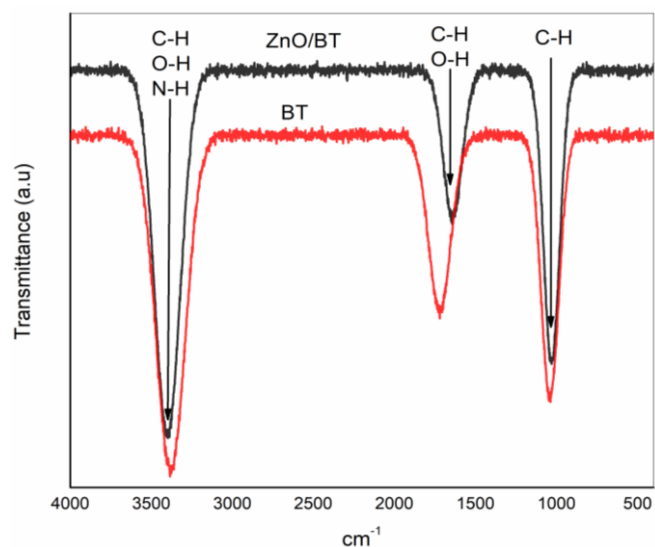


Figure 3: FTIR of BT and ZnO/BT catalyst.

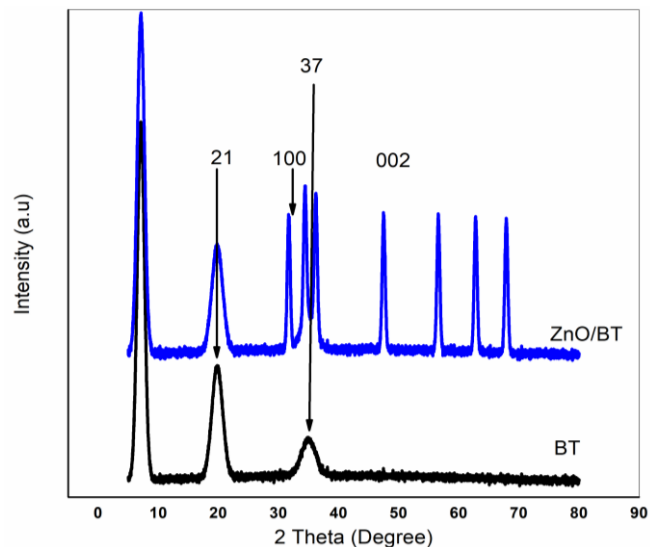


Figure 4: XRD of bentonite and the new catalyst.

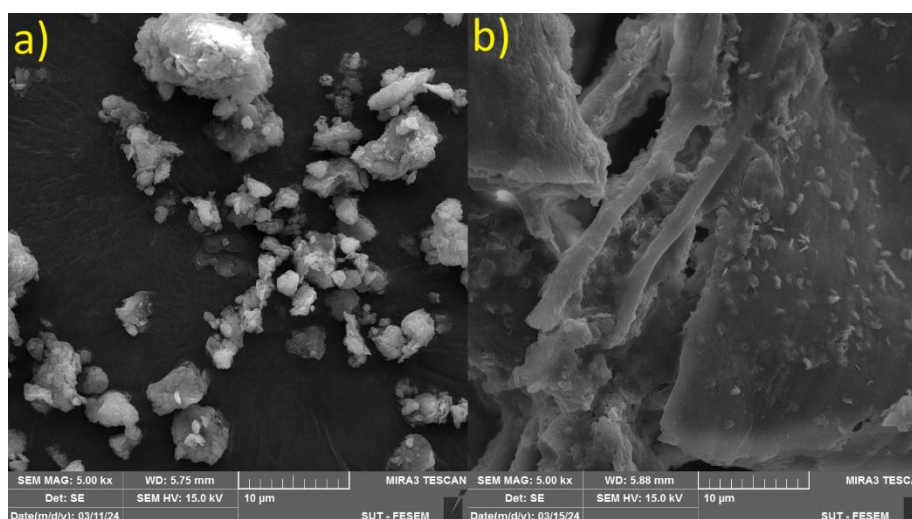


Figure 5: FE-SEM analysis of (a) nano clay and (b) new composite.

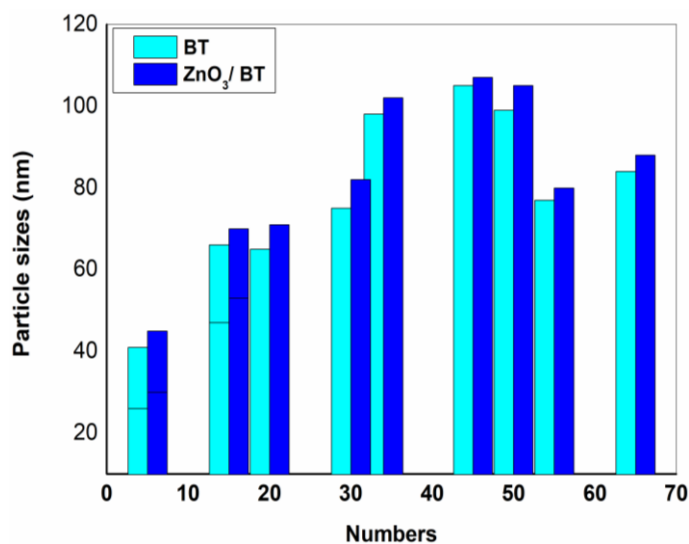


Figure 6: Particle size distribution.

The slight reduction in surface area from 453 m²/g for bentonite to 429 m²/g for the ZnO/BT composite suggests that the adsorption-desorption isotherm type remains similar, likely Type IV with hysteresis. However, the pore-size distribution indicates minimal blockage or coverage of the narrowest pores by the incorporated zinc oxide nanoparticles, as shown in Figure 7a. The pore-size distribution analysis (often using the BJH method for mesopores) reveals how the pore structure changes upon modification, as shown in Figure 7b. Pristine bentonite with a very high surface area usually contains a significant number of micropores and/or accessible mesopores. The initial broad peak is centered in the mesoporous range. Incorporating a metal oxide onto the support surface, which results in a slight decrease in surface area, indicates that a portion of the original pore surface or volume has been covered or filled [23]. The analysis of the Diffuse Reflectance Spectroscopy (DRS) spectrum is critical because it confirms the optical properties of the ZnO/BT composite, most importantly the 2.21 eV band gap, which has profound implications for its use as a photocatalyst. The DRS spectrum of the new composite would show a sharp decrease in reflectance (or a sharp increase in absorption) at an energy corresponding to the 2.21 eV band gap, as shown in Figure 8. This marks the onset of fundamental light absorption, where photons possess sufficient energy to promote electrons from the valence band to the

conduction band. The immobilization process can also form a heterojunction between the metal oxide and the support surface or create defects/oxygen vacancies within the zinc oxide crystal lattice. These defects introduce new energy levels within the band gap, effectively lowering the energy required for electron excitation [24].

