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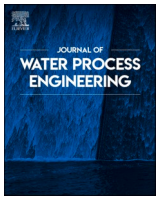

Remediation of textile wastewater by hybrid technique using ZIF-67 catalyzed ozonation coupled with electrocoagulation

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ABSTRACT

Large-scale industrial wet processing generates high volumes of wastewater, causing a continuous disruption of the clean environment. Textile wastewater contains high mass loadings of contaminants, which poses a challenge to the environment and requires adequate treatment. This study aims to investigate the treatment of textile wastewater by catalytic ozonation coupled with electrocoagulation using ZIF 67 as a catalyst in a hybrid reactor. This research explores the first application of ZIF-67 in a hybrid system with catalytic ozonation and electrocoagulation processes to treat real textile effluent. The initial characterization of wastewater indicated high pollutant loads such as 480 mg/L chemical oxygen demand (COD) and 210 mg/L biological oxygen demand (COD). The influence of operational parameters like current density, ozone dose, pH, and catalyst dose were studied. The heterogeneous catalytic ozonation-electrocoagulation (HCOP-EC) process achieved 79.6 % decolorization, 73.3 % COD removal, and 69.04 % BOD after 30 min of treatment at optimal conditions of pH 9, ozone dose 0.3 mg/min, current density 15.2 mA/cm^2, and catalyst dose 50 mg/L. The catalyst reusability study showed an efficient performance of up to 3 cycles. Due to the complex matrix nature of the real effluents, the HCOP-EC combined process may be effectively applied to remediate pollutant loads in real textile wastewater.

1. Introduction

Water scarcity has become a global issue. Water is a vital necessity for life. Ineffective water consumption and discharge are continuously producing anthropogenic water pollution. The expansion of communities and industrialization have led to high water demands and enhanced water pollution. Among various industries, the textile sector is the second-highest effluent-generating industry in the world, emitting a large amount of wastewater during wet processing [1]. The wastewater includes organic matter, dyes, and toxic chemicals that affect humans and aquatic life [2]. According to recent reports, wastewater discharged from the textile industry accounts for 80 % of the overall release of industrial wastewater and comprises highly toxic dyes. [3,4]. Multiple research studies have been conducted on various conventional and advanced treatment technologies to treat toxic contaminated wastewater. However, due to its complex nature, advanced treatment processes and hybrid techniques were suggested for wastewater treatment [1].

Recent research has reported several methods for the treatment of wastewater, including physical, chemical, and biological methods. These methods include filtration membranes [5], ions exchange [6], coagulation [7], and advanced oxidation processes. Physical methods are more effective when dealing with a small volume of wastewater. The hybrid techniques are highly efficient due to the rapid remediation of wastewater in compact units. The advanced oxidation process (AOP) has attracted much attention to degrading many types of organic pollutants in wastewater. AOP generates free hydroxyl •OH radicals, which are the strongest among the reactive oxidant species, with a redox potential of 2.80 ev [8]. These radicals rapidly degrade resistive dyes and pollutants present in wastewater. Among the AOPs, the most applied methods for the remediation of wastewater include catalytic ozonation [9], hydrogen peroxide-based treatment [10], Fenton-based oxidation [11], and electrochemical oxidation [12].

Catalytic ozonation is an effective technique for treating wastewater

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effluents released by the textile sector [13] since ozone has a high redox potential (2.70 v), acting as an excellent oxidant to degrade organic pollutants in wastewater [14]. Ozonation has many advantages over other processes, such as no sludge generation, minor space requirement, and a fast decomposition process [15]. The disadvantages of simple ozonation involve low stability due to short half-life, low solubility, and high cost. The effectiveness of the oxidation process and pollutant decomposition rate is significantly enhanced in catalytic ozonation [15].

Electrocoagulation is an electro-oxidation process in which an anode is sacrificed to produce coagulants that remove pollutants from the textile wastewater. When the current passes through the anode, made up of metal, it sacrifices to produce M^{n+} metal ions; on the other hand, the cathode produces •OH radicals [16]. These metal ions and hydroxyl radicals combine to produce electro-flocs which are responsible for the adsorption of organic pollutants in wastewater. Moreover, gases are generated at the electrodes which float the pollutant at the top of the water surface [17,18]. Previous research works [19–21] have reported the productive elimination of textile dyes and organics in textile wastewater by the electrocoagulation process. Yildiz et al. [19] applied advanced peroxi-coagulation for the degradation of real textile wastewater by *in-situ* H_2O_2 generation. A complete decolorization and more than 65 % TOC were reported at optimum parameters of pH 3, current 100 mA after 100 min treatment time. Gökkuş et al. [20] investigated the advanced sequential treatment comprising electrocoagulation and photo electro-Fenton process for the treatment of dye-contaminated wastewater. Up to 100 % color elimination and 68 % total organics were removed at optimum pH 3 and j 50 mA/cm^2. Cardoso et al. [22] studied the carbon dot-based catalytic ozonation for textile dye effluent and reported 90 % efficiency at pH 7 after 30 min. Sequential treatment technologies certainly have higher efficiency than standalone technologies; however, on a large industrial scale, sequential treatment may involve multiple steps in series, requiring a high capital cost and area. Therefore, this research explores the hybrid one-step electrocoagulation-catalytic ozonation process, which provides definite advantages such as high efficiency, low area requirement with compact units, and reduced treatment time and cost. The present research is in line with the sustainable development goals (SDG 6 and SDG 14).

Effective adsorbents with high surface area and large porosity enhance the removal ability of pollutants from wastewater. Metal-organic frameworks (MOFs) have exhibited favorable distinct properties such as significant surface area, good adsorbent capacity, and high thermal stability. Generally, MOF consists of a metal linked to organic matter using a linker [23]. MOFs perform more effectively in wastewater treatment than other catalysts, such as carbon-based catalysts, zeolites, and metal oxides. The porosity and pore diameter of MOF will change by changing the metal salt linked with the organic linker. MOFs have broad applications in different fields, like energy storage, wastewater treatment, gas absorption, gas separation, and supercapacitor batteries [24]. Zeolitic imidazole frameworks (ZIFs) have a good surface area, thermal stability, and pore diameter. Among the studied ZIFs, ZIF 67 is famous due to its effective surface area and efficient removal ability in the wastewater treatment process [25].

