

Article

Treatment of Textile Wastewater by a Novel Clay/TiO₂/ZnO-Based Catalyst, Applying a Synergic Catalytic Ozonation–Electrofloculation Process

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Abstract: This study aims to investigate the treatment of real textile wastewater using a novel bentonite clay/TiO₂/ZnO-based ozonation catalyst. In this study, synergic electrofloculation/catalytic ozonation, catalytic ozonation, and ozonation processes are applied in a modified hybrid reactor. To the authors' knowledge, this is the first application of bentonite clay/TiO₂/ZnO as an ozonation catalyst for treating real textile wastewater. The four operational variables—ozone dose (0.2–0.8 mg/min), reaction time (0–120 min), DC voltage supply (5–15 V), and catalyst dose (0.5–2 g/L)—were studied for decolorization and for the removal of chemical oxygen demand (COD). The results showed that the combined process (electrofloculation + clay/TiO₂/ZnO/O₃) had the highest removal efficiencies for COD and color (97.86% and 97.90%, respectively) at optimum parameters of 10 DC volts, an ozone dose of 0.8 mg/min, and a catalyst dose of 2 g/L in textile wastewater. The results further revealed that the initial pH of wastewater plays an essential role in the process's overall performance. The studied synergic process was efficient for real wastewater treatment under alkaline pH (6–9). Based on empirical work, we established that the synergic process is suitable for effectively treating textile wastewater.

Keywords: catalytic ozonation; electrofloculation; decolorization; COD; textile wastewater



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1. Introduction

Water is an essential requirement for the survival of human beings. However, water pollution is one of the critical problems leading to the inefficient utilization of water resources. Increases in population and industrialization may lead to increased water pollution, and untreated wastewater discharge may be a reason for such pollution.

Textile industries are the second-most-prominent industries in the world [1]. The organic pollutants in the wastewater of textile industries include toxic chemicals, complex organic pollutants, and mutagenic organic compounds that may harm humans and aquatic life [2]. For many years, scientists have investigated various conventional and advanced treatment technologies for converting complex organic pollutants into less toxic substances. Because many organic pollutants are non-biodegradable and chemically unstable, their treatment with conventional biological processes may not be effective. Therefore, advanced treatment technologies are an utmost priority [1].

To date, several conventional wastewater-treatment methods have been studied, including adsorption [3], coagulation–flocculation [4], incineration [5], and biological treatment [4]. However, these methods may not be able to completely treat wastewater due to the presence of toxic and biological-resistant pollutants. Moreover, they may be time-consuming and provide incomplete removal of recalcitrant compounds [6].

Currently, advanced oxidation processes (AOPs) receive much attention. AOPs are applied to degrade various recalcitrant organic compounds in wastewater [6]. The processes generate free hydroxyl radicals ($\text{HO}\cdot$) that are among the most powerful and non-selective oxidants, which may lead to the removal of persistent dyes and other organic pollutants in wastewater [7]. Among AOPs, the most widely used treatment methods are hydrogen-peroxide-based processes, Fenton-like processes [8], electrochemical oxidation, oxidation combined with hydrodynamic acoustic cavitation [9], and catalytic ozonation processes [6].

Catalytic ozonation has been widely studied in recent years, due to its efficient performance in removing various pollutants. However, most of the studies used aqueous solutions instead of real industrial wastewater. Testing a catalytic process in a more challenging environment is essential. Therefore, in recent years, real wastewater has been used for such testing. Many materials have been used as catalysts, including activated carbons, metal-organic frameworks, metal oxides, zeolites, and clays. However, economic factors, as well as the effectiveness of such materials, must be considered. Clay-based catalysts may be more economical than many other materials that have been tested as catalysts in ozonation processes. Therefore, in the current investigation, we prepared a bentonite-based catalyst (clay-TiO₂-ZnO) to study the treatment of real textile wastewater.

Electroflocculation is a process that is widely used in the textile industry to degrade persistent dyes from wastewater. The process depends, mainly, on the type, nature, pH, and material of the electrodes that affect the overall removal-process efficiency [10,11]. Electroflocculation has been applied to treat various industrial and domestic effluents, such as paper, textiles, paint, and distillery effluents. During electroflocculation, oxidation at the anode produces the situ electrocoagulants to remove organic materials from wastewater [12].

Additionally, catalytic ozonation and electroflocculation processes are essential in the synergic process. Electroflocculation is very helpful for reducing turbidity and the catalytic ozonation process is helpful for removing COD and color. The stand-alone processes cannot perform efficiently in very high turbidity conditions. Therefore, a synergic process, applying both techniques, may improve the efficiency of the process [13]. Applying hybrid treatment methods may overcome the limitations of the stand-alone processes by providing fast degradation of antibiotics with less time and lower operating costs [14].

In recent years, advanced oxidation processes (AOPs) have gained much attention for the future treatment of real wastewater. Among these processes, catalytic ozonation showed better performance for treating effluents using a synergic process, which is essential. One study investigated the removal of reactive black 5 dye using CuMn₂O₄/gC₃N₄ (coated zeolites 4A) in a combined electroflocculation–catalytic ozonation hybrid reactor [15]. The results showed that maximum removal efficiency was achieved at an optimum pH of 10 in 30 min. The radical scavenger reduced the removal efficiency, indicating a radical-scavenger-based mechanism for the synergic process. Thus, CuMn₂O₄/gC₃N₄–zeolite catalysts seem to be promising in the synergic process for textile wastewater treatment [15].

In a few recent studies involving several processes, such as ozonation, electroflocculation, catalytic ozonation, and combined electro-flocculation–catalytic ozonation, hybrid processes were found to be highly effective for treating textile wastewater. However, it is difficult to degrade real textile effluents by applying only one technique, due to the complexity and persistent nature of dyes. S Electroflocculation combined with catalytic ozonation increases overall removal efficiency in real conditions and enhances the applicability of the treatment at a more comprehensive pH range, due to the mechanisms involved in the hybrid process [16]. Electroflocculation has been successfully applied for removing dyes from textile wastewater, depending mainly on the pH of the solution. Successful

application also depends on type, nature, and material of the electrode, which affect the overall efficiency of the removal process [11].

Nanomaterials, such as nanoclay, titanium dioxide (TiO₂), and zinc oxide (ZnO), have been used to sequester a variety of persistent dyes in wastewater [14]. The photocatalysts TiO₂ and ZnO immobilized on bentonite clay seem to be promising sequesters, and they have been explored for wastewater remediation via nanotechnology. Titanium dioxide and zinc oxide are cheap and non-toxic; however, their large-scale use is limited due to significant band-energy gaps and other issues. To overcome these limitations, the photocatalysts are combined or immobilized on other adsorbent surfaces such as clay and sodium [17]. Due to its low cost, availability, reusability, porosity, and enhanced adsorption capacity, clay is most widely used for wastewater treatment [18].

The current study involves the first-time application of a novel bentonite clay/TiO₂/ZnO nanocomposite for removing the color and the COD from real textile wastewater. The four operational parameters—pH, voltage, time, and ozone dose—were optimized for single ozonation, catalytic ozonation, and a synergic catalytic ozonation–electrofloculation process in a hybrid electrochemical reactor. This study may provide economic and environmental benefits and help to achieve sustainable development goals.