3.2 Statistical analysis of hybrid treatment

To measure and enhance the combined effect of the working variables, attention was paid to an exact standard of procedure restraints. Statistically significant manufacturing investigations were presented in Table 2 to analyze the experimental data for adsorption and oxidation treatment using a digital baffled reactor. The organic removal based on a linear model was used to determine the development variable amount and signify it in real units [25]. The equations 1 and 2 of the model for organic compounds in refinery wastewater by Minitab software with box-behnken design (BBD) with first order polynomial that show the effect of parameters on the organic removal are:

$$\text{Organic Removal by BT} = 30.10 + 1.728X_1 + 0.0672X_2 + 18.48X_3 + 0.248X_4 \quad (1)$$

$$\text{Organic Removal by ZnO/BT} = 47.99 + 1.636X_1 + 0.055X_2 + 14.60X_3 + 0.1652X_4 \quad (2)$$

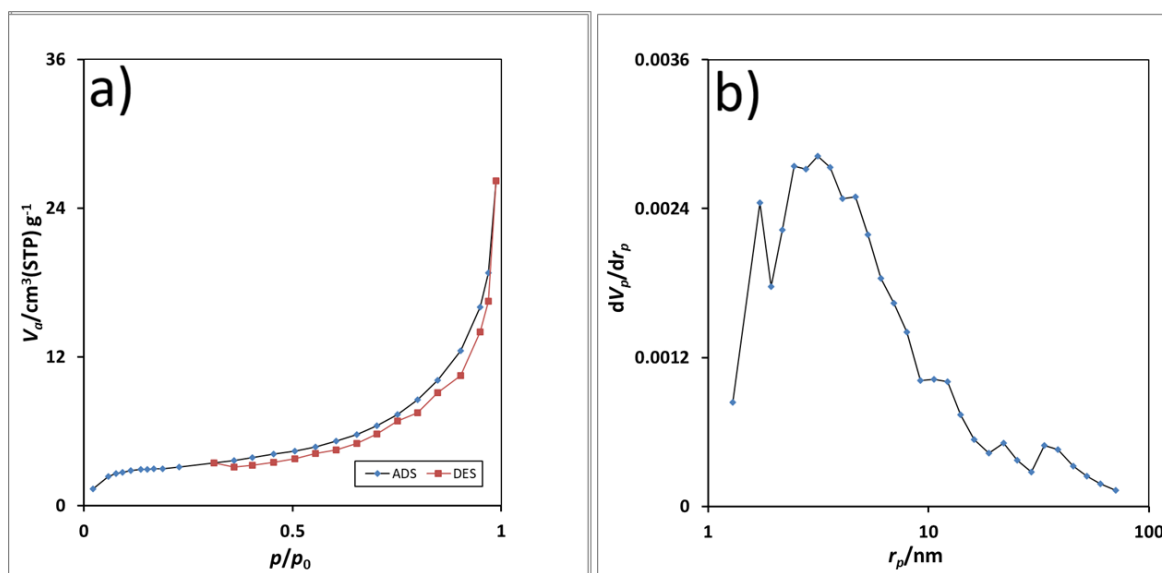


Figure 7: (a) Adsorption-desorption isotherms and (b) The new composite distribution.

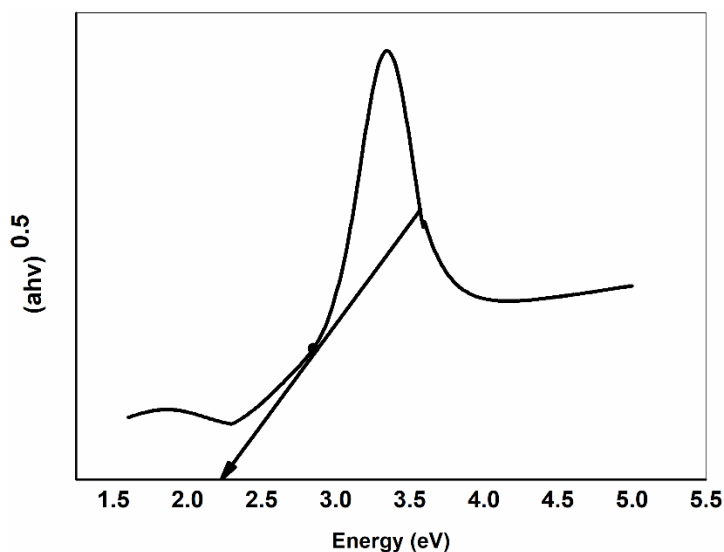


Figure 8: Diffuse Reflectance Spectroscopy of ZnO/BT.

The effects of organic removal on the parameters pH, time, dose, and temperature are confirmed. Positive coefficient values indicate improved elimination, whereas negative coefficient values indicate adverse effects. The model's capability remained unchanged in the Analysis of Variance in Table 3 for bentonite with metal oxide developed for pollutant removal, based on F and P tests aimed at the use of changing parts and

completing detailed sources of variation. Consistent p-values were used as indicators of significance, where values less than 0.05 indicate that the variable has a strong effect on organic elimination. This statistical behavior validates that the experimental results are not due to random variation but are indeed attributable to the studied limits [26].

Table 2: Hybrid treatment data of adsorption/oxidation.

Run	X ₁ : pH	X ₂ : time (min)	X ₃ : Dose (g)	X ₃ : Temperature (°C)	Organic removal by BT	Organic removal by ZnO/BT
1	3	30	0.9	43	72.4	80.4
2	9	30	0.9	43	84.9	92.3
3	3	120	0.9	43	77.4	85.4
4	9	120	0.9	43	89.3	96.3
5	6	75	0.25	25	55.4	70.3
6	6	75	1.5	25	77.5	87.4
7	6	75	0.25	60	66.7	73.4
8	6	75	1.5	60	82.5	89.3
9	3	75	0.9	25	69.5	79.2
10	9	75	0.9	25	78.8	87.4
11	3	75	0.9	60	77.4	85.2
12	9	75	0.9	60	90.3	97.2
13	6	30	0.25	43	51.4	69.4
14	6	120	0.25	43	60.3	72.5

Table 2: Continue.

Run	X ₁ : pH	X ₂ : time (min)	X ₃ Dose (g)	X ₃ Temperature (°C)	Organic removal by BT	Organic removal by ZnO/BT
15	6	30	1.5	43	76.3	83.5
16	6	120	1.5	43	80.3	88.2
17	3	75	0.25	43	49.6	60
18	9	75	0.25	43	59.4	71.5
19	3	75	1.5	43	78.6	86.1
20	9	75	1.5	43	84.4	90.5
21	6	30	0.9	25	62.5	71.6
22	6	120	0.9	25	70.4	78.8
23	6	30	0.9	60	71.8	79.2
24	6	120	0.9	60	77.9	85.1
25	6	75	0.9	43	71.5	84.2
26	6	75	0.9	43	70.9	85
27	6	75	0.9	43	72	84.8

The competence of the developed response surface models was additionally assessed using the coefficient of determination (R^2) and the adjusted coefficient of determination (adjusted R^2). For the bentonite clay model, the statistical analysis yielded an R^2 value of 79.8 % and an adjusted R^2 value of 71.5 %, representative that the model adequately defines the experimental data and clarifies most of the observed variability. In comparison, the nano composite model

showed a higher R^2 value of 89.5 % and an adjusted R^2 value of 77.5 %, representing a better overall fit and improved capability to signify the experimental response. These statistical indicators indicate that the developed quadratic models are appropriate for describing the adsorption treatment, with the nano-composite model providing superior predictive performance compared to the bentonite clay model in Table 4 [27].

Table 3: The variance analysis for the nanocomposite.

Foundation	DOF	Seq. SS	Adj. MS	Fisher Value	P-test Value
1-Model	14	2766.26	197.59	10.96	0
Linear	4	2232.13	558.03	30.96	0
X ₁	1	322.4	322.4	17.89	0.001
X ₂	1	112.49	112.49	6.24	0.028
X ₃	1	1565.66	1565.66	86.88	0
X ₄	1	233.42	233.42	12.95	0.004
Square	4	481.33	120.33	6.68	0.005
X ₁ ²	1	164.76	164.76	9.14	0.011
X ₂ ²	1	4.52	4.52	0.25	0.626
X ₃ ²	1	143.32	143.32	7.95	0.015
X ₄ ²	1	16.72	16.72	0.93	0.354

Table 3: Continue.

Foundation	DOF	Seq. SS	Adj. MS	Fisher Value	P–test Value
2-Way Interaction	6	22.82	3.8	0.21	0.966
$X_1 \times X_2$	1	0.09	0.09	0	0.945
$X_1 \times X_3$	1	3.59	3.59	0.2	0.663
$X_1 \times X_4$	1	3.16	3.16	0.18	0.683
$X_2 \times X_3$	1	6.08	6.08	0.34	0.572
$X_2 \times X_4$	1	0.86	0.86	0.05	0.831
$X_3 \times X_4$	1	9.04	9.04	0.5	0.492
Error	12	216.26	18.02	--	--
Lack-of-Fit	10	215.65	21.57	71.09	0.014
Pure Error	2	0.61	0.3	--	--
Total	26	2982.52	--	--	--

Table 4: Model summary for BT and ZnO/BT.