Various MOFs, such as MOF 5 [26], MIL 53(Al) [27], UIO 66 [28], ZIF 8, and ZIF 67, have been effectively applied for wastewater treatment. Among these, ZIF 67 has gained superiority due to a significant surface area of up to 2058 m^2/g [29]. One of the most highlighted features of ZIF 67 is that it can be synthesized easily in mild conditions as compared to other MOFs, which require elevated conditions for synthesis. ZIF 67 has a higher adsorption capacity (1683.8 mg/g) than other MOFs. Previous research has studied the potential of ZIF 67 as an efficient catalyst in the reduction of organic pollutants. However, the performance of ZIF 67 in advanced hybrid processes has never been explored. Current research focuses on the first application of ZIF 67 in a hybrid technique employing a catalytic ozonation combined electrocoagulation process to treat real textile effluent. The experiments were conducted in a hybrid heterogeneous catalytic ozonation-electrocoagulation (HCOP-EC) reactor using Al electrodes. Wastewater was characterized by color, COD, BOD, TDS, and turbidity parameters. The effect of critical parameters such as current density, pH, catalyst amount, and ozone dose were elucidated for reducing color and COD from the textile wastewater. The catalyst was characterized by FTIR, SEM-EDX, and BET techniques before and after the treatment.

2. Materials and methods

2.1. Materials and reagents

The raw textile wastewater samples were collected from the well-reputed textile company near Kasur, Lahore, Pakistan. Samples were taken to the lab and stored in an incubator on the same day at 4 °C. The samples were characterized before the treatment.

The following chemicals were procured from Sigma Aldrich UK. Sodium hydroxide (NaOH), hydrochloric acid (HCl), cobalt (II) nitrate hexahydrate Co $(NO_3)_2{\cdot}6H_2O$, 2-methylimidazole, NaCl, and methanol. All chemicals used were of analytical quality and were employed without additional purification.

2.2. Catalyst preparation

The catalyst ZIF 67 was prepared using the method described in the literature (Fig. 1a) [30]. In this method, 0.74 g of Co $(NO_3)_2{\cdot}6H_2O$ was added to the 200 mL of methanol and mixed for 8 h at 250 rpm to obtain a clear solution using a magnetic hot plate stirrer (Model 79-1A, Canfort, China). After that, 1.45 g of 2-methylimidazole was added to the methanol solution. The solution was stirred for 8 h at 200 rpm. Then, it was centrifuged at 3000 rpm for 25 min using a centrifuge (Model 800D, Canfort, China) and washed with water and methanol three times to acquire purple crystals. Then, the obtained purple crystals were dried in Oven (Model DW-LVO-1B-6050, Drawell, China) for 12 h at 80 °C.

2.3. Experimental procedure

Experimental runs were conducted in a hybrid electrochemical reactor made up of plexiglass (Fig. 1b). The reactor was made up of two Aluminum (Al) electrodes having (3.5 cm × 6.5 cm) L × W dimensions, respectively, with an effective area of 45.2 cm^2 fixed at a 2 cm gap. The ozone produced in an ozone generator (Model DA12025B12L (0–5 g/h), Sky Zone, Pakistan) was bubbled continuously from the diffuser at the bottom of the reactor. The electric current was provided by a DC power supply (Model TN-605DS, Axis, Pakistan) purchased from the local market, which had a voltage variation of 0–5 V. For each run, the reactor was filled with 1 L wastewater, the pH of the solution was set, the catalyst was suspended using a porous nylon bag, the voltage and ozone dose were regulated, and after equal intervals of time, samples were taken out for analysis. 2 % KI traps were used to capture unreacted excess ozone gas coming out of the reactor to avoid discharge to the environment (Table 1).

2.4. Analytical methods

The color reduction in the textile wastewater after treatment was determined using a Perkin Elmer lambda double beam UV–Vis Spectrophotometer for absorbance analysis. Every sample absorbance was analyzed at a maximum wavelength of 510 nm. Using a digital meter (Hanna HI-9811), the effluent pH, TDS, and conductivity were measured. The standard procedure was followed to test turbidity using a turbidity unit (HACH 2100P). The standard iodometric method was used for the measurement of ozone dose. The ozone gas generated by the ozone generator was sent into the 2 % KI solution by adding 5 mL 0.1 N H_2SO_4 extra amount of iodide quenched. The solution was titrated against 0.025 N sodium thiosulphate using drops of starch as an indicator [31,32]. BOD was determined using the standard Winkler method