2. Results and Discussion

2.1. Characterization

The FTIR spectrum of clay/TiO₂/ZnO before and after adsorption was determined. The peak observed in the 1032.61 cm⁻¹ region assigned the vibrations of the TiO₂ coating, as shown in Figure 1. After the process, the peak was shifted slightly toward the left, as shown in Figure 1, due to the organic pollutants becoming adsorbed after treatment. The two peaks depicted at 1120–1000 cm⁻¹ in the raw bentonite were due to vibrations of Si-O-Si. The two peaks at 914 cm⁻¹ and 990 cm⁻¹ depict the vibration of Al-Al-OH and Si-O-Al in the raw bentonite sheets [19]. The small peaks at 688 cm⁻¹, 778 cm⁻¹, and 528 cm⁻¹ were due to Si-O-Al, Al-Mg-OH, and Si-O-Al vibrational stretching, which may have been caused by the octahedral and tetrahedral crystal lattice of the raw bentonite [19]. The fact that no sharp peaks were detected below 3000–1800 cm⁻¹ in the raw bentonite indicated that there were no organic impurities in the bentonite. The broad peak at 521 cm⁻¹ was attributed to the coating of ZnO. The peaks that appeared at 552 and 529 cm⁻¹, respectively, showed the Si-O-Si and Al-O-Si bond-stretching of bentonite clay, and the peaks observed at 739 cm⁻¹ and 689 cm⁻¹ reflected quartz vibrations in the composite [20]. The stretching vibrations of the Si-O bond can be seen in the clay sample at 1028 cm⁻¹; the weak peaks appeared at the 530 cm⁻¹–610 cm⁻¹ regions, showing zinc in the composite [20]. The peaks that appeared at 512 cm⁻¹ showed the vibrations of titania, as shown in Figure 1 [21]. The peaks at 512 cm⁻¹ and 521 cm⁻¹ confirmed the successful coating of photocatalyst on the bentonite surface.

In the SEM images of the prepared clay/ZnO/TiO₂ composite, as shown in Figure 2a,b, the uniform distribution of TiO₂ and bentonite particles can be detected, and the bentonite particles are located on the TiO₂ surface. The SEM images determined the synthesized composite's size and surface morphology before and after the synergic process. The distribution of the ZnO particles on the composite can be seen in Figure 2a, where the sample surface is covered with zinc oxide particles, and there are no remarkable changes in morphology after coating with ZnO. The SEM images of zinc oxide particles show clusters connected to the sample surface. The TiO₂ particles reduced spherically in this image, unlike the pristine titania [21]. The ZnO particles showed flower-like and spherical morphology; however, when combined with the TiO₂/clay sample, the composition morphology of these particles was entirely changed, as shown in Figure 2a. After the treatment process, the surface became porous and rough, as shown in Figure 2b. The elemental composition of the synthesized composite before and after the process has been presented on Table 1 and shown in Figure 3.

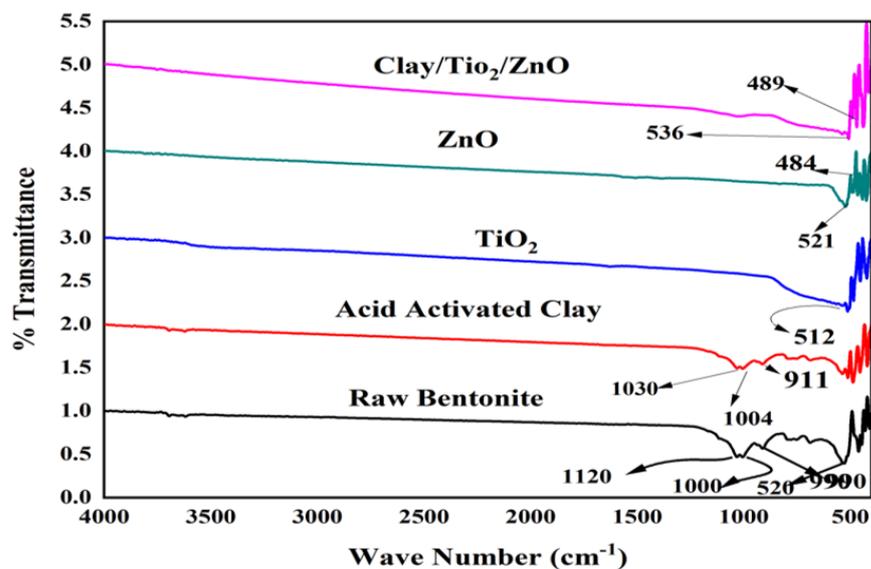


Figure 1. FTIR analysis before and after adsorption.

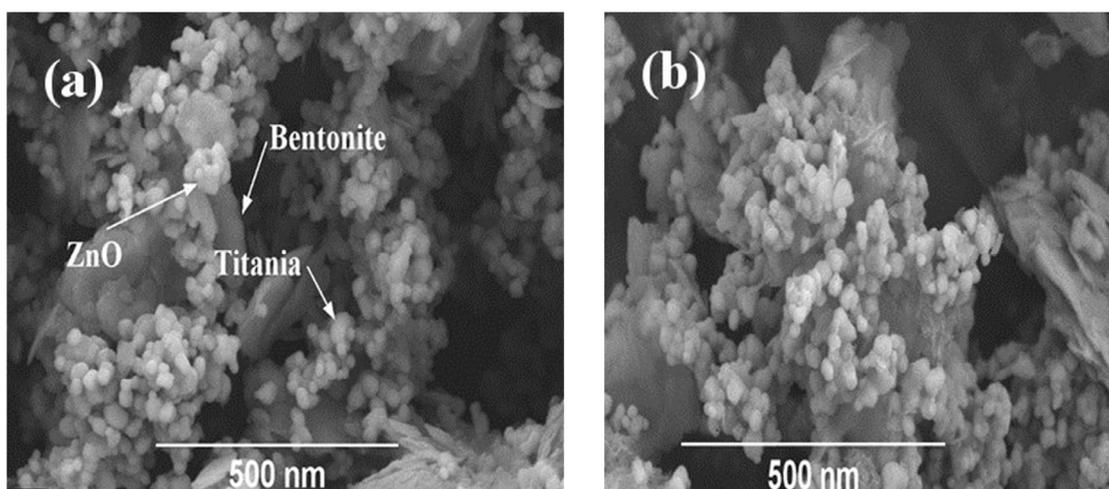


Figure 2. SEM images before and after adsorption (a,b).

Table 1. EDX analysis before and after the process.

Elements	Before Process	After Process
O	68.46	67.25
Na	3.71	4.2
Al	4.58	7.16
Si	4.97	4.11
Nb	1.63	1.44
K	0.45	0.38
Ti	13.78	14.33
Cu	0.28	0.31
W	0.38	0.27
Zn	1.41	0.55

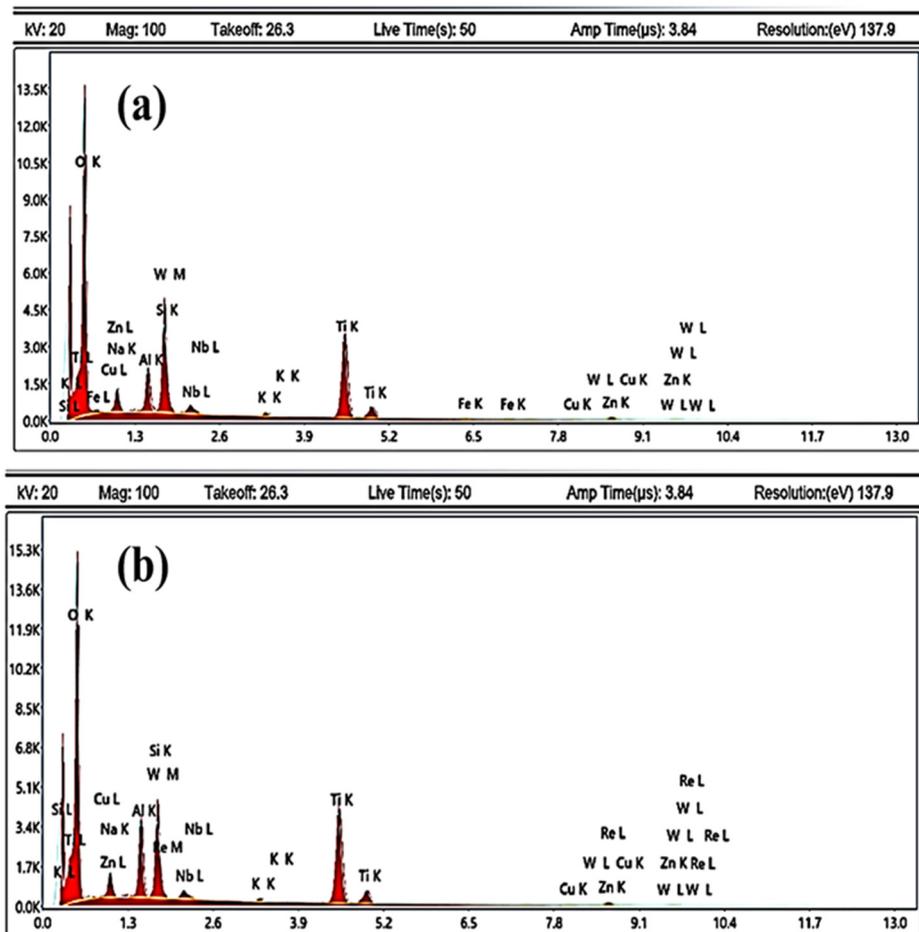


Figure 3. EDX analysis of nanocomposite before and after adsorption (a,b).