Model	R ² (%)	Adjusted R ² (%)	Predicted R ² (%)
BT	79.8	71.5	62.3
ZnO/BT	89.5	77.5	68.7

The results in Figures 9 show that elimination increases over time, pH, dose, and temperature, and that all parameters have a positive effect on the hybrid for all organic compounds in wastewater, with values in bentonite with metal oxide, respectively, which incline to droplet formation for a certain time, due to the lack of passable places on the adsorption surface and increased free radical production that reacts with

organic compounds more than organic adsorption in the basic solution [25]. As previously stated, the statistics were analyzed using response surface methods with the Box-Behnken design to calculate the main effects of the independent variables. The variation in organic removal produced by varying the state level describes the consequences of the problem [34].

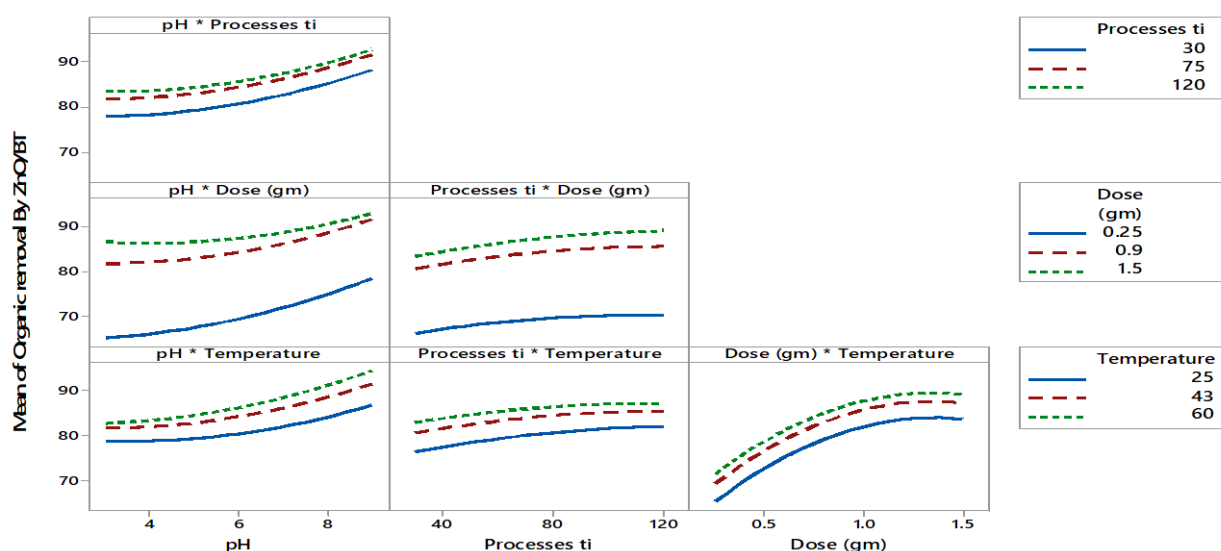


Figure 9: The interaction between the organic removal and independent parameters for ZnO/BT.

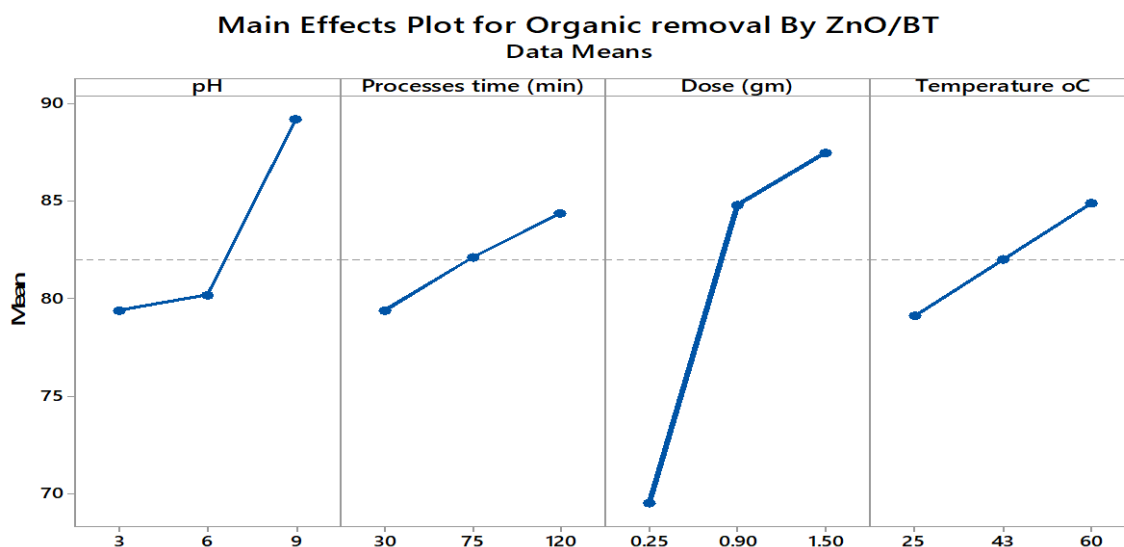


Figure 10: The main plot for the organic removal for ZnO/BT.

Figure 10 depicts the main effects of each independent variable on pollutant removal for bentonite with metal oxide. The most significant variables influencing organic removal were pH, time, dose, and temperature. These coefficients are positive, indicating that increasing the parameters within the inspected range would increase organic removal. Also, increasing the parameters increases the amount of free radicals in the prepared catalyst [28].

3.3. Working variables for hybrid treatment

To assess the effect of dose on hybrid treatment performance, experiments were conducted at doses ranging from 0.2 to 1.5 g. Organic elimination increased with dose due to the amount effect on adsorption and oxidation, reaching 88.4 and 75.3 % at 1.5 g. Lower organic elimination was observed at doses ≤ 0.2 g, with values of 57.2 and 68.8 % at 0.2 g for bentonite and bentonite with metal oxide, respectively (Figure 11a). A higher amount would lead to a higher degradation rate of adsorption and oxidation on the support surface. Consequently, more free hydroxyl radicals would accumulate in the wastewater, leading to greater oxidation of organic compounds and their conversion to carbon dioxide and water [29]. Figure 11b demonstrates that the organic elimination capability is enhanced as the hybrid treatment time increases, through adsorption onto bentonite with a high surface area, oxidation by free radicals produced from zinc oxide on the support, and conversion of organic compounds to water and carbon dioxide in wastewater treatment. Longer treatment time

results in greater organic elimination in wastewater by the digital baffle catalytic reactor, increasing mass transfer and free radical production. This could be attributed to the presence of important adsorption action via the photooxidation process due to the length of the process time, and to increasing the organic adsorption with more generation of free radicals in wastewater by hybrid treatment [30]. The pH has a significant effect on the overall performance of hybrid treatment and associated growth. It increases pollutant removal, while all other parameters remain relatively low, raising additional issues. Figure 11c shows the pH results in the range (3-9) for the adsorption and oxidation of compound pollutants. It was observed that organic removal reached 71.4 and 90.6 % in basic solution compared with 71.2 and 79.6 % in acid solution for bentonite and bentonite with metal oxide, respectively. This indicates high organic removal in oxidation compared with adsorption treatment and high free radical production that degrades organic compounds in wastewater [31]. This behavior can be attributed to the surface chemistry and catalytic activity of the new composite. In a basic solution, the metal oxide surface carries a negative charge that increases organic adsorption and facilitates the formation of free radicals and reactive oxygen species. These oxidants are chiefly responsible for organic degradation in wastewater. In an acidic solution, protonation of active sites decreases adsorption effectiveness and suppresses free radical production, thereby limiting pollutant removal [32]. The influence of temperature on adsorption and oxidation by

the new composite for organic removal from wastewater can vary with changes from low to high temperatures. Increasing temperature can enhance adsorption kinetics and squalor treatment by increasing the oxidation rate involved in adsorption and free radical production from metal oxide on the support [33]. However, disproportionately high temperatures might similarly result in deterioration of the support structure itself, affecting its efficiency. Increasing the temperature from 25 to 60 °C led to an increased removal of pollutant compounds, as shown in Figure 11d [34]. The elevated temperature enhances mass transfer rates and reduces wastewater viscosity, easing the diffusion of pollutant molecules toward active support sites. Higher thermal energy also promotes the production of reactive oxidants, accelerating oxidative degradation kinetics. So, the synergistic combined mechanism of the nanocomposite becomes more active at high temperatures, leading to enhanced organic compound removal in wastewater [35]. The optimal conditions for independent variables that

affect organic removal by hybrid treatment, such as pH, process time, dose, and temperature, were determined using a response surface method design, as shown in Figure 12 for bentonite and bentonite with metal oxide.