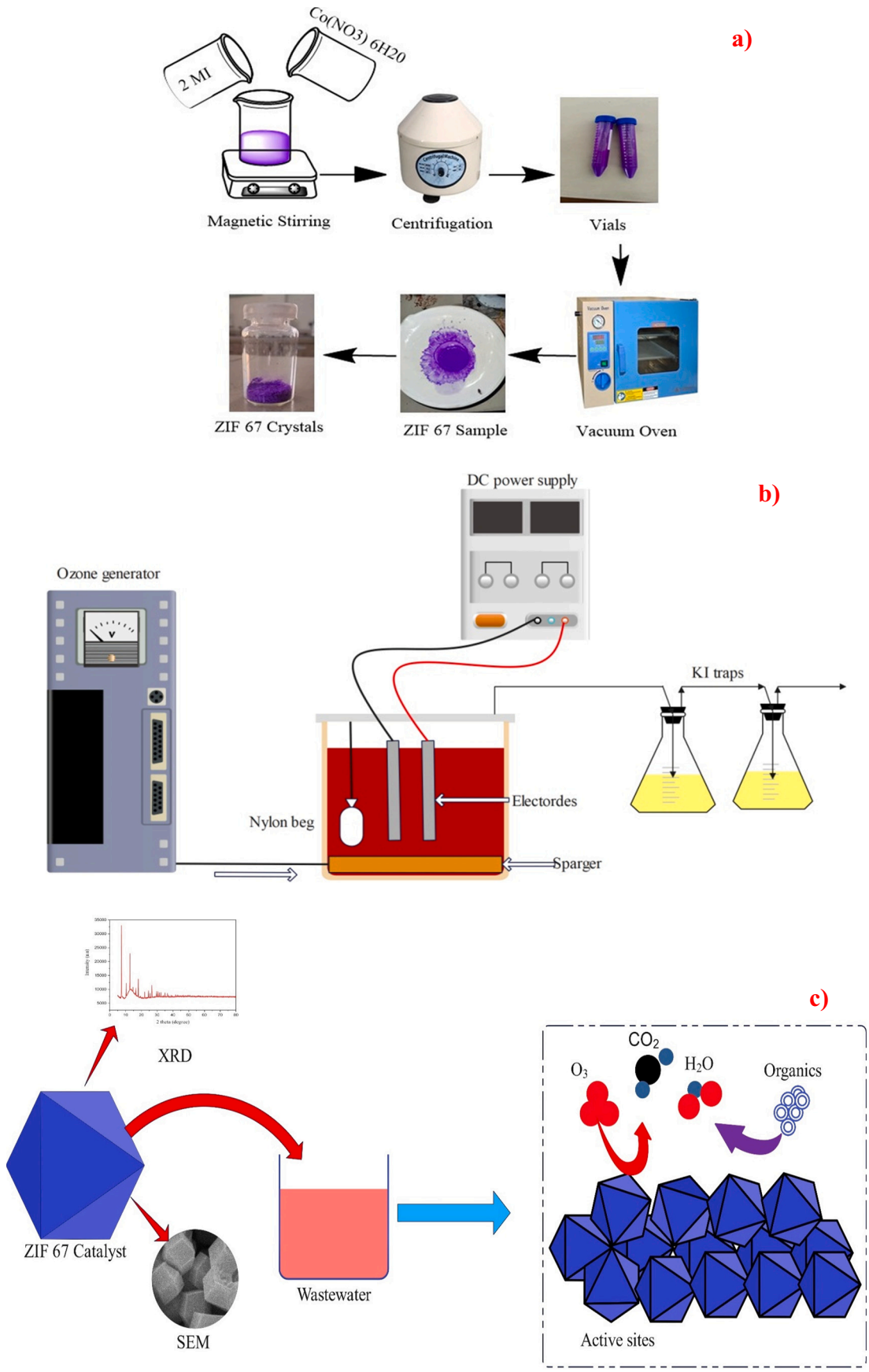

Fig. 1. a) Catalyst synthesis steps, b) Experimental setup, c) ZIF 67 catalytic activities.

Table 1
Characterization of textile wastewater.

Parameter	Before treatment	After treatment	NEQs[34]
PH	9	9	6–9
COD (mg/L)	480	128	150 mg/L
TDS (mg/L)	3800	440	3500 mg/L
BOD	210	65	80 mg/L
Color	Purple reddish	Color less	–
Turbidity (NTU)	45.7	7.2	–
Electrical conductivity (μs/cm)	6520	1150	–

[32]. The initial and final COD of the wastewater sample was analyzed by the standard HACH 8000 method using digestion vials [33].

3. Results and discussion

3.1. Characterization of catalyst

The Bruker Alpha-E FTIR spectrometer was used to analyze the functional groups of ZIF 67 across a wavelength range of 500 to 4000 cm^{-1}. The morphological study of the catalyst was performed on a Nova Nano SEM 450 analyzer. The electron beam was used to take pictures at a 10 kV acceleration voltage. Energy-dispersive X-ray spectroscopy (EDX) was used to determine the elemental composition of the produced catalyst. The solid catalyst crystallinity and chemical makeup were assessed by X-ray diffraction Analysis (XRD). The X-ray diffractometer (Bruker D2 Phraser) was used to investigate the ZIF 67 catalyst XRD spectrum in the 2θ range of 10–80°, using X-ray production by Cu Kα irradiation operating at 30 kV and 10 mA. Using the Micrometrics-ASAP-2020 analyzer, the surface area and pore size were examined by the Brunauer-Emmett-Teller (BET) method. Samples were degassed for 8 h at 150 °C while under vacuum. At 77 K and 99.99 %, pure nitrogen adsorption-desorption isotherms were determined.

The functional groups attached to the catalyst surface ZIF 67 were determined by using the Fourier Transform Infrared Spectrometer (FTIR) analysis. The infrared radiation (IR) spectra displayed various stretching and bending peaks, as represented in Fig. 2. The corresponding bands at 1141.99 cm^{-1}, 1304.56 cm^{-1}, 1474.92 cm^{-1}, 1580.35 cm^{-1} and 3772.12 cm^{-1} reflect the stretching modes of C═N and C═C bonds of 2-methylimidazole, as well as those of C—H in the aromatic ring and aliphatic sections of 2-methylimidazole [25,35,36]. The region from 1500 to 1700 cm^{-1} relates to the stretching of C═N in the 2-methylimidazole ligand [25,37]. The peaks at 3772.12 cm^{-1} and 3832.17 cm^{-1} correspond to the O—H stretch of the hydroxyl group and water adsorbed. After the treatment, there was a change observed in the peaks from 1141.99 cm^{-1} to 1140.6 cm^{-1}, 1474.92 cm^{-1} to 1416.4 cm^{-1}, and 3772.12 cm^{-1} to 3383.3 cm^{-1} represented C—N, C═C, and C—H bindings. The drift in the peaks confirms the adsorption of organic pollutants (such as residual dyes, surfactants, and aromatic compounds added in wet processing steps) on the surface of the ZIF 67 catalyst.

A surface structure analysis of catalyst ZIF 67 was performed to elucidate changes after and before the treatment. The SEM image 2 (c, d) shows that the ZIF 67 has rhombic dodecahedral crystals. After treatment, the SEM images revealed that the surface of the catalyst becomes more rough, and amorphous after the loading of organic molecules on the surface [38,39].

Energy dispersive x-ray spectroscopy (EDX) analysis was used for the elemental analysis of the ZIF 67 catalyst [40,41]. The EDX spectra of the ZIF 67 catalyst are displayed in Fig. 2(e, f). Further, the composition of the components is shown in Table 2. A drift in the peak intensities of the elements, mainly of C, N, and Co, indicates the adsorption of aromatic ring organics onto the ZIF 67 surface and also the presence of azo dyes. The Brunauer–Emmett–Teller (BET) method was used for determining the surface area and pore volume of the prepared catalyst ZIF 67 [42]. The catalyst ZIF 67 exhibited a surface area of 1906.25 m^2/g and a pore volume of 0.755 cc/g.

The XRD was assessed to determine the composition and structural characteristics of the ZIF-67 Fig. 2(g). The notable reflections at 2θ of 7.4, 10.4, 12.7, 14.8, 16.5, and 17.9 corresponded to the ZIF-67 single crystal's (011), (002), (112), (022), (013), and (222) planes [43]. The strong, narrow peaks showed that high crystalline ZIF-67 had been synthesized successfully. Fig. 2(g) illustrates that there is a variation in intensity attributable to the adsorption of organic pollutants onto the surface of ZIF-67 crystals.

3.2. Parametric effects study

3.2.1. Effect of ozone dose

The ozone (O_3) rate is essential in controlling the degradation rate of organic pollutants in HCOP. A single ozonation process was applied to wastewater to determine an optimum ozone dose level for the process. Since the oxidizing power of ozone (O_3) is exceptional, it can be used to mineralize organic dyes and pollutants in textile wastewater. The result in Fig. 3a shows that by increasing the ozone dose up to 0.4 mg/min, maximum removal of 62.3 % was achieved after 30 min of treatment [44,45]. Practically, •OH radicals' generation is enhanced at higher ozone doses, which rapidly attacks the organic molecules, leading to degradation and accelerating the mineralization process. Meanwhile, the decolorization achieved at 0.2 mg/min, 0.3 mg/min, and 0.4 mg/min were 44.2 %, 56.2 %, and 62.3 %, respectively. The COD removal achieved in that case was 31.21 %, 44.9 %, and 52.4 % at ozone doses 0.2 mg/min, 0.3 mg/min, and 0.4 mg/min, respectively.