2.2. Surface Area, Porosity, and Pore-Size Distribution

The percentage of porosity, the surface area, and the pore-size distribution could be calculated from the SEM images using an open-source image-processing image-j (1.51p) software [22]. This technique undergoes repetitive computational processes and reduced times by using thresholding algorithms in the image j software. The surface area and the pore-size distribution of 100 particles, before and after the process, are shown in Figure 4. The SEM images were converted to binarized-image 8-bite grayscale pixel-selected threshold values of 0–255 after applying the bandpass filter. The red region represents the pores, as shown in Figure 4c,d.

The percentages of porosity were determined to be 69.37% and 55.96%. After the process, the percentage of porosity was reduced, showing that the surface became porous after this process, due to the removal of water molecules, organic molecules, and inorganic molecules that were present in the textile wastewater. The average pore radius was determined to be 2.3225 nm, which constituted mesopores according to the International Union of Pure and Applied Chemistry (IUPAC) rules; after the process, the pore radius decreased to 2.2078 nm, as shown in Figure 4e,f, due to the large available surface area. The histogram indicated that excellent removal efficiency was found in the particles that had a smaller pore radius, due to the larger surface area. Because small particles had a shorter diffusion path, allowing the pollutants to penetrate more deeply and more quickly into the catalyst particle—resulting in a higher adsorption rate for large particles—the internal diffusion path was enhanced and, therefore, there was a greater probability of encountering small-sized pores [23]. The pore-size histogram became narrow after the process, showing uniform pore-size distribution after the process, as shown in Figure 4e,f [23].

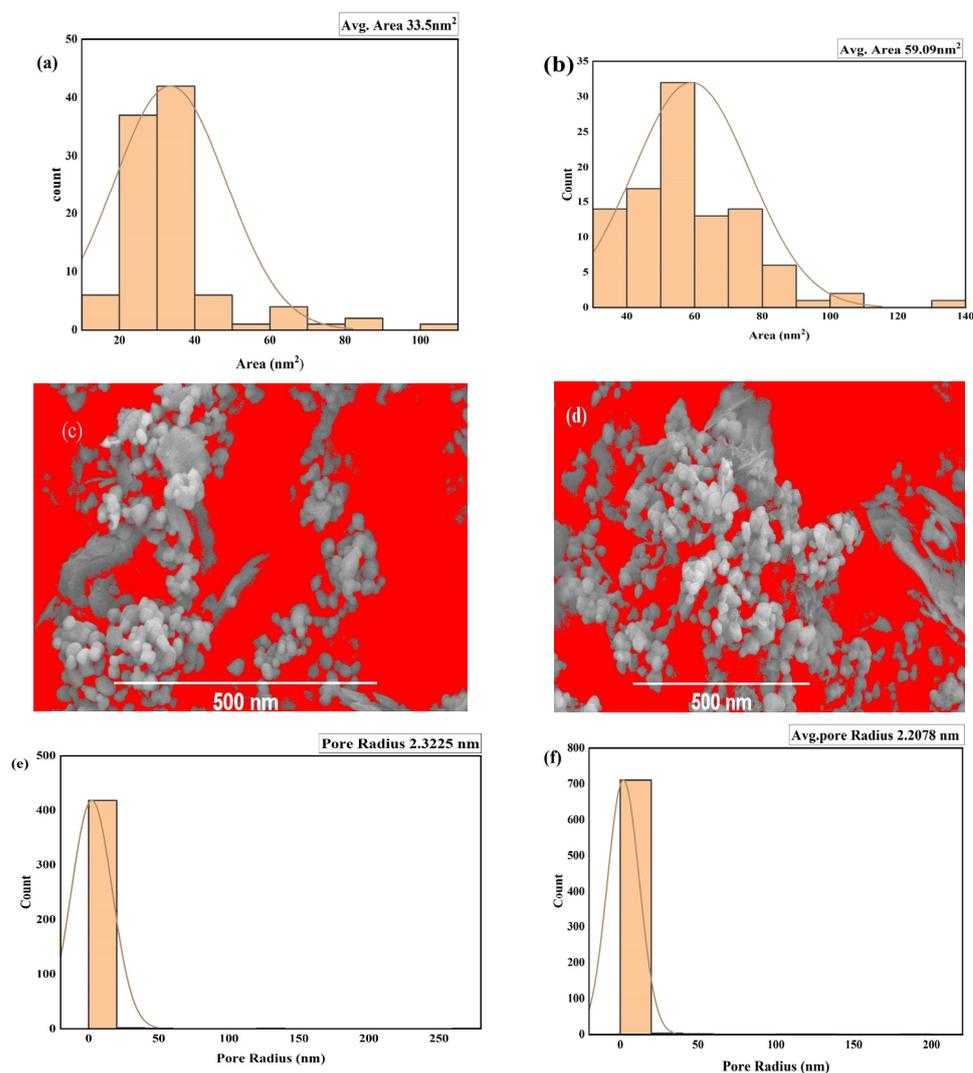


Figure 4. Surface area, porosity, and pore-size distribution before process (a,c,e) and after process (b,d,f).

2.3. Ozone Dose Optimization

Ozone, the most efficient oxidant, readily oxidizes the organic pollutants present in textile wastewater and plays a vital role in the removal of COD and color. The ozone dose was optimized at three different ozone doses, 0.2, 0.6, and 0.8 mg/min. The efficiency of color removal increased with increases in the ozone dose by 83.05%, 90.87%, and 95.035% within 120 min of ozonation [7]. The optimum removals of COD and color were achieved to be 78.3% and 95.035%, respectively, at 0.8 mg/min. By increasing the ozone dose, more organic compounds degraded, because the ozone accelerated the oxidation process, resulting in the decomposition of organic pollutants by breaking down their chemical structures [24]. The rate of color removal was increased with increases in the ozone dose, due to the formation of free hydroxyl radicals (OH), resulting in increased ozone transfer from the gaseous phase to the liquid phase, as shown in Figure 5a.