3.4. Regeneration and cycle for the nanocomposite

Regeneration remains a major challenge, and the use of commercial catalysts, such as low-surface-area titanium dioxide, at high cost has spurred the search for low-cost alternative photocatalyst materials. After bentonite, which has a high surface area and a lower cost than activated carbon, adsorbs organic pollutants, it must be regenerated to restore its adsorption capacity. This is typically achieved by desorption, in which organic compounds are removed from the support. Heating the new composite releases adsorbed organic compounds from wastewater. This technique requires careful control to avoid damaging the new composite.

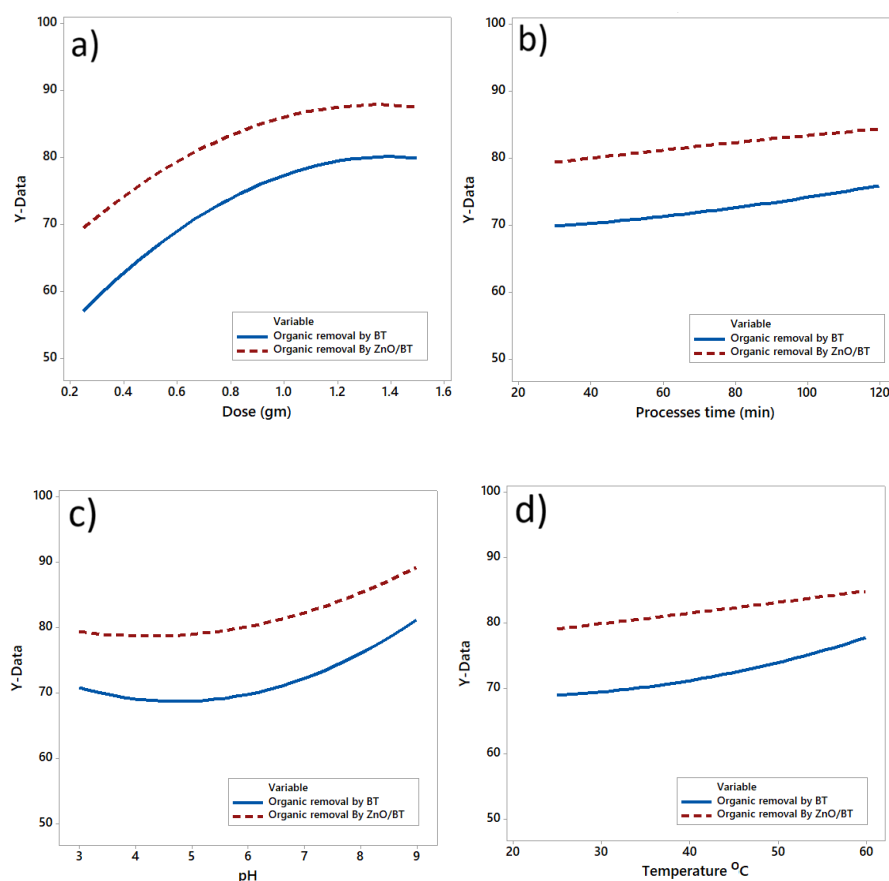


Figure 11: The effect of working variables (a) dose, (b) process time, (c) pH, and (d) temperature.

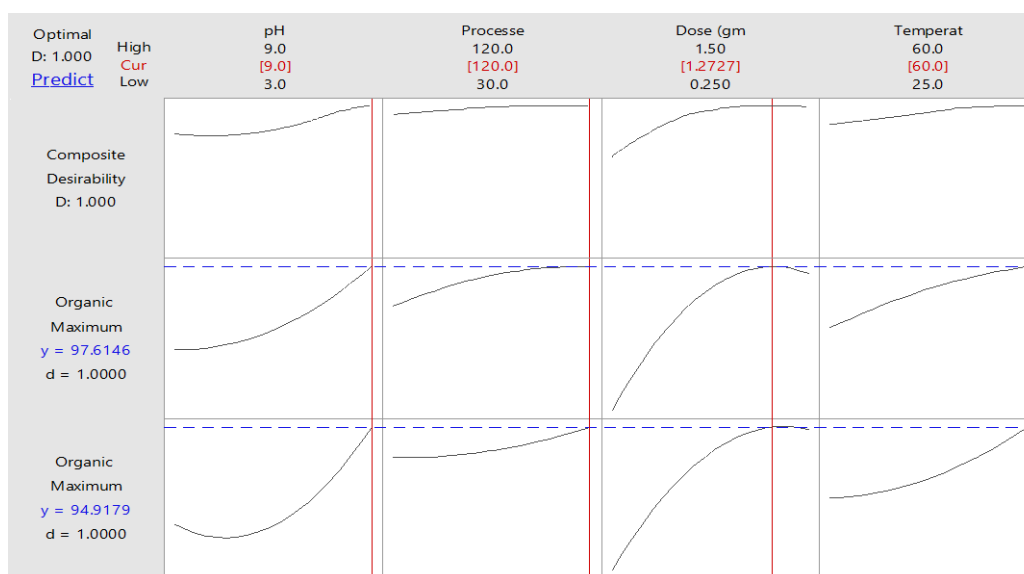


Figure 12: The best conditions for hybrid treatment of adsorption and oxidation.

Regeneration efficiency values at 80 and 30 °C, respectively, were 86.4 and 71.5 % for new composites at pH 6 and 300 rpm with 1.5 g. The reusability of the photocatalyst was examined through successive oxidation treatments over 6 cycles under the best conditions shown in Figure 13. The composite heterojunction photocatalyst maintained its outstanding performance even after 3 cycles, with only a slight decrease from 99.4 to 82.5 %. Thus, the prepared composite heterojunction effectively treated organic compounds in wastewater. The reduced activity of the catalyst could be attributed to the loss of catalyst weight throughout the hybrid treatment [36].

3.5. Simulated empirical analysis and Minitab results

Based on the independent variables for Organic Removal by adsorption and photooxidation with a new nano catalyst prepared from bentonite and a metal oxide, using a Box-Behnken design to optimize the Organic Removal Percentage, as shown in Figure 14, the expected consequences, plots, and a structured conversation, as would be classically generated in a statistical analysis of a Design of Experiments, would be suitable. This is the main organic removal. While a full CFD replication is multifaceted, the Empirical CFD term proposes that the fluid dynamics of the stirred batch reactor affect the observed experiential consequences (R %). At 0.5 hours, organic removal is often incomplete due to external mass transfer how quickly organic molecules move from the bulk solution

to the composite surface. After 120 min, the treatment transitions to being limited by intra-particle mass transfer via molecular diffusion (molecules moving into the porous support of the new composite). The CFD model suggests that adequate mixing ensures that the external mass-transfer resistance is negligible, meaning that the true oxidation/adsorption kinetics control the treatment at 120 min. A CFD simulation would predict that excessive support could lead to poor particle separation or agglomeration, possibly reducing the effective adsorption surface area despite a higher total mass. The empirical data presentation shows high elimination at 1.5 g, suggesting that, in the new setup, mixing was adequate to overcome this negative CFD result [37].

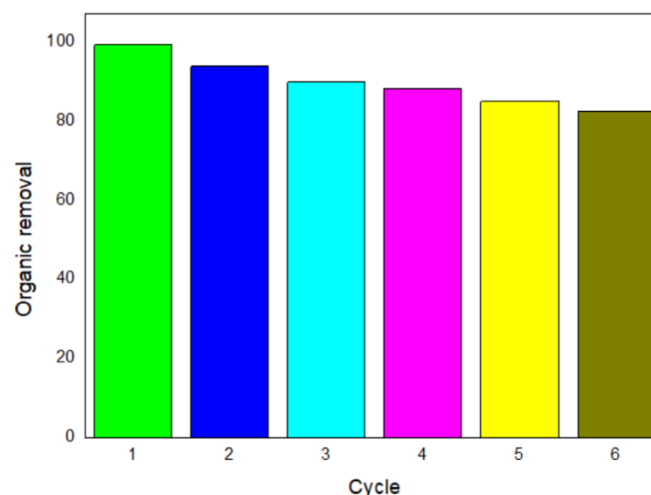


Figure 13: ZnO/BT reusability.