Ozone is a highly reactive oxidant that degrades the organic pollutants present in textile wastewater and plays a crucial role in removing color and COD. The concentration of dissolved ozone rises to quickly attack the organic materials as the concentration of ozone gas increases, which directly improves the diffusion through the gas-liquid interface. Ozone dose enhanced the removal ability in the combined catalytic ozonation–electrocoagulation process, as shown in Fig. 3b. The color removal achieved was 69.2 %, 79.6 %, and 82.1 % at 0.2 mg/min, 0.3 mg/min, and 0.4 mg/min ozone dose, respectively. The decrement in COD was 58.2 %, 73.3 %, and 77.8 % at the respective doses [46,47]. The increase in ozone dose generates more hydroxyl radicals, which attack the pollutants at the prevailing pH of 9. These •OH radicals rapidly degrade and mineralize the organic compounds in wastewater, reducing color and COD. Moreover, the EC electro-flocs provide extra surface for capturing the organic pollutants in wastewater.

3.2.2. Effect of current density

Current density (CD) is a crucial parameter that augments the rate of electrochemical reactions in the EC process, which controls the formation of *in-situ* electro-flocs. The current density augments the electrocoagulation process to produce metal ion coagulants, bobble formation, and mixing in the aqueous solution [48–50]. The three different current densities, 21.7 mA/cm^2, 15.2 mA/cm^2, and 7.92 mA/cm^2, were applied for the removal of organic pollutants from the textile wastewater [51]. The experimental result of a single EC process is shown in Fig. 4a, which shows the color removal of 52.3 %, 44.2 %, and 37.3 % at current densities of 21.7 mA/cm^2, 15.2 mA/cm^2, and 7.92 mA/cm^2 each. At the lower current density of 15.2 mA/cm^2 and 7.92 mA/cm^2, the color removal declined to 44.2 % and 37.3 %, respectively, since the electrochemical reactions become sluggish at lower current density, thereby decreasing the rate of flocs formation and sweep coagulation to remove the organics. The COD was reduced to 23.7 %, 30.21 %, and 35.01 % by applying 7.92 mA/cm^2, 15.2 mA/cm^2, and 21.7 mA/cm^2, respectively.

The economics and the performance of electrocoagulation highly depend upon the current density. The effect of current density on the removal of color and degradation of organic pollutants in the combined process is shown in Fig. 4b. With the treatment time, pollutant removal

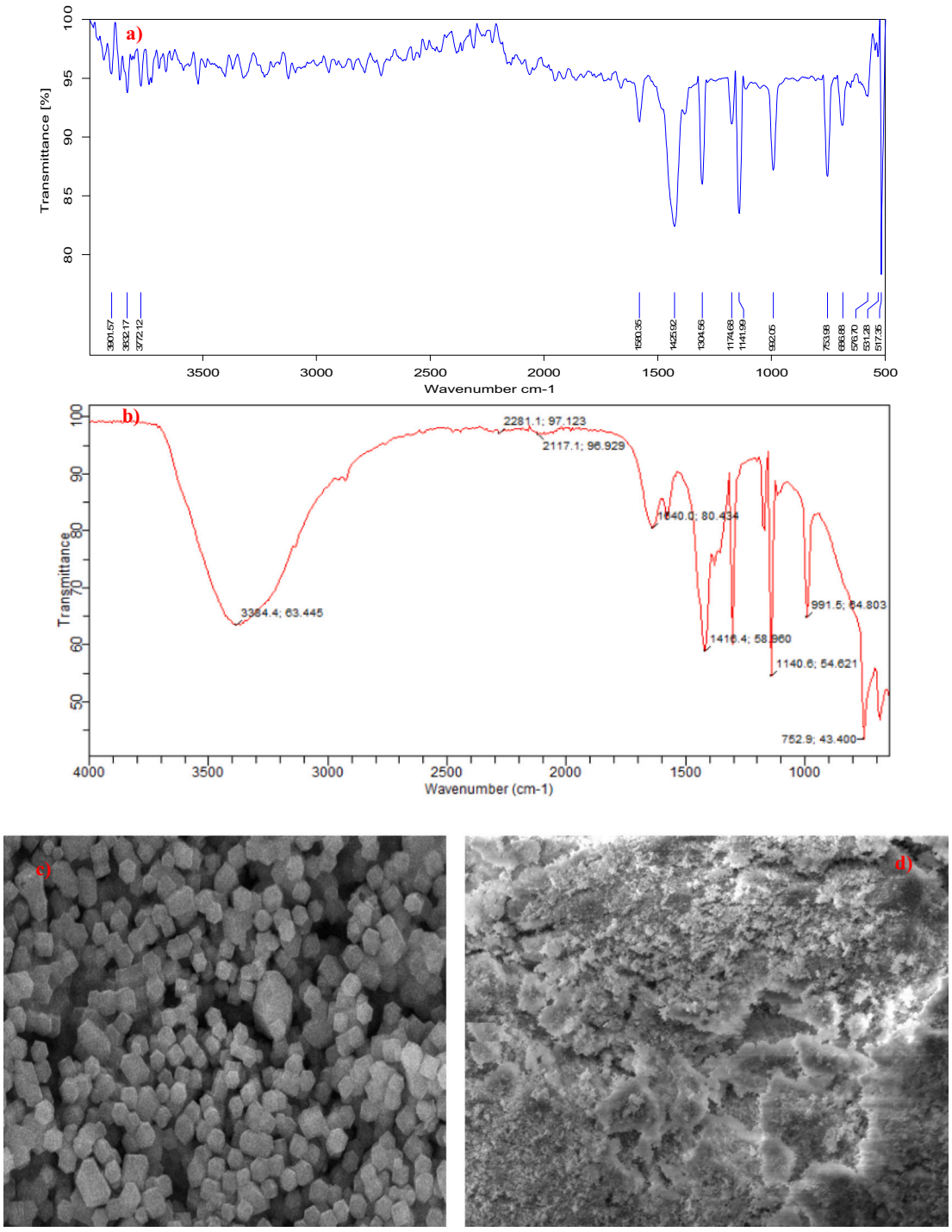

Fig. 2. FTIR of ZIF 67 a) before treatment and b) After treatment, SEM images of ZIF 67 c) before treatment, and d) after treatment, and EDX of ZIF 67 e) before treatment and f) after treatment and g) XRD spectrum of ZIF 67.

increased with enhanced current density. At high current density, more metal ions produce electro-flocs, which cause the adsorption of organic pollutants. However, In the presence of ozone, an increase in voltage gives rise to more •OH radicals being produced through O_2 reduction, which produces H_2O_2, which encourages the conversion of O_3 to •OH radicals and improves the reduction of organics [52,53]. The color removal achieved was 80.1 %, 78.01 %, and 73.1 % at the current density of 21.7 mA/cm^2, 15.2 mA/cm^2, and 7.92 mA/cm^2. The COD removal declined to 59.2 %, 72.2 %, and 76.5 % when the current density varied to 7.92 mA/cm^2, 15.2 mA/cm^2, and 21.7 mA/cm^2 respectively.