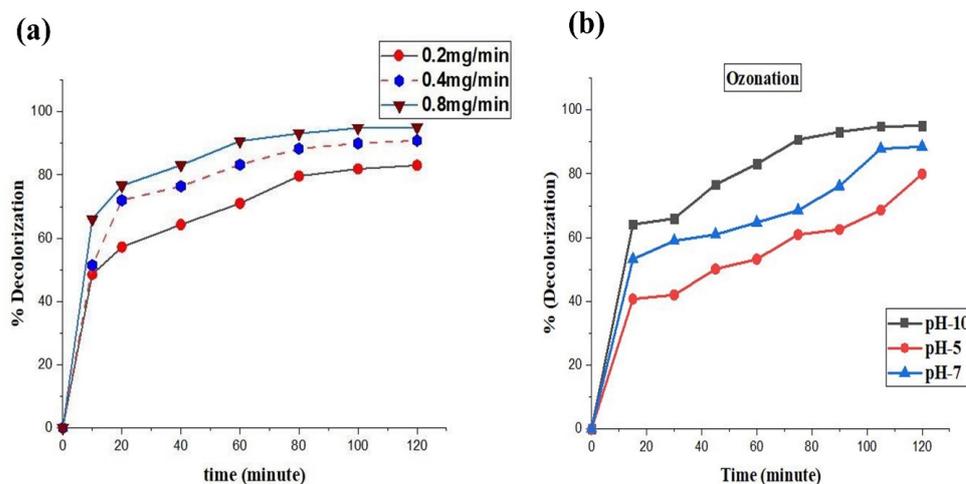


Figure 5. (a) Ozone dose optimization at $\text{pH} = 10$, time = 120 min; (b) pH optimization at ozone dose = 0.8 mg/min, time = 120 min.

In addition, in the case of the catalytic, the synergic catalytic ozonation–electroflocculation at this optimum ozone dose was analyzed. The concentration of the ozone/ O_2 mixture in the solution was ensured to trigger the production of oxidants, enhancing the removal efficiency of color and COD to 97.90% and 97.83%, respectively, in one hour, as shown in Figure 6. Thus, the synergic process provided better removal efficiency for COD and color in a reduced time, compared to that of the single-ozonation and catalytic-ozonation processes [16].

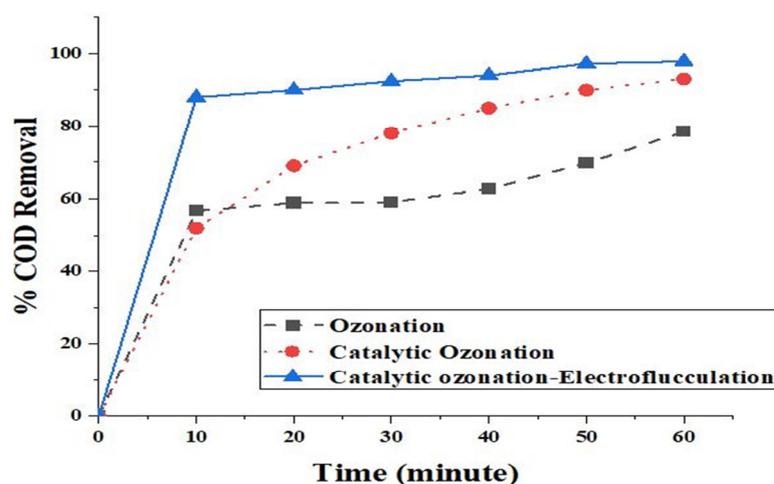


Figure 6. Comparison of COD removal for all process at $\text{pH} = 10$, time = 120 min. ozone dose 0.8 mg/min and adsorbent dose 2 g/L.

2.4. pH Optimization

The initial pH had a profound impact on exploring the ozonation mechanism. We optimized the pH at three different values (5, 7, and 10) for single ozonation. The pH_{zc} of the photocatalyst was determined to be 6.7. At an acidic medium (a pH of 5), molecular oxygen was released, which removed only selective aromatics and organic compounds. However, the decolorization rate was slow [25]. Figure 6 shows that the color-removal efficiency increased with increases in pH from 41% to 95%. The maximum removal of COD and color was determined to be 78.9% at a pH of 10 for single ozonation. Under alkaline conditions, the ozonation was more favorable for both COD and color removal, because at a basic pH of 10, more ozone decomposed due to free hydroxyl ($\cdot\text{OH}$) radicals that reacted with the organic compounds that were present in the textile wastewater; on the other hand, in acidic conditions (pH of 5), the molecular ozone (O_3) reacted directly with the organic

contaminants. Therefore, the radicals ($\bullet\text{OH}$) had a robust oxidizing potential under alkaline conditions and were less selective than the molecular ozone [6].

Ozonation in the presence of a nanocatalyst provided more removal of color (96.4%) and COD (93%) under the optimum condition of a pH of 10 than single ozonation, due to the enhanced adsorption capacity and porosity of the nanocomposite, as shown in Figure 5b. The surface charges of a nanocatalyst are governed by reaction kinetics, in the case of catalytic ozonation, for the removal of real effluents. For electroflocculation, which is a self-pH-neutralizing process, the pH was initially enhanced to the alkaline range, due to the H_2O electrolysis and the generation of (OH^-) ions and hydrogen evolution [11]. Under primary conditions (pH of 7–10), more insoluble $\text{Al}(\text{OH})_3$ was formed, and the ultimate Al ions conversion achieved pH stability. For combined catalytic ozonation–electroflocculation, the percentage of color removal was higher compared to that achieved with ozonation and catalytic ozonation at a pH of 10, due to the formation of the predominant species, $\text{Al}(\text{OH})_4^-$ [26]. The percentage of color removal increased from 91% to 97% with the move from acidic to alkaline medium, and in the presence of a nanocatalyst enhanced the color-removal efficiency to 97.90% in one hour. In contrast, the COD removal was 97.83%, as shown in Figure 6. At alkaline conditions (pH of 10), synergic catalytic ozonation and electroflocculation contained the maximum reduction of real effluents from textile wastewater; the ozonation enhanced the self-decomposition and provided more hydroxyl-free radicals that promptly degraded the pollutants [15]. The pH_{zpc} of the nanocomposite was 6.7; thus, $\text{pH} > \text{pH}_{\text{zpc}}$ showed that the surface of the nanocatalyst was negatively charged. Under the acidic condition, the reduced removal of COD and color was found to be due to the electrostatic repulsion, hydrogen bonding, and the π – π interaction between the pollutants and the nanocatalyst [27].

Moreover, at high pH, the synergy effect of the H_2 bubbles generated during electroflocculation, combined with ozonation, develops bubbling in the system, predominantly inducing mixing, turbulence, and gas–solid–liquid contact via the enhanced mobility of ions, causing a prompt removal of real effluents from the textile wastewater [13].

It is important to emphasize that the pH of water may significantly affect the efficiency of a treatment process. In the case of catalytic ozonation and the ozonation process, the overall removal efficiency tends to increase with the increase in pH. This may be due to the increase in the production of hydroxyl radicals at higher pH values. Even in an aqueous environment, hydroxide ions react with the molecular ozone, leading to the production of hydroxide radicals. However, at low pH values, a molecular ozone reaction dominates, while at higher pH values, a hydroxyl radical-based mechanism dominates [6].

The studied process may also follow another mechanism simultaneously, along with the radical-based process, as described above. Electroflocculation not only leads to the generation of reactive oxygen species; the removal of pollutants also contributes by the sweep flocculation mechanism at higher pH values, where alumina lead to the formation of $\text{Al}(\text{OH})_3$ flocculation and to the adsorption of dyes and color from textile wastewater [13].

In the current study, the maximum color and COD reductions of 97.90% and 97.83%, respectively, were achieved at a pH of 10, while at a pH of 7 and a pH of 5, the maximum reductions were 95.7% and 91%, respectively. A reduction in color removal was obtained. Thus, the real experiments were performed at the optimum conditions of a pH of 10 and an ozone dose of 0.8 mg/min.

2.5. Time Optimization

As shown in Figure 7a, the time was optimized for ozonation by increasing the time, producing more hydroxyl free radicals (OH) and increased degradation of organic pollutants in textile wastewater. The decolorization rate increased from 50% to 95%, as shown in Figure 7a. Ozone caused the degradation of dye or other real effluents present in textile wastewater by splitting the unsaturated bonds in their structures. Thus, the increased time provided more gas–liquid contact for decolorization and the degradation of organics and byproducts, achieving higher efficiencies of decolorization and COD-

removal. The oxidation capacity was also increased by increasing the time, due to additional generation of free hydroxyl radicals. However, in the case of combined catalytic ozonation–electrofloculation, the degradation time was reduced to one hour, due to water electrolysis, hydrogen evolution, and the generation of a more predominant species of $\text{Al}(\text{OH})^{-4}$ [24].