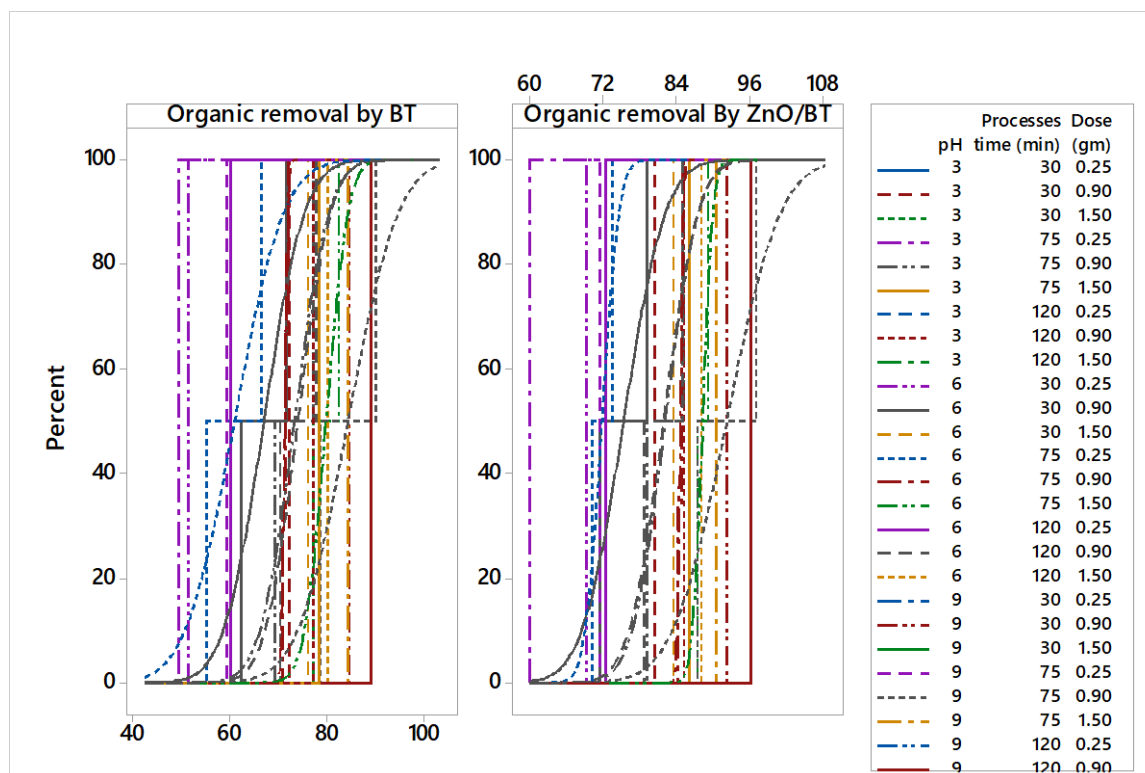
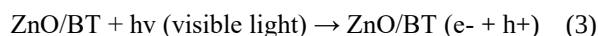


Figure 14: Empirical CFD of organic removal by BT and ZnO/BT.

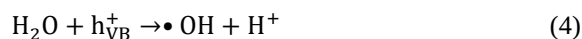
3.6. The mechanism for the nanocomposite

The improved performance of the new composite in the photo-oxidation reactor can be attributed to the synergistic relationship between zinc oxide and the Nano clay matrix. The metal oxide provides highly active oxidation and adsorption sites, while the clay contributes a layered, porous structure with a high specific surface area and abundant surface hydroxyl functional groups. The addition of the metal oxide to the nano-support surface enhances the dispersion of active sites and promotes a well-organized interaction between organic compounds and the nanocomposite surface. The organic elimination mechanism is primarily governed by electrostatic interactions, surface complexation, and composite surface oxidation. Under optimal pH conditions, the nanocomposite surface becomes negatively charged, facilitating the adsorption of positively charged pollutant species onto its active surface sites. Hydroxyl groups present on both zinc oxide and bentonite surfaces participate in the formation of surface complexes with organic compounds, thereby improving adsorption stability and elimination efficiency [38]. Many catalysts, such as titanium and zinc oxides, are known as photocatalysts

and semiconductors with low surface area. In this work, a new nanocomposite was prepared as a high-surface-area semiconductor. Like zinc oxide, it cannot be used for ecological cleansing because it can dissolve and form toxic by-products. Through the hybrid treatment of adsorption and oxidation, the photon energy of the valence band is sufficient to reach the conduction band, producing an electron-hole pair, as exemplified in Figure 15 [22]. UV radiation can provide photons with energy, which is vital for overcoming the band gap of lower-energy commercial zinc oxide and for driving an electron from the valence band to the conduction band [10]. Equations 3-8 expand on the significant photocatalytic oxidation treatment.



The photo-produced holes (h^+) in the valence band react with surface-adsorbed water molecules or (OH^-) to produce highly oxidized free radicals ($\bullet\text{OH}$) in equation 4.

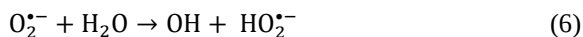


At the same time, photo-produced electrons (e^-) in the conduction band react with dissolved oxygen to

produce superoxide radical anions ($\bullet\text{O}_2^-$). In equation 5:



These superoxide radicals additionally interact with water molecules to produce additional free radicals and hydroperoxyl species in equation 6.



In photo-oxidation, discrete catalyst particles efficiently absorb light from the UV source and generate free radicals from the new composite and hydroxyls in RWW or dissolved oxygen in situ, which produce super reactive oxygen species. The organic oxidation is accelerated by the presence of zinc oxide in the combined construction, which eases real electron transfer across heterojunctions. The organizations defined for bimetallic composites, where the interface varies, improve composite performance, and are consistent with this contemporary charge transfer dynamic [39]. The use of UV light in the oxidation treatment has been the topic of many studies. Miserably, only a small fraction of light energy that may theoretically be used as a direct exciter to ZnO/BT reaches the Earth's surface. Organic pollutants in a waste stream might be oxidized with free radicals and start the photooxidation in wastewater. (Eq. 7) [40].



The kinetics of the organic oxidation treatment by the prepared composite were examined using pseudo-first- and second-order kinetic models in equations 8–10, respectively. The kinetic equation was initiated to provide a better fit with the pseudo-second-order kinetic model. The straight-line plots were obtained with the first-order kinetics model [41]. Figures 16 and 17 exemplify the linearized form of the second-order model using [9] and [11], with variations in pH, emphasizing the significant effects of these independent variables on photo-oxidation to eliminate pollutant compounds in wastewater, and varying time over the range (10–60 min). The results indicated that the oxidation rate improved with a basic solution and the new composite, whereas it increased with acid solution, leading to the production of more free radicals, easing the degradation of organic compounds, and promoting oxidation [42].