3.2.3. *Effect of pH*

The pH level significantly affects the reaction pathway in the combined catalytic ozonation and electrocoagulation process. Electrocoagulation leads to an initial rise in pH due to water electrolysis, generating OH^- ions and H_2 gas, which shift the pH into the basic range. The process then stabilizes at a neutral pH due to the conversion of aluminum species and the formation of insoluble $Al(OH)_3$ [54]. Similarly, ozonation is a pH-driven process that promotes the radical

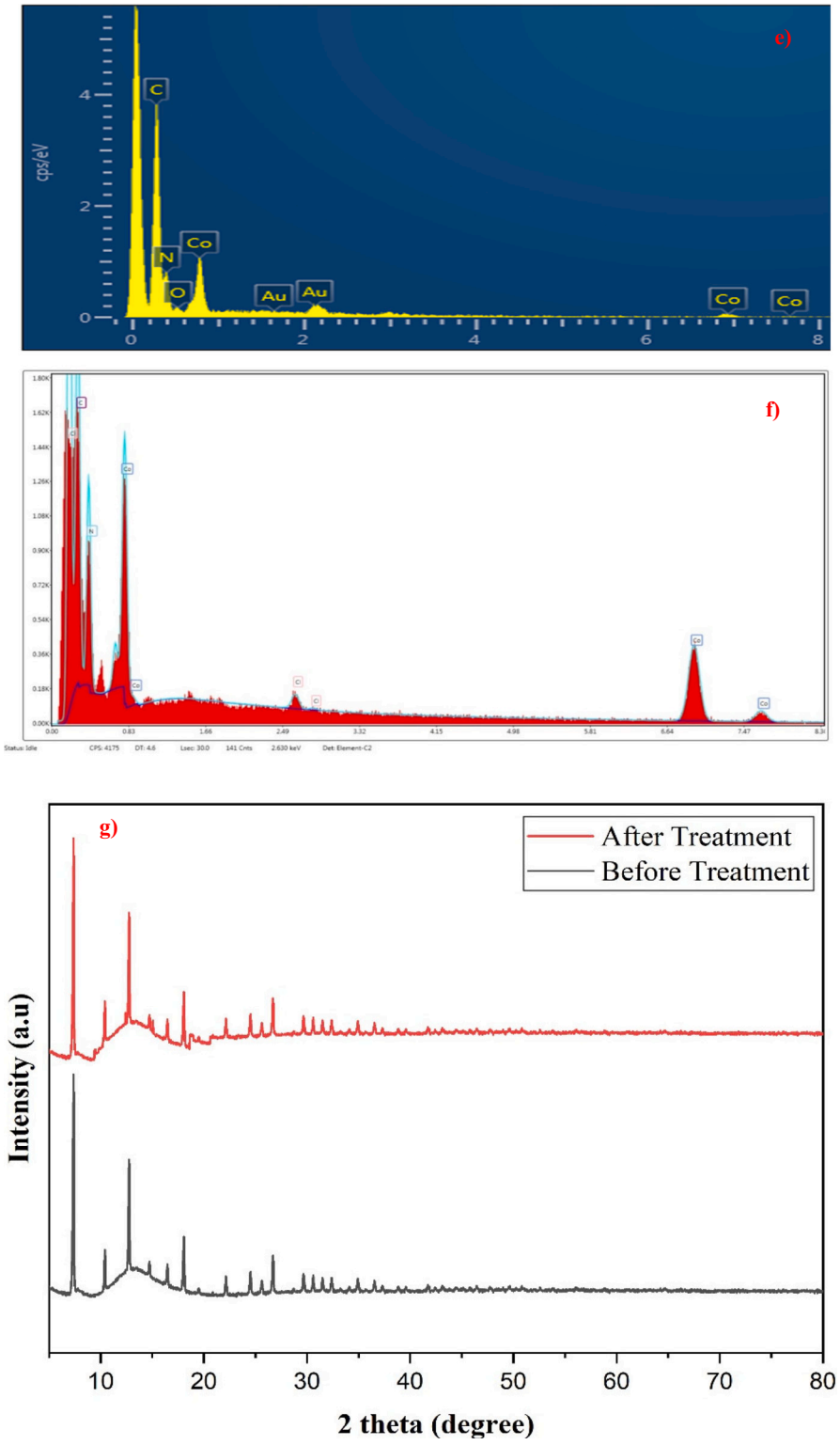

Fig. 2. (*continued*).

mechanism in alkaline pH by generating •OH radicals and directly oxidizing organic materials with O_3 in acidic pH ranges [31,55]. The surface charges of the catalyst significantly influence the reaction kinetics in the catalytic ozonation process for organic abatement. We conducted a study to assess the impact of pH levels (5, 7.5, and 9) on color removal from real textile wastewater. After 30 min, the color reduction percentages were 79.6 % at pH 9, 71 % at pH 7.5, and 63.32 % at pH 5, as depicted in Fig. 5a. The wastewater contains highly positively charged organic contaminants, with the most substantial decreases observed at pH 9. Combining electrocoagulation and catalytic ozonation at an alkaline pH of 9 improved organic removal. At pH 9, the most prevalent species produced in the electrocoagulation process is Al $(OH)^{-4}$ [56,57]. The ozone-enhanced self-decomposition at pH 9 gives •OH radicals, which promptly degrade organics by a radical mechanism [52]. The abundance of negative charges on the catalyst surface is a crucial factor contributing to the degradation of the organic material at

Table 2
EDX composition of ZIF 67.