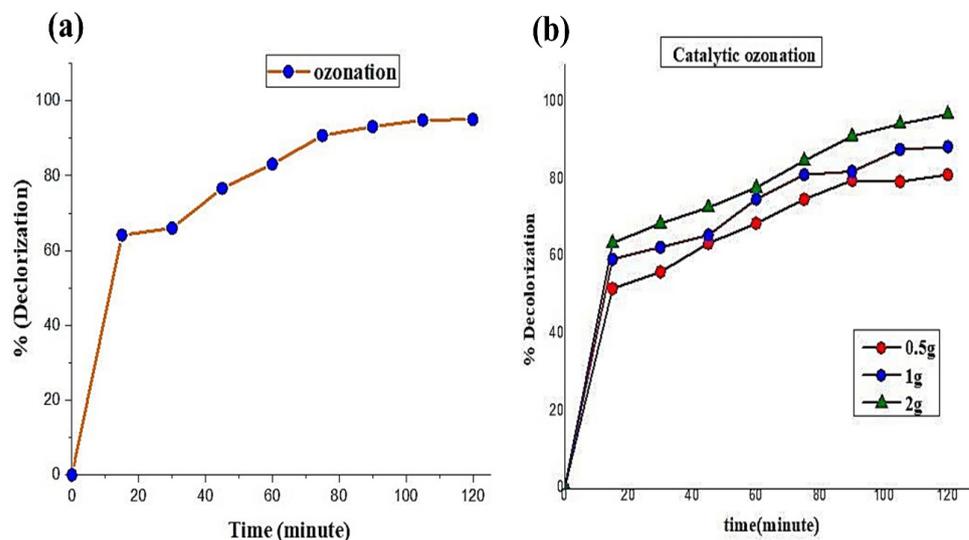


Figure 7. (a) Time optimization at pH 10, ozone dose = 0.8 mg/min; (b) catalyst dose optimization at pH = 10, ozone dose = 0.8 mg/min, time = 120 min.

2.6. Catalyst Dose Optimization

The catalyst dose was optimized at three different values—0.5 g/L, 1 g/L, and 2 g/L—on the modified bentonite clay/TiO₂/ZnO oxidation process to treat real textile effluents. The optimum color removal was achieved at the catalyst dose of 2 g/L. This showed that the percentage of decolorization increased with an increase in the catalyst dose, as shown in Figure 7b. The maximum removals of color and COD were achieved at 97.05% and 93%, respectively, with the optimum conditions of time, pH, and a catalyst dose of 2 g. The ozone dose of 0.8 mg/min 120 min may have been due to an increase in the adsorption rate at which the catalyst played a vital role in removing textile effluents in the combined ozonation process [25]. The catalyst played a vital role in the synergy by enhancing the kinetics and adsorption capacity for removing organics in textile wastewater [16]. In the synergic process, varying the catalytic dose from 0.5 g/L to 2 g/L provided remarkable reductions in the color and COD of textile wastewater, as shown in Figure 8a. The COD removal increased from 88% to 97.83% and color removal increased from 59% to 97.9%, consuming only 2 g/L of catalyst. The nanocatalyst provided the exposed surface area for the rapid adsorption of real effluents and a platform to accelerate the radical chain reactions. In the case of the synergic process, the catalyst dose of 2 g/L triggered these reactions, which promptly attacked the real effluents that were present in the wastewater. That does was selected for the optimum values of 97.90% [27].

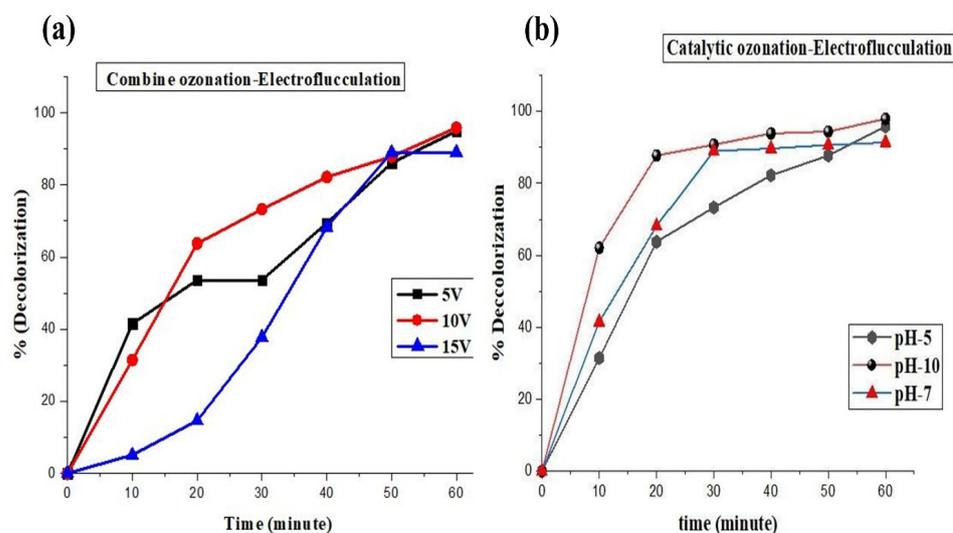


Figure 8. (a) Voltage optimization for at (ozone dose = 0.8 mg/min, time = 120 min, catalyst dose = 2 g/L); (b) pH optimization at (ozone dose = 0.8 mg/min, time = 120 min, pH = 10).

2.7. Voltage Optimization

The removal efficiency of the synergic process depends highly upon the applied voltage, as shown in Figure 8a. The effect of voltage on the removal of color from textile wastewater was studied at three different levels—5 V, 10 V, and 15 V—at the optimum conditions of a pH of 10, time of 60 min, and an ozone dose of 0.8 mg min⁻¹ [15]. The color removal of 97.90% and the COD removal of 97.8% were achieved after 60 min using the synergic process. The rise in the voltage (V) during ozonation generated additional free hydroxyl radicals (\bullet OH) by reducing O₂, which may have led to the generation of H₂O₂, accelerating the ozone conversion to accessible \bullet OH radicals, thereby increasing the organic pollutants and the abatement of inorganics. However, an abrupt decrease in the color, with the voltage (V) applied at 15 V, was observed [11]. This may have occurred because by increasing the voltage, the ions produced by the dissolution of the electrodes (Al) may also increase, producing different species of metal hydroxides Al(OH)₃ that cause the charge neutralization of the organic pollutants present in the wastewater, reducing the Van der Waals attraction and the electrostatic repulsion, causing ultimate removal and sweep coagulation/flocculation [15]. In this process, the DC voltage of 10 was considered the optimum value because of the economic considerations, as the operational cost increases with the electrical-energy increase.

Kinetics Study

First-order kinetics was applied to check the reaction kinetics of the catalytic ozonation and the synergic catalytic ozonation–electroflocculation process based on COD removal for each process, as shown in Figure 3 [6]. The ozone concentration and the pH were kept constant, using the equation given below:

$$-\ln\left(\frac{-COD_t}{COD_0}\right) = k \times t \quad (1)$$

Linear plots were obtained for both catalytic ozonation and the synergic catalytic ozonation–electroflocculation. Values of rate constants and regression coefficients are shown in Figure 9. The highest value of the rate constant, $1.5 \times 10^{-3} \text{ min}^{-1}$, was achieved for catalytic ozonation under the optimum conditions (pH = 10, time = 120 min, and a catalyst dose of 2 g/L) [28].