$$-\frac{dc}{dt} = K_1 C \quad (8)$$

$$\ln \frac{C_0}{C} = K_1 t \quad (9)$$

$$-\frac{dc}{dt} = K_2 C^2 \quad (10)$$

$$\frac{1}{C} - \frac{1}{C_0} = K_2 t \quad (11)$$

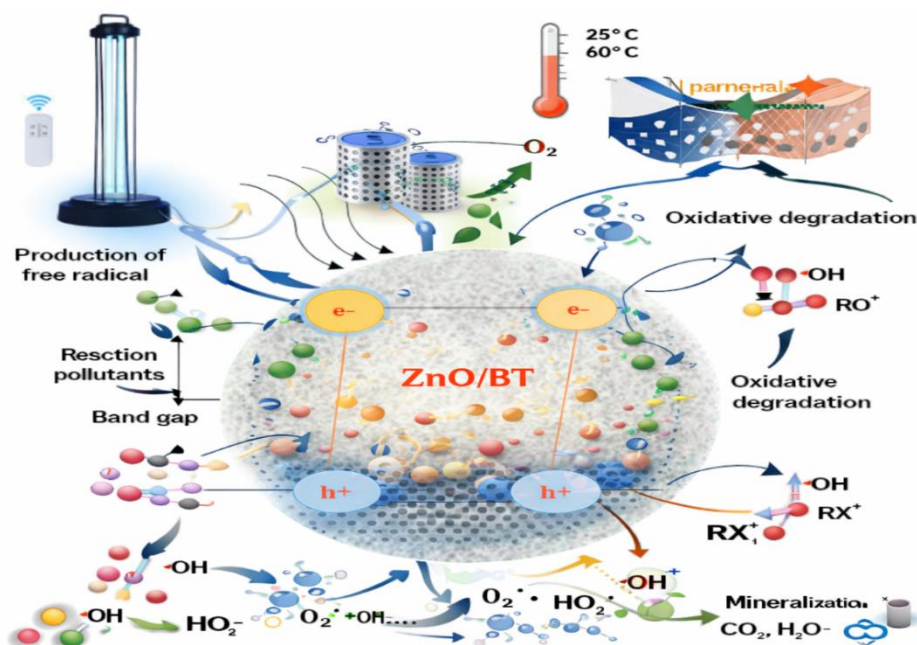


Figure 15: The mechanism of the prepared composite.

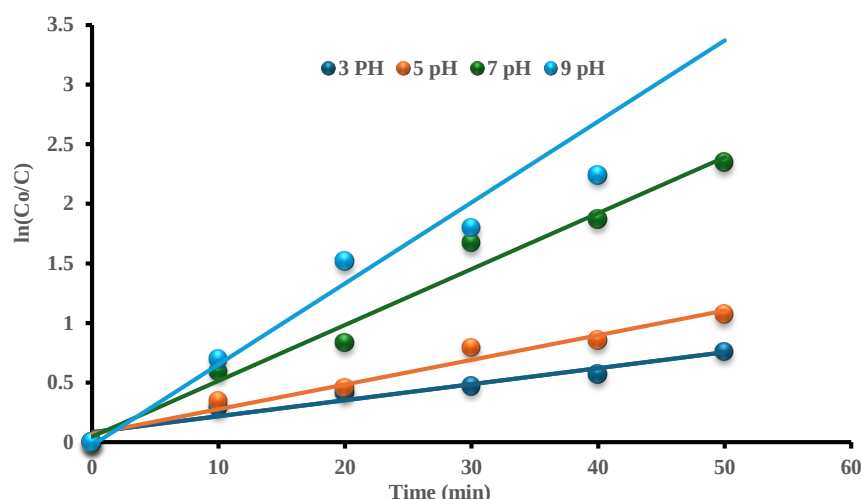


Figure 16: The first-order kinetic organic oxidation.

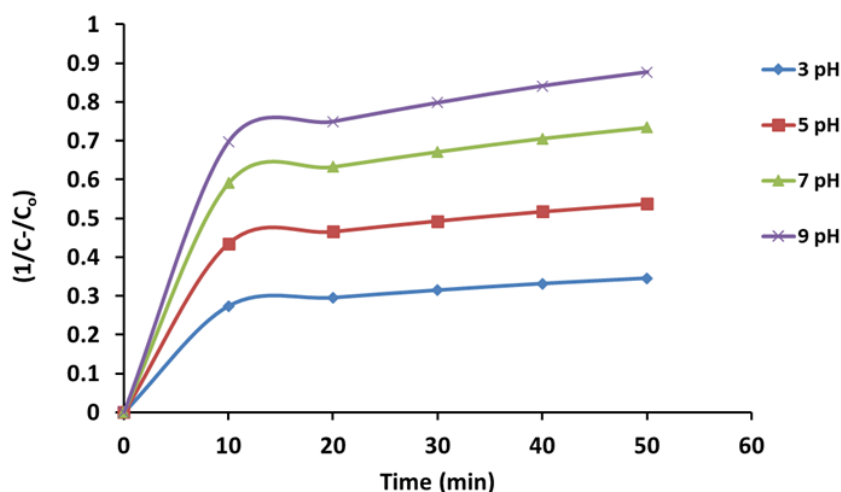


Figure 17: The second-order kinetic organic oxidation.

The oxidation kinetics were examined using both the pseudo-first-order and pseudo-second-order kinetic models to fix the rate-controlling mechanism. Comparison of the linear regressions and their consistent coefficients of determination (R^2) indicated that the pseudo-first-order oxidation showed a better agreement with the experimental data than the pseudo-second-order model. The pseudo-first-order plots presented higher linearity over the examined contact time, whereas the pseudo-second-order plots deviated from linear performance, chiefly during the initial oxidation stage. So, the oxidation treatment is more suitably described by pseudo-first-order kinetic oxidation, signifying that the oxidation rate is chiefly governed by the availability of active photodegradation sites during the initial stages of the treatment in Table 5 [43].

Table 5: Comparisons of rate constants for organic oxidation.

pH	First order		Second order	
	K_1 (1/min)	R^2	K_2 (L/mg.min)	R^2
3	0.0048	0.92	0.0003	0.88
5	0.0058	0.91	0.0004	0.89
7	0.0066	0.94	0.0006	0.9
9	0.0057	0.95	0.0005	0.89

Table 6: Comparison results between the methods.

Method	Working circumstances	Feedstock	Removal (%)	Requirement	Reff.
Batch oxidation reactor	300 rpm, medium pH, and 60 min	Malachite Green Dye	99.4	Photo-catalytic ZnO/bentonite/Ag	[44]
Photocatalytic oxidation	300 rpm, 6 g/L Dose, pH 10, and 90 min	Ciproxin Antibiotic	85	Photo catalyst and bentonite	[45]
Photocatalytic oxidation	200 rpm, 1.2 g/L Dose, 9 pH and 120 min	Rhodamine B Dye	96.3	photocatalytic and Oxidant Ag-ZnO/rGO	[46]
Photocatalytic oxidation	300 rpm, 5 ppm solution, pH 8, and 40 min	Methylene Blue Dye	98	Sol-Gel synthesized ZnO	[30]
Batch digital oxidation with BT	300 rpm, 1.5 g dose, pH 9, 60 °C and 120 min	RWW	90.5	Nano bentonite	This study
Batch digital oxidation with ZnO/BT	300 rpm, 1.5 g dose, pH 9, 60 °C and 120 min; 60 oC temperature : 120 min oxidation time:	RWW	99.7	Photocatalytic and Oxidant (ZnO/BT)	This study

3.7. Ecological implications and catalyst constancy

It is significant to note that the treated wastewater examined in this work is intended for manufacturing reuse within refinery processes rather than for direct human consumption. The main objective of the treatment procedure is to reduce the organic load and restore water recyclability for working reuse. In this context, the new composite established satisfactory working stability under the examined circumstances. Also, the immobilization of zinc oxide nanoparticles within the bentonite matrix is expected to reduce zinc metal release into the treated wastewater and to reduce the free radicals produced by oxidation, which react with any metals in wastewater and are converted to harmless byproducts in treated wastewater. The structural incorporation of metal oxide and Nano clay helps minimize nanoparticle dissolution while preserving catalytic activity during the oxidation process. So, the proposed system offers a practical, ecologically sound approach to requests for refinery wastewater reuse.

3.8. Comparison of the catalyst and previous catalysts

High levels of organic removal in wastewater produced from feedstock used in crude oil production. There are

many types of linked pollutant compounds, such as aromatics and phenols. Reliable adsorption and photocatalytic treatment, along with a variety of skills, are typically used to eliminate organic compounds. The hybrid treatment, which combines physical and chemical processes to remove pollutants from wastewater, is shown in Table 6 for comparison with this work and other works.