Element	Atomic weight before treatment (%)	Atomic weight after treatment (%)
C	49.45	44.7
N	21.97	26.61
O	1.58	0.66
Co	21.33	24.78
Au	5.67	3.25

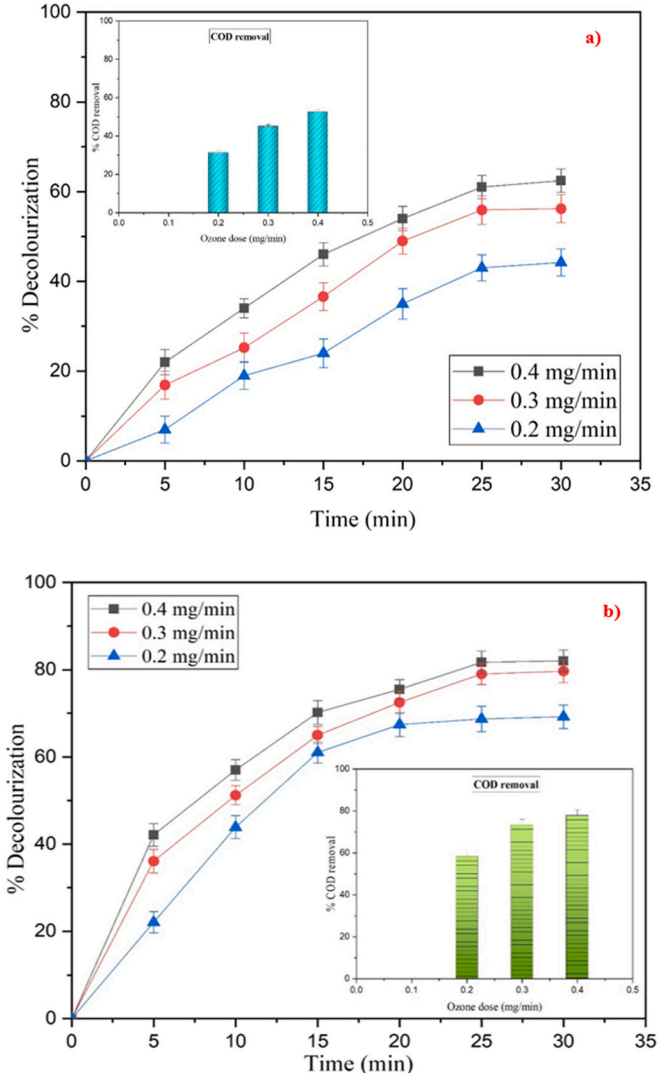

Fig. 3. a) Effect of ozone dose in the simple ozonation process (pH 9, V = 1.0 L, catalyst dose = 0 g/L) and b) Effect of ozone dose in the Catalytic ozonation-electro coagulation process (pH 9, V = 1.0 L, catalyst dose = 50 mg/L).

pH 9 compared to other pH levels studied. Additionally, at higher pH levels, the combined effect of fine H_2 bubble generation in electro-coagulation and ozonation bubbling in the system significantly promotes turbulence, mixing, and contact between gas, solid, and liquid interfaces. This enhances ionic mobility, leading to rapid organic degradation and removal.

3.2.4. *Effect of catalyst dose*

In the heterogeneous catalytic ozonation process, the catalyst offers a platform that enhances degradation reactions by either direct adsorption of organics onto the surface or by ozone molecules and •OH radicals'

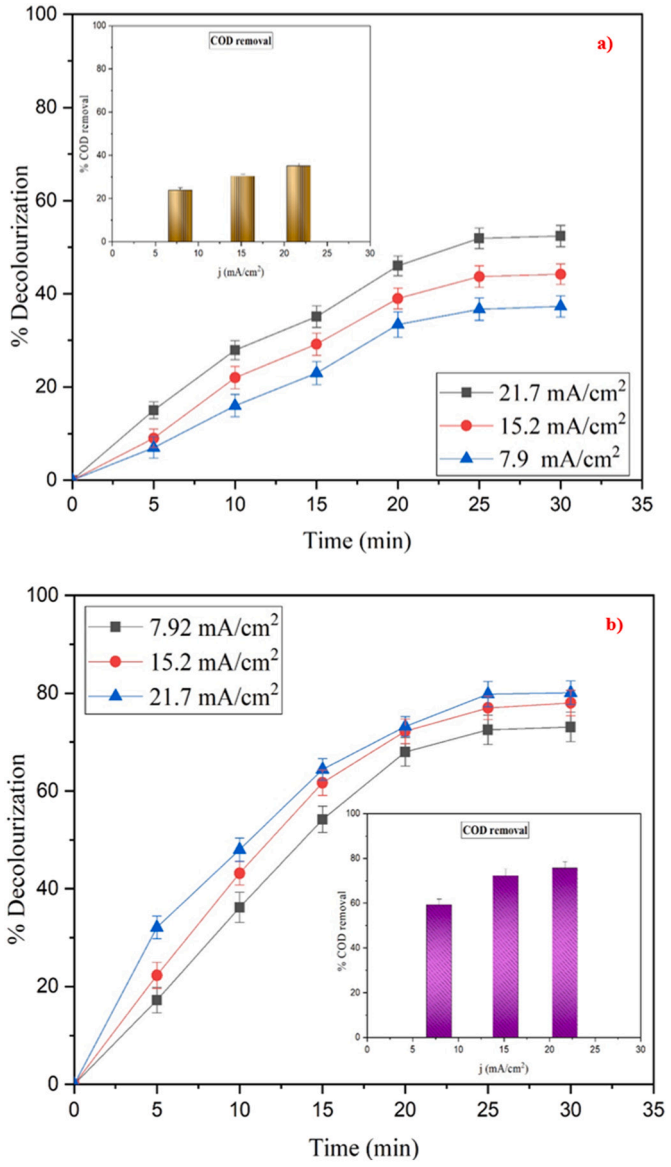

Fig. 4. a) Effect of current density in the simple EC process (pH 9, V = 1.0 L, catalyst dose = 0 mg/L), and b) Effect of current density on the EC+ catalytic ozonation process (pH 9, V = 1.0 L, catalyst dose = 50 mg/L, Ozone dose = 0.3 mg/min).

attachment and subsequent attacks on pollutants. The catalyst plays a vital role in electrocoagulation and catalytic ozonation due to its good adsorption ability for the removal of organic contaminants in textile wastewater by enhancing the •OH.

-based degradations. The optimum catalyst dose plays a vital role in the generation of hydroxyl radicals and the adsorption of the organic pollutants on their surface. The applied catalyst ZIF 67 was studied in this combined hybrid process by changing the catalyst dose from 25 to 75 ppm and noting the color removal as their result shown in Fig. 5b. The color removal increased from 70.1 % to 81.26 % by raising the catalyst ZIF 67 dose from 25 ppm to 75 ppm [45,58]. It may be due to the excellent adsorption capacity of ZIF 67 and enhanced surface availability at high catalyst doses.