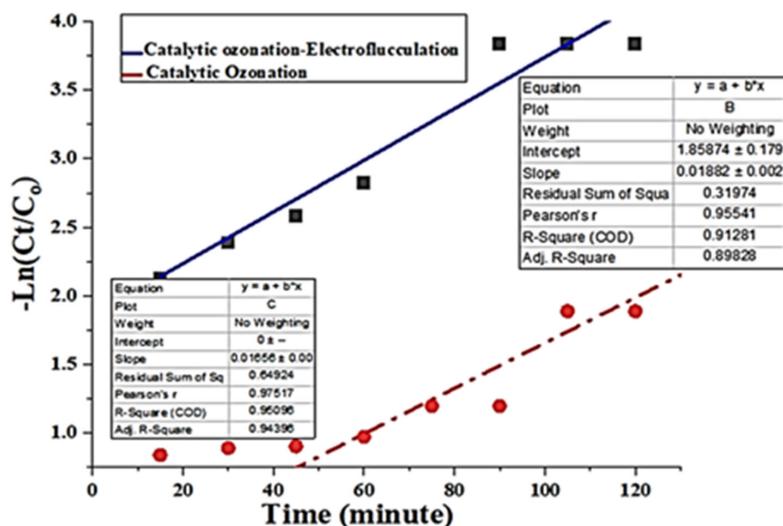


Figure 9. Kinetic study at 0.8 mg/min, catalyst dose of 2 g/L, time of 60 min, and pH of 10.

2.8. Scavenger Analysis of Catalytic Ozonation and Synergic Process

Effect of NaHCO₃ on the Removal Efficiency for Catalytic Ozonation and Catalytic Ozonation–Electroflocculation on Bentonite Clay/TiO₂/ZnO

To determine whether the modified clay/TiO₂/ZnO facilitated the ozone decomposition and the formation of hydroxyl radicals, sodium bicarbonate (NaHCO₃, a potent radical scavenger) was used at the optimum conditions of a pH of 10, an ozone dose of 0.8 mg/min, a catalyst dose of 2 g, and a time of 120 min. The results are shown in Figure 10b, which indicates that NaHCO₃ inhibited the color removal for catalytic ozonation [8]. In particular, at alkaline pH, higher removal was usually expected, due to the presence of (OH) free radicals [8]. The removal efficiency achieved in the case of the synergic catalytic ozonation–electroflocculation process was as follows: the percentage of color removal with a scavenger was 23%, and the percentage removal without scavenger was 94.94%, indicating that a scavenger inhabited the effect of color removal for real textile wastewater, confirming that the mechanism was radically based [15]. The pollutant removal in the absence of a scavenger was greater (94.94%) than the pollutant removal with a scavenger (23%), which restricted the adsorption of real textile effluents on the surface [8]. Thus, the composite decomposed the aqueous O₃ in the absence of textile pollutants, leading to the generation of more hydroxyl radicals. These results further supported our hypothesis [29].

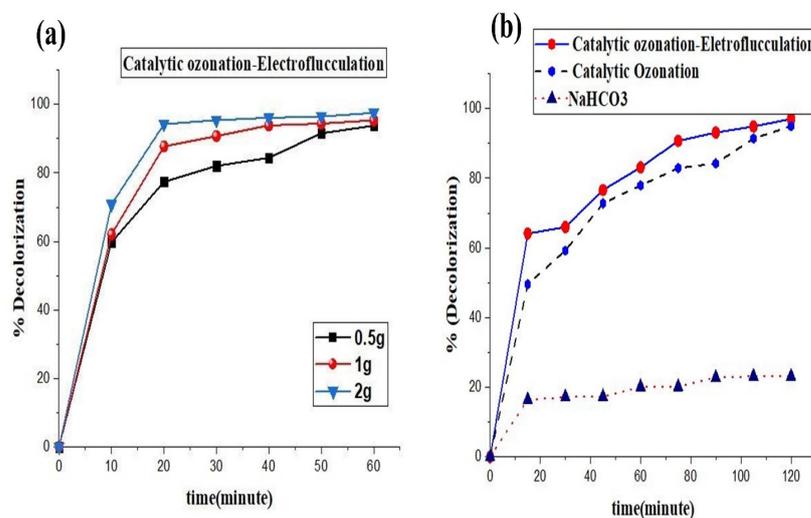


Figure 10. (a) Dose optimization at pH 10, ozone dose = 0.8 mg/min for the synergic process; (b) scavenger analysis at pH 10, time 120 min, catalyst dose = 2 g/L.

2.9. Catalyst Reuse

To check the reusability of the catalyst, the modified clay/TiO₂/ZnO was washed, heated, and dried, using the established technique [30]. The percentage of removal of color was calculated after 120 min and subsequent calculations were made for up to five cycles; hence, the percentage of color removal was observed up to five cycles, as shown in Figure 11b. These calculations confirmed the nanocomposite's stability for long-term usage in real conditions, due to the porous surface being covered by organic pollutants. In the synergic process, the nanocatalyst surface was auto-regenerated continuously, due to the hybrid mechanisms of ozone oxidation, electrochemical oxidation, and the oxidation of radicals; thus, the adsorption capacity of the nanocatalyst had to be maintained to enhance the need for replacement and to enhance catalyst life. The slight titania from the surface of the clay/TiO₂/ZnO catalyst continuously reacted with accessible OH⁻ ions that were present in the solution and formed titanium hydroxides (H₄O₄Ti₃) that acted as a coagulant/flocculants, imparting a positive effect on the removal efficiency [6]. The generation of aluminum hydroxides were considered as a prime coagulant because the Al electrode present in the hybrid reactor produces a very negligible amount of titanium hydroxides (H₄O₄Ti₃) [11]. Therefore, after each experimental run, a minor layer of sludge appeared at the surface, due to Al(OH)₃ caused by oxygen generated at the anode floating at the surface and the ozonation effect. The surface sludge was removed and scraped [15].

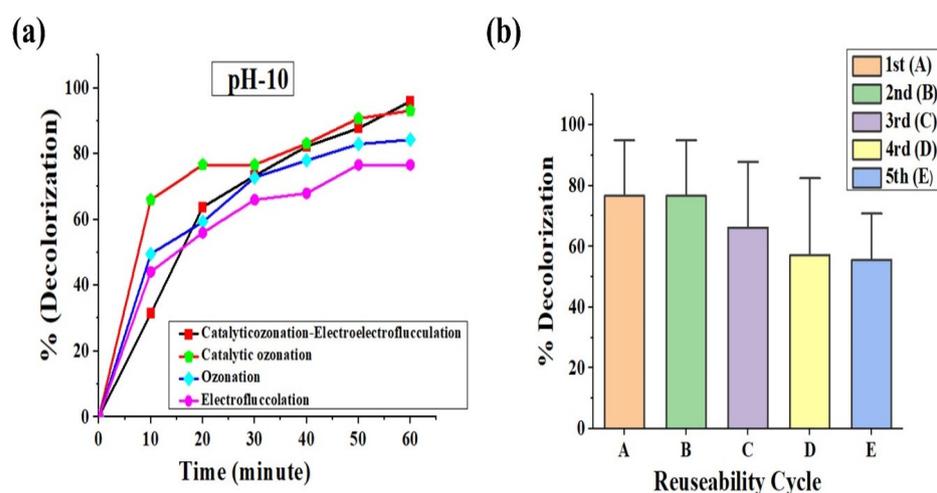


Figure 11. (a) Comparison of all processes at pH = 10, o dose = 0.8 mg/min, time = 120 min catalyst dose = 2 g/L; (b) catalyst reusability at pH = 10, t = 60 min, catalyst dose = 2 g/L.

2.10. Comparison of Various Processes

In the optimum conditions of applied voltage (10 V), ozone dose (0.8 mg/min), time (60 min), and catalyst dose (2 g), the color removal and the COD removal via all processes were studied and compared, as shown in Figure 5a. The results indicated that the synergic process of catalytic ozonation–electroflocculation provided the highest color and COD for real textile wastewater treatment in just one hour, compared to the other processes that required two hours. However, the removal efficiency was in the order of synergy > catalytic ozonation > ozonation process, because ozonation-based processes under alkaline conditions of pH (pH = 10) promoted the generation of additional free hydroxyl radicals, leading to an increase in the rate of degradation compared to that of oxidant (O₂) that was generated in the process of electroflocculation [6]. In addition, electroflocculation involved forming aluminum hydroxide flocculation, which may adsorb the suspended particles in wastewater [6]. Hence, the synergic process may be a preferred alternative for treating textile wastewater in real conditions.