4. Conclusions

The sustainable construction of the new composite, prepared by precipitation methods from bentonite clay and zinc oxide, yielded a structurally stable, highly active multifunctional substance capable of hybrid adsorption and oxidation degradation. The prepared composite achieved stable dispersion within the digitally baffled combined adsorption and oxidation. Hybrid treatment optimization using the Box–Behnken design showed that pH, amount, process time, and temperature exerted strong interactive effects on adsorption and oxidation treatment. The degradation pathway closely followed first-order kinetics, confirming that organic concentration was the rate-determining factor and that the active oxidative species were reliably available throughout the process. Under optimal conditions of 2 hours process time, pH 9, 60 °C, and a 1.5 g dose, the new

composite achieved an overall pollutant elimination efficiency of 99.7 %, while nano clay achieved 90.5 %, confirming the superior performance of the new composite for organic contaminant elimination. The results confirmed that the combined treatment significantly increases reactive oxygen species and free radical production, resulting in greater adsorption and photocatalytic activity than pristine bentonite.

Importantly, the ZnO–BT nanocomposite demonstrates promising potential for hybrid processes in a digital baffle oxidation batch reactor, with composite amount and operating parameters to maintain high organic efficiency in wastewater. Overall, the nano catalyst in the digital baffle catalytic reactor proves strong potential as a maintainable, scalable, and energy-efficient solution for wastewater treatment.

5. References

1. Abdullah R, Astira D, Zulfiani U, Widyanto AR, Hidayat ARP, Sulistiono DO, et al. Fabrication of composite membrane with microcrystalline cellulose from lignocellulosic biomass as filler on cellulose acetate based membrane for water containing methylene blue treatment. *Bioresour Technol Reports*. 2024;25:101728. <https://doi.org/10.1016/j.biteb.2023.101728>.
2. Moawed EA, Eissa MS, Al-Tantawy SA. Application of polyurethane foam/zinc oxide nanocomposite for antibacterial activity, detection, and removal of basic dyes from wastewater. *Int J Environ Sci Technol*. 2023; 20(7):7767-74. <https://doi.org/10.1007/s13762-022-04428-w>.
3. Nawaf AT, Humadi JI, Jarullah AT, Ahmed MA, Hameed SA, Mujtaba IM. Design of nano-catalyst for removal of phenolic compounds from wastewater by oxidation using modified digital basket baffle batch reactor: experiments and modeling. *Processes*. 2023; 11(7):1990. <https://doi.org/10.3390/pr11071990>.
4. Zhang P, Zhang S, Xu M, Jiang S, Ou X, Wang C, et al. Bio-electro-Fenton systems in wastewater treatment: Research progress and prospects. *J Electroanal Chem*. 2025;981:118959. <https://doi.org/10.1016/j.jelechem.2025.118959>.
5. Ugurlu M, Ilterisyilmaz S, Köleoglu M. Synthesis of activated carbon supported catalysis systems and research for sonocatalytic performance on wastewater treatment. *Mater Today Proc*. 2021; 46(1):6908-12. <https://doi.org/10.1016/j.matpr.2021.01.556>.
6. Nawaf AT, Hassan AA. Design of (MnO₂/GO) for removal of organic compounds from wastewater using a digital baffle batch reactor. *Int J Environ Sci Technol*. 2025; 1-20. <https://doi.org/10.1007/s13762-025-06414-4>.
7. Nsaif RD, Alturki SF, Suwaed MS, Hassan AA. Lead removal from refinery wastewater by using photo-voltaic electro Fenton oxidation. In: *AIP Conference Proceedings*. AIP Publishing; 2023. <https://doi.org/10.1063/5.0163378>.
8. Hamza S, Swadi A, Yasser AA, Saleh A, Al-khateeb RT, Hassan AA, et al. Modelling Hybrid New Design Electrocoagulation-Electro Fenton Oxidation Systems for Efficient Wastewater Treatment. *Russ J Electrochem*. 2025;61(9):516-30. <https://doi.org/10.1134/S1023193525700089>.
9. Khan MSH, Rahaman MT, Pranta AD, Hasan MK. Eco-friendly organic nanomaterials for multi-functional textiles: sources, applications, recent advances and future prospects towards sustainability. *Int J Environ Sci Technol*. 2025;22(8):7353-410. <https://doi.org/10.1007/s13762-024-06299-9>.
10. Hassan AA, Shakir IK. Kinetic Insights into Solar-Assisted Fabrication and Photocatalytic Performance of CoWO₄/NCW Heterostructure. *Bull Chem React Eng Catal*. 2024;10. <https://doi.org/10.9767/bcrec.20198>.
11. Fernández De Dios MÁ, Iglesias O, Pazos M, Sanromán MÁ. Application of electro-fenton technology to remediation of polluted effluents by self-sustaining process. *Sci World J*. 2014. <https://doi.org/10.1155/2014/801870>.
12. Parven A, Meftaul IM, Venkateswarlu K, Megharaj M. Herbicides in modern sustainable agriculture: environmental fate, ecological implications, and human health concerns. *Int J Environ Sci Technol*. 2025; 22(2):1181-202. <https://doi.org/10.1007/s13762-024-05818-y>.
13. Nawaf AT, Abdulmajeed BA. Design of oscillatory helical baffled reactor and dual functional mesoporous catalyst for oxidative desulfurization of real diesel fuel. *Chem Eng Res Des*. 2024; 209:193-209. <https://doi.org/10.1016/j.cherd.2024.07.032>.
14. Li Y, Li Y, Ni BJ, Li YZ, Ni SQ. Towards scalable anammox: mechanistic insights and emerging strategies. *Trends Biotechnol*. 2025. <https://doi.org/10.1016/j.tibtech.2025.08.013>.
15. Jiang F, Zhang Y, Xu X, Mao Y, Wang M, Yang B, et al. Application of cysteine with Cu²⁺ to strengthen Fenton-based treatment of coking wastewater used ferric sludge as a source of iron catalyst: Cl-removal and Fe³⁺/Fe²⁺ cycling. *J Environ Chem Eng*. 2025; 13(5):117556. <https://doi.org/10.1016/j.jece.2025.117556>.
16. Meneceur S, Laouini SE, Mohammed HA, Bouafia A, Salmi C, Abdullah JAA, et al. Eco-Friendly ZnO/CuO/Ni Nanocomposites: Enhanced photocatalytic dye adsorption and hydrogen evolution for sustainable