3.2.5. *Catalyst reusability*

The reusability investigation determines the catalyst's effectiveness, life, and affordability. Fig. 5c shows the outcomes of the ZIF 67-employed EC + O_3 process, in which the ZIF 67 catalyst was reused

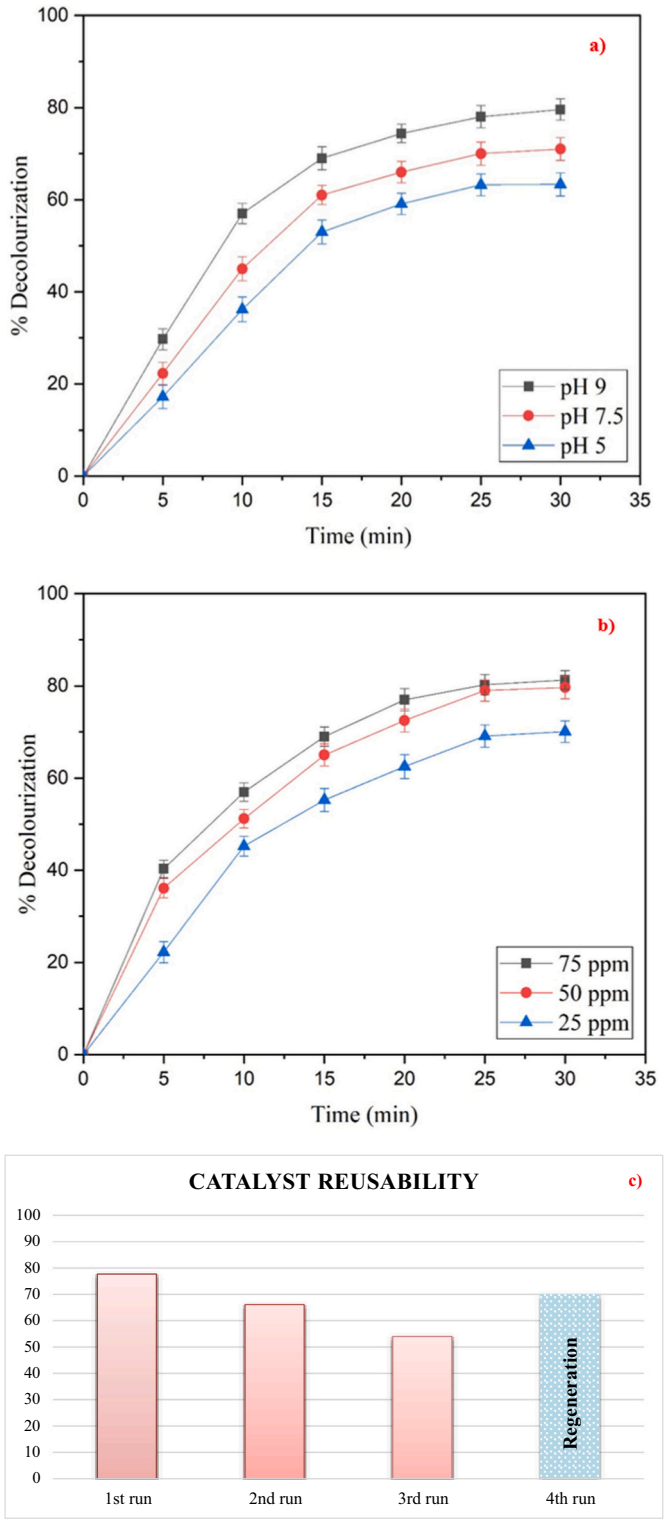

Fig. 5. a) Effect of pH in the EC+ catalytic ozonation process (j = 15.2 mA/cm^2, V = 1.0 L, catalyst dose = 50 mg/L, Ozone dose = 0.3 mg/min) b) Effect of MOF dose in the EC+ catalytic ozonation process (j = 15.2 mA/cm^2, V = 1.0 L, pH = 9, Ozone dose = 0.3 mg/min), and c) Catalyst reusability study (t = 30 min, pH 9, j = 15.2 mA/cm^2, ozone dose = 0.3 mg/min, V = 1.0 L, catalyst dose = 50 mg/L).

for up to three consecutive runs. The catalyst was washed three times with distilled water and repurposed for the subsequent cycle. In the subsequent runs, the removal efficiency decreased: in the first run, it was 77.9 %; in the second, it was 67.2 %; in the third, it was 55.80 %. Even when the catalyst efficacy has decreased, it can still remove pollutants. This decrease in the catalyst efficiency could be caused by the pore becoming choke-leached, causing the dye molecules to adhere to the catalyst surface and pores. After the 3rd run, the catalyst was regenerated using the method described in the literature [59]. In this method, the ZIF-67 surface was regenerated through eluents, *i.e.*, 0.1 mol/L HCl and ethanol washing technique. The mixture was stirred and dried at 70 °C in the oven. The resulting regenerated adsorbent was then reused under the same conditions during the subsequent adsorption test. According to the reusability study, the catalyst is sufficiently stable to be used for industrial applications. According to the reusability study, the catalyst is sufficiently stable to be used for industrial applications.

3.2.6. *Comparison of processes*

At optimum parameters, the processes were compared for decolorization and COD abatement in textile wastewater. The result presented in Fig. 6a showed that the maximum color removal is achieved in the combined HCOP-EC process. The order of decolorization efficiency is as HCOP-EC > Simple ozonation > simple EC > MOF adsorption. Simple ozonation showed a higher decolorization rate than simple EC because at pH = 9, •OH radicals are produced, so ozone readily attacks the organic pollutant.

COD removal achieved at various processes is shown in Fig. 6b. Results showed that more removal in the hybrid HCOP-EC process is achieved than in the single ozonation process. The addition of a catalyst significantly increases the generation of hydroxyl radicals, which degrades organic pollutants more effectively in a hybrid process as compared to single ozonation or single EC process. The COD removal efficiency attained 73.3 % in the case of hybrid catalytic ozonation and electrocoagulation process after 30 min [46,60].

Table 3 compares this research work in terms of parameters and process efficiency with various research studies reported in the literature. The parametric effects investigated in this research for the studied variables (treatment time, ozone dose, current density, pH, and catalyst dose) are in agreement with those of previous research studies [19,20,61,62].

Florenza et al. [61] utilized the electro-Fenton process to treat dye-containing textile wastewater, achieving complete color removal after 120 min of treatment at pH 3 and a high current density of 100 mA/cm^2. Bener et al. [62] examined the removal of organic pollutants from textile wastewater using the electrocoagulation method, achieving a color removal of 94.6 %, with a COD reduction of 18.6 % at pH 5 after 120 min. Recently, Munir et al. [67] explored the catalytic ozonation process employing Fe-Zeolite as a catalyst, resulting in a color removal rate of 90.0 % and a COD reduction of 74.0 %. Although extensive research has been conducted on the performance of standalone technologies such as catalytic ozonation and electrocoagulation, demonstrating favorable removal efficiencies [59,65,69,70], the current study exhibited an outstanding color removal of 79.6 % and a COD reduction of 73.3 % at pH 9. The color and CD removal was achieved with a minimal ozone dosage of 0.3 mg/min and a current density of 15.7 mA/cm^2 following a treatment duration of 30 min. Hence, the hybrid ZIF 67 catalytic ozonation-electrocoagulation process exhibits advantageous performance and rapid elimination of pollutants in textile wastewater.