2.11. Proposed Mechanism

The proposed mechanism of the synergic process for the removal of organic pollutants and COD is shown in Figure 12. The results showed that the synergic process increased the organic pollutants' rate of degradation, resulting in a decreased in color and COD. The maximum removal of organic pollutants was achieved at pH 10. In a modified hybrid reactor, the catalytic ozonation, sweep coagulation/flocculation, and electroflocculation simultaneously occurred in the side-by-side oxidation mechanisms. The oxidation facilitates the production of O_2 at the anode and metal ions, whereas a reduction in the cathode produces OH radicals. The aluminum flocculation is produced and captured by the pollutants via neutralization and destabilization. At a pH of 10, radical and direct oxidation mechanisms for ozonation occurred. [15]. The bentonite (Be) provided the platform for rapidly generating OH radicals in a solution by various possible mechanisms. In addition, due to its enhanced adsorption capacity, the nanocatalyst provided the surface for the rapid generation of $\bullet OH$ radicals that killed the organic pollutants, reducing O_3 to O_3^- and O_2^- , and producing more H_2O_2 , leading to the leaching of organic pollutants [27]. The synergic mechanism significantly enhanced the removal of COD and color in textile wastewater.

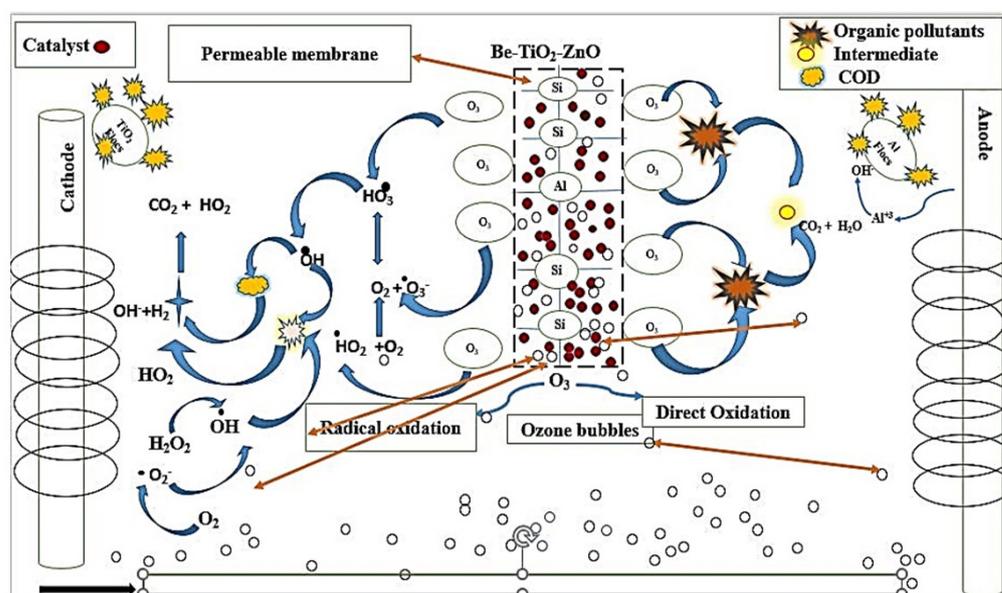


Figure 12. Proposed mechanism for synergic process [31].

3. Materials and Methods

3.1. Materials

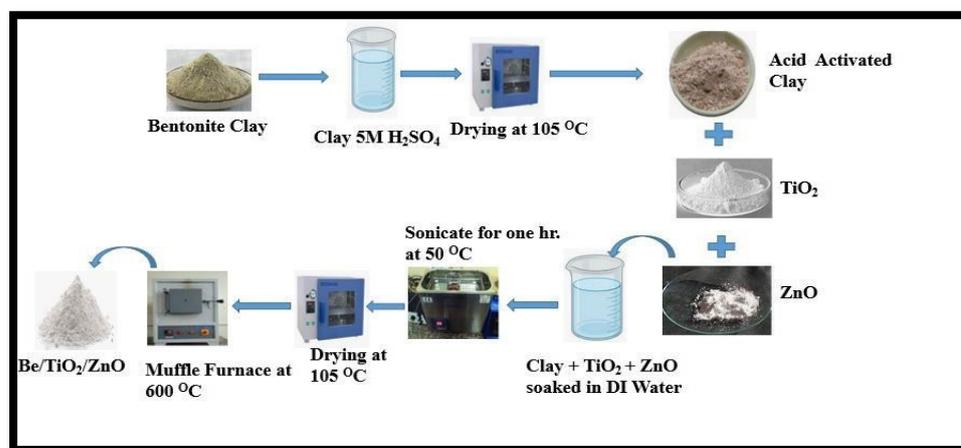
The sample of real textile wastewater was collected from Sadiq Sons Dyeing and Printing Industries, Lahore, Pakistan. It was collected from the inlet section and stored in a refrigerator at 4 °C. The characteristics of the textile wastewater are mentioned in Table 2. The bentonite clay (2 μm , Merck, Berling, Germany), commercial powder TiO_2 (P25, Merck), and ZnO (P25, Merck) were purchased from Merck, 64271 Darmstadt, Germany. The 0.1 M hydrochloric acid (37% purity) and the 0.1 M sodium hydroxide pellets were collected from Active Fine Chemicals Limited (Dhaka, Bangladesh) and used to maintain the pH of the solution. All the chemicals were analytically graded and used without further purification.

Table 2. Characterization of textile wastewater.

Parameters	Before Treatment	After Treatment	NEQs [32]
pH	11	7	6–9
TDS (mg/L)	1750	890	-
Electrical conductivity ($\mu\text{s}/\text{cm}$)	3550	1500	-
Chemical oxygen demand (mg/L)	1200	40	150 mg/L
Biological oxygen demand (BOD)	510	30	80 mg/L
Turbidity (NTU)	0.90	0.20	-
Maximum wavelength	518 nm		-
Color	Dark red	Colorless	Colorless

3.2. Catalyst Preparation

Commercial TiO_2 (P_{25}) and ZnO (P_{25}) powder were obtained from Merck Germany. For the fabrication of the ternary composite, bentonite (natural montmorillonite, $>2 \mu\text{m}$) was modified with 5 M sulfuric acid via the incipient impregnation method [12], i.e., 200 g of clay was mixed with a 1000 mL aqueous solution of 5 M sulfuric acid (271 mL) at 80°C for different contact hours; the sample was then washed with distilled water to obtain neutral pH. It was then dried in a conventional oven at 105°C for pH adjustment of the dye solution. The acid-activated bentonite clay (50% *w/w*) was then mixed with TiO_2 (45% *w/w*) and ZnO (5% *w/w*) in distilled water and placed in a sonicator (40 KH, 100 W, universal ultrasonic cleaner DSA-100-SK1-2.8L stainless-steel digital-timed heater ultrasound cleaning tank) to obtain one resultant mixture that was dried in a conventional oven for 24 h and calcined in a muffle furnace (heating rate $10^\circ\text{C}/\text{min}$) at 660°C for 3 h to remove any impurities. The TiO_2 and ZnO attached to the clay's surface [33], as shown in Figure 13.

**Figure 13.** Synthesis of modified bentonite clay/ TiO_2 / ZnO .

3.3. Experimental Setup

The experimental setup of the synergic catalytic ozonation–electrofloculation used is shown in Figure 14. The experiments for ozonation and catalytic ozonation were performed in a borosilicate glass reactor with a capacity of 1500 mL at a semi-batch mode. Two aluminum electrodes with the surface of a semi-batch of 20 inch² were placed in the reactor tank and connected to the DC power supply. Two sets of ozone traps were filled with 100 mL of 2% KI (potassium iodide) solution. Membrane bags (nylon, 25 μm) held the catalyst and could be quickly recovered after each run.