- energy and water purification. *J Cryst Growth*. 2025; 650:127984. <https://doi.org/10.1016/j.jcrysgro.2024.127984>.
17. Ameen S, Fatima R, Kadhem AA, Abbas T, Khan MA, Abbas A, et al. Enhanced photocatalytic degradation of methylene blue using aluminum and cerium co-doped ZnO nanocomposite. *Int J Environ Sci Technol*. 2025;22(16):16549-58. <https://doi.org/10.1007/s13762-025-06683-z>.
 18. Hassan AA, Shakir IK. Synthesis of nanocellulose using ultrasound-assisted acid hydrolysis for adsorption/oxidation of organic pollutants in wastewater under UV and solar light. *J Sustain Sci Manag*. 2024;19(12):120-140. <https://doi.org/10.46754/jssm.2024.12.008>.
 19. Del Sole R, Fogel AA, Somin VA, Vasapollo G, Mergola L. Evaluation of effective composite biosorbents based on wood sawdust and natural clay for heavy metals removal from water. *Materials (Basel)*. 2023;16(15). <https://doi.org/10.3390/ma16155322>.
 20. Navidpour AH, Fakhrzad M, Tahari M, Abbasi S. Novel photocatalytic coatings based on tin oxide semiconductor. *Surf Eng*. 2019; 35(3):216-26. <https://doi.org/10.1080/02670844.2018.1477559>.
 21. Akbari, Mona and Akbari M. Modeling of preparation of chitosan/tripolyphosphate nanoparticles using machine-learning techniques. *Iran J Chem Chem Eng*. 2024;43(1). <https://doi.org/10.30492/ijcce>. 2023. 1996385.5925.
 22. Al-Hassan AA, Shakir I. Enhanced photocatalytic activity of CuO/NCW via adsorption optimization for refinery wastewater. *Iran J Chem Chem Eng*. 2024. <https://doi.org/10.30492/IJCCE.2024.2034599.6684>.
 23. Cao L, Li Z, Xiang S, Huang Z, Ruan R, Liu Y. Preparation and characteristics of bentonite-zeolite adsorbent and its application in swine wastewater. *Bioresour Technol*. 2019;284:448-55. <https://doi.org/10.1016/j.biortech.2019.03.098>.
 24. Hadi HJ, Ali ND, Ahmed T, Al-khateeb RT, Hassan AA, Humadi JI. Cotton-derived activated Carbon/CuO nano-photocatalyst for Organic-rich produced water treatment in a digital baffle adsorption-oxidation reactor. *Nanotechnol Environ Eng*. 2026; 11(2):45. <https://doi.org/10.1007/s41204-026-00548-7>
 25. Farise SB, Alabdly HA, Hasan AA. Lead removal from simulated wastewater using magnetite as adsorbent with box-behnken design. *IOP Conf Ser Earth Environ Sci*. 2021;790(1). <https://doi.org/10.1088/1755-1315/790/1/012043>.
 26. AlJaberi FY, Abdulmajeed BA, Hassan AA, Ghadban ML. Assessment of an electrocoagulation reactor for the removal of oil content and turbidity from real oily wastewater using response surface method. *Recent Innov Chem Eng* 2020;13(1):55-71. <https://doi.org/10.2174/2405520412666190830091842>.
 27. Farhan MASOI, Hassan MIFAA, Humadi ATNJI. Hydrocarbon removal from refinery wastewater by photo - Fenton oxidation process: a new digital baffled photo batch reactor. *Int J Environ Sci Technol*. 2026; 9. <https://doi.org/10.1007/s13762-025-06865-9>.
 28. Amdeha E. Biochar-based nanocomposites for industrial wastewater treatment via adsorption and photocatalytic degradation and the parameters affecting these processes. *Biomass Convers Biorefinery*. 2023; (0123456789). <https://doi.org/10.1007/s13399-023-04512-2>
 29. Atiyah AS, Al-Samawi AAA, Hassan AA. Photovoltaic cell electro-Fenton oxidation for treatment of oily wastewater. *AIP Conf Proc*. 2020;2235 (May). <https://doi.org/10.1063/5.0008937>.
 30. Hassan AA, Al-Zobai KMM. Chemical oxidation for oil separation from oilfield produced water under UV irradiation using titanium dioxide as a nano-photo-catalyst by batch and continuous techniques. *Int J Chem Eng*. 2019;2019. <https://doi.org/10.1155/2019/5064527>.
 31. Alturki SF, Ghareeb AH, Hadi RT, Hassan AA. Evaluation of using photovoltaic cell in the electro-fenton oxidation for the removal of oil content in refinery wastewater. *IOP Conf Ser Mater Sci Eng*. 2021; 1090(1):012012. <https://doi.org/10.1088/1757-899X/1090/1/012012>.
 32. Yan S, Lai X, Fan L, Wang T, Yao Y, Wang W. Integrating adsorption and in situ advanced oxidation for the treatment of organic wastewater by 3D carbon aerogel embedded with Fe-doped carbonitrides. *Environ Sci Pollut Res*. 2023; 30(1):1386-98. <https://doi.org/10.1007/s11356-022-22275-7>.
 33. Peralta-Hernández JM, Vijay S, Rodríguez-Narváez O, Pacheco-Álvarez MA. Photo and solar fenton processes for wastewater treatment. *Electrochem Water Wastewater Treat*. 2018;223-37. <https://doi.org/10.1002/9781119283675.ch9>.
 34. Hassan AA. Integrated treatment of refinery wastewater using oxidized cotton waste (H₂O₂/NaOH/CW) as adsorbent and photodegradation. *J Chem Pet Eng*. 2025;9(2):237-55. <https://doi.org/10.22059/jchpe.2025.377224.1519>.
 35. Pipil H, Yadav S, Chawla H, Taneja S, Verma M, Singla N, et al. Comparison of TiO₂ catalysis and Fenton's treatment for rapid degradation of Remazol Red dye in textile industry effluent. *Rend Lincei*. 2022; 33(1):105-14. <https://doi.org/10.1007/s12210-021-01040-x>.
 36. Adday AS, Al-Jubouri SM. Photocatalytic oxidative removal of the organic pollutant from wastewater using recyclable Ag₂O@CRA heterojunction photocatalyst. *Case Stud Chem Environ Eng*. 2024; 10: 100852. <https://doi.org/10.1016/j.cscee.2024.100852>.
 37. Li X, Wu YY, Peng YF, Wu B, Chen K, Ji LJ. CFD simulation of mass transfer in adsorption column: Numerical analysis of molecular diffusion and convection. *J Water Process Eng*. 2025; 79:108967. <https://doi.org/10.1016/j.jwpe.2025.108967>.
 38. Hassan A, Sharshoh M, Nawaf A, Humadi J. Synthesis of Mn₃O₄/nano-activated carbon composite and its application for heavy metal removal in a digital

- baffle adsorption reactor. *Nanotechnol Environ Eng.* 2026;7:1-21. <https://doi.org/10.1007/s41204-025-00467-4>.
39. Li X, Wang Z, Zhang Y, Zhang W, Zhang H, Liu P, et al. Hydrogen-rich gas formation from catalytic pyrolysis of biomass tar by aluminum dross coupled HZSM-5 co-loaded Ni-Fe bimetallic catalysts: Influence of co-carrier characteristics. *J Environ Manage.* 2025;389:126016. <https://doi.org/10.1016/j.jenvman.2025.126016>.
40. Hussein MG, Nawaf AT, Jafer AS, Hassan AA. New design electro-catalytic digital baffle batch oxidation reactor for organic removal from refinery wastewater. *Glob Nest J.* 2025;27(4). <https://doi.org/10.30955/gnj.07218>.
41. Pal DB, Lavania R, Srivastava P, Singh P, Srivastava KR, Madhav S, et al. Photo-catalytic degradation of methyl tertiary butyl ether from wastewater using CuO/CeO₂ composite nanofiber catalyst. *J Environ Chem Eng.* 2018;6(2):2577-87. <https://doi.org/10.1016/j.jece.2018.04.001>
42. Teymori M, Khorsandi H, Aghapour AA, Jafari SJ, Maleki R. Electro-Fenton method for the removal of Malachite Green: effect of operational parameters. *Appl Water Sci.* 2020; 10(1). <https://doi.org/10.1007/s13201-019-1123-5>.
43. Yin Z, Liu S, Tian Z, Zhao X, He J, Wang C. Carbon-based nanomaterials mediated adsorption and photodegradation of typical organic contaminants in aqueous fulvic acid solution. *Water Sci Technol.* 2023;88(7):1863-74. <https://doi.org/10.2166/wst.2023.250>.
44. Fajar ABN, Safitri N, Naufal WM, Fadhillah AM, Arsenalia S, Nugrahaningtyas KD, et al. ZnO/Bentonite composites for environmental remediation: The influence of preparation method on composite structural characteristics and dye removal effectivity. *Next Mater.* 2025;9:101332. <https://doi.org/10.1016/j.nxmater.2025.101332>.
45. Hamada MA, Sadek OM, Mekhamer WK, Al-Balawi SM, Elsafi M, Saleh IH. Green preparation and evaluation of bentonite-supported Bi₂O₃/polyester nanocomposites as gamma radiation shielding materials. *Sci Rep.* 2026;16:17847. <https://doi.org/10.1038/s41598-026-53392-9>.
46. Kadhem AA, Alshamsi HA. Biosynthesis of Ag-ZnO/rGO nanocomposites mediated *Ceratophyllum demersum* L. leaf extract for photocatalytic degradation of Rhodamine B under visible light. *Biomass Convers Biorefinery.* 2024;14(19):24655-69. <https://doi.org/10.1007/s13399-023-05069-w>.

How to cite this article:

Aziz JS, Rashid AH, Jassim NJ, Hassan AA, Abood SA. Bio-Assisted Synthesis and Photocatalytic Performance of ZnO–Bentonite Nanocomposite in a Digital Baffle Catalytic Reactor for Organic Pollutant Removal. *Prog Color Colorants Coat.* 2027;20(3): 251-269. <https://doi.org/10.30509/pccc.2026.167826.1518>.