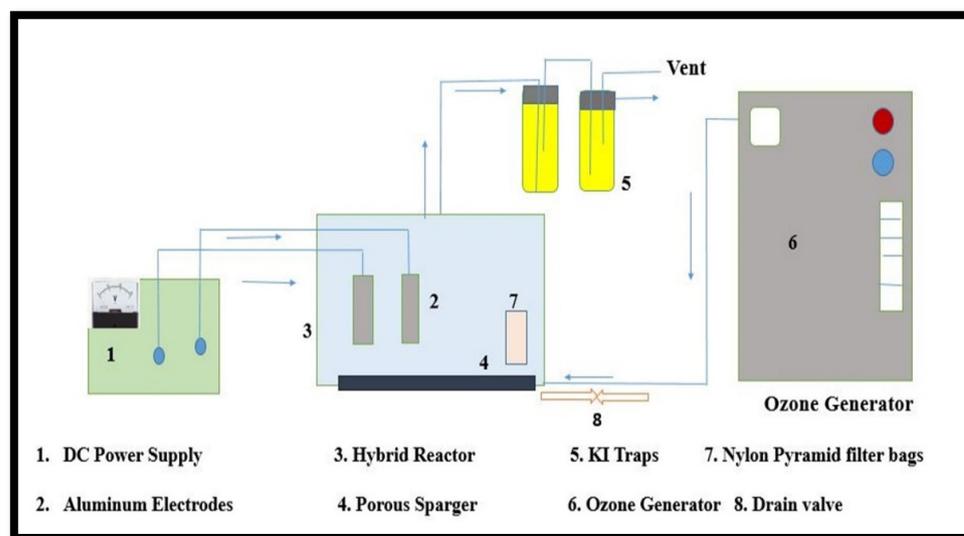


Figure 14. Schematic representation of synergic ozonation/catalytic ozonation–electroflocculation setup [15].

3.4. Characterization

Chemical structural changes before and after the synergic process were determined using a Fourier-transform infrared spectrophotometer (FTIR) (Shimadzu FTIR-8400S) in the range of $4000\text{--}500\text{ cm}^{-1}$. Surface morphological changes before and after adsorption were analyzed by a scanning electron microscope (SEM) (VPFESEM Model Supra 35VP) at an accelerating voltage of 10 KV. The elemental composition before and after adsorption was measured by an energy-dispersive X-ray (EDX) spectroscope. The pH_{z} was measured by the typical salt-addition method [34].

3.5. Experimental Procedure

A sample of 1.5 L of textile wastewater was obtained in the reactor for every experimental run. Ozone was adjusted; through the ozone generator (DA12025B12L, Sky Zone, Karachi, Pakistan) supplied at the bottom of the borosilicate glass reactor at the Sparger (porous gas diffusor). A rotameter was installed to regulate the flow of ozone gas. The ozone dose was measured by the standard iodometric titration method [35]. The sample was filtered after each run to remove any impurities. The unreacted ozone was scrubbed with a 2% potassium iodide solution from the top (when leaving the reactor). The 1.5 L textile water samples were charged into the borosilicate reactor, with a continuous ozone supply, for 2 h [36]. Membrane filter bags (nylon, $25\ \mu\text{m}$) were used for catalyst holding, substrates/pollutants were transported through the membrane via transport phenomenon, and the nanocatalyst was retained due to its size. The driving force was a concentration of ΔC , pressure Δp , voltage, or electrical potential difference ΔV .

Different membrane-based reactors have been reported in the literature, a few of which require sophisticated engineering. The novel or most straightforward approach was used in this study, based on nanocatalyst trapping or holding within a nylon permeable membrane “bag”, which provides an adequate dispersion of the nanocatalyst and ensures minimal interaction between the nanocatalyst and the pollutants, thereby allowing the use of labile catalyst systems [10] that may “dip” into a sample solution and be recycled many times [37]. However, for combining catalytic ozonation and electroflocculation, a specific amount of adsorbent was added, and the values of voltage and the ozone rate were adjusted accordingly.

3.6. Analytical Method

The color removal was studied by measuring absorbance using a UV–Vis spectrophotometer (Perkin Lambda 35) at a lambda maximum of 518 nm, as shown in Figure 15. The

pH was adjusted using a pH meter (Portable Hanna HI9811-5, Hanna Instruments, Smithfield, RI, USA). The initial and final COD concentrations of treated and raw samples were determined using the standard HACH method with an 8000 reactor digestion method [38].

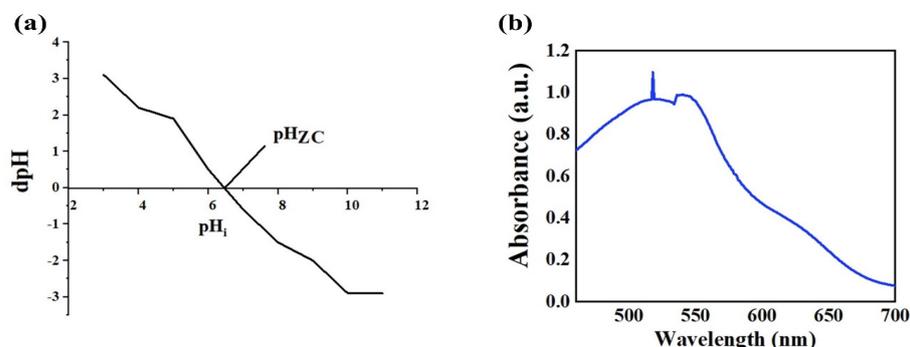


Figure 15. (a) pH_{pzc} of synthesized nanocomposite; (b) calibration curve for raw textile wastewater.

The percentages of color removal and COD were found using the following formulae:

$$\% \text{ Color Removal} = \frac{A_i - A_f}{A_i} \times 100 \quad (2)$$

where A_i and A_f are the initial and final absorbance;

$$\% \text{ COD Removal} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \times 100 \quad (3)$$

where COD_i and COD_f are the initial and final concentrations.

Ozone Dose Analysis

The iodometric method was used for the ozone dose analysis. Ozone gas from the ozone generator was charged into two 100 mL solutions of 2% KI traps. The solution was quenched with 5 mL 2N sulfuric acid to liberate iodine and titrated against the 0.005 N sodium thiosulfate, using starch as an indicator. The formula used for calculating the ozone dose was as follows [28]:

$$\text{Ozone dose} \left(\frac{\text{mg}}{\text{min}} \right) = \frac{V \times N \times 24}{T} \quad (4)$$

4. Conclusions

Real textile effluents were removed using a novel modified bentonite clay/ TiO_2 / ZnO catalyst, and the four operational parameters—pH, time, applied voltage, and catalyst dose—were optimized. The efficiencies of various ozonation processes, catalytic ozonation, and synergic electroflocculation–catalytic ozonation in the removal of color and chemical oxygen demand (COD) were determined and compared. The reaction kinetics showed the pseudo-first-order kinetics for both catalytic ozonation and the synergic process. The synergic process's maximum removal of COD and color was found to be 97.83% and 97.90%, respectively, at the optimum conditions of pH of 10, time of 60 min, catalyst dose of 2 g, and ozone dose of 0.8 mg/min. in reduced time compared to other processes. The efficiency of color removal was inhibited by a potent scavenger of NaHCO_3 , which confirmed the radical-based mechanism for ozonation. Ozone degradation of real textile effluents using clay/ TiO_2 / ZnO occurred by a radical mechanism involving hydroxyl. The catalyst showed satisfactory removal for up to five cycles. Thus, the synthesized nanocomposite proved to be an effective alternative for treating real effluents.

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