Fig. 7 illustrates the time-dependent UV–visible spectrum of real textile wastewater during the hybrid ZIF 67 catalytic ozonation-electrocoagulation (HCOP-EC) process. The results show that the absorption peaks were progressively suppressed and ultimately vanished throughout the reaction, signifying the degradation of organics in wastewater, and the color was effectively removed. Furthermore, there were no newly observed absorption bands in either the visible or ultraviolet regions.

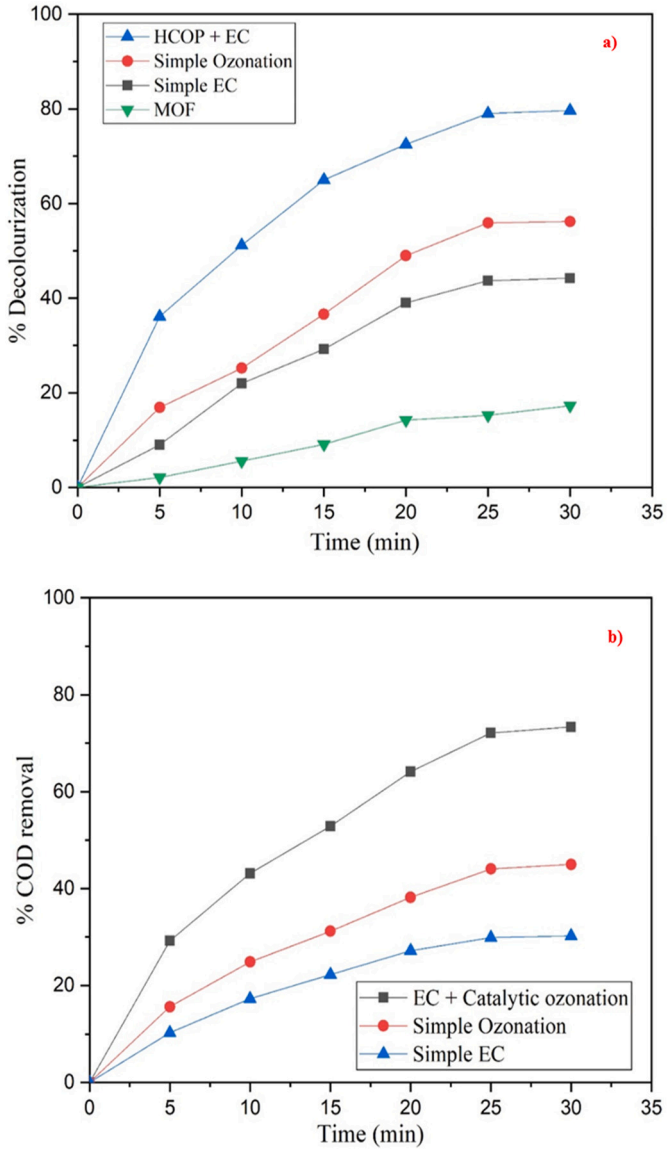

Fig. 6. a) Comparative study of various processes (t = 30 min, pH 9, j = 15.2 mA/cm^2, ozone dose = 0.3 mg/min, V = 1.0 L, catalyst dose = 50 mg/L) and b) COD removal study (t = 30 min, pH 9, j = 15.2 mA/cm^2, ozone dose = 0.3 mg/min, V = 1.0 L, catalyst dose = 50 mg/L).

3.2.7. *Proposed mechanism*

The mechanism for the hybrid HCOP-EC is below Fig. 8. The highest elimination of organic pollutants was attained at pH 9. Catalytic ozonation free radical mechanism at prevailing pH, combined with sweep coagulation/flocculation induced by electro-flocs, all happened concurrently in the side-by-side oxidation processes of the hybrid reactor. Meanwhile, at the cathode, •OH radicals produced by reduction and oxidation promote the generation of O_2 at the anode, which helps as a flotation media for the trapped organics. By way of destabilization along with neutralization, the contaminants are swept and adsorbed by the aluminum flocculation. Ozonation processes involve indirect and direct oxidation at a pH of 9 [69]. There is a large diversity of possible methods, and the ZIF 67 supplied the platform for fast-generating •OH radicals in a solution. Moreover, the catalyst's improved adsorption capacity made it possible for it to act as an active surface for the rapid production of •OH ions, which break down the organic pollutants by changing O_3 into O_3^- and O_2^- and producing more H_2O_2, which in turn led the organic contaminants to leach [44,71]. Hence, the hybrid HCOP-EC process leads to a multi-mechanistic pathway to eliminate the

Table 3
Hybrid HCOP-EC process performance comparison with other wastewater treatment processes.

Technology	Targeted pollutant	Operational parameters	Removal efficiency[a]	Reference
Electro-Fenton	Acid Red 1	(Electrode material: BDD, pH: 3.0, Time = 120 min, j = 100 mA/cm^2)	% R_{cod} = 100, % R_{CR} = 100	[61]
Electrocoagulation	Real textile effluent	(Electrode material: Fe, pH: 5.0, Time = 120 min, j = 25 mA/cm^2)	% R_{cod} = 18.6, % R_{CR} = 94.6	[62]
Electrooxidation	Basic Blue 9	(Electrode material: Al, pH: 7.0, Time = 20 min, j = 20.27 mA/cm^2)	% R_{cod} = 90.01, % R_{CR} = 99.90	[63]
Electrooxidation	Acid Orange 74	(Electrode material: Al, pH: 8.0, Time = 50 min, j = 40 mA/cm^2)	% R_{cod} = 28.7, % R_{CR} = 65.7	[64]
Catalytic ozonation	Textile effluent	(Catalyst: Fe (II), nZVI, ozone dose = 0.2 g/L, Time = 40 min, catalyst dose = 0.7 g/L)	% R_{cod} = 73.5, % R_{CR} = 87.00	[65]
Catalytic ozonation	Real textile effluent	(Catalyst: Copper (II)-doped carbon, ozone dose = 1.98 g/L, Time = 60 min, pH = 7.0)	% R_{CR} = 41.00	[66]
Catalytic ozonation	Real paper and pulp wastewater	(Catalyst: Copper (II)-doped carbon, ozone dose = 1.98 g/L, Time = 60 min, pH = 7.0)	% R_{cod} = 74.00, % R_{CR} = 90.00	[67]
Catalytic ozonation	Real industrial textile wastewater	(Catalyst: carbon aerogel supported copper oxide, ozone dose = 4 mg/min, Time = 60 min, catalyst dose = 1 g/L, pH = 7.8)	% R_{cod} = 46.00,	[68]
Electro-Fenton	Acid Brown 14	(Electrode material: Fe, pH: 3.0, Time = 60 min, j = 50 mA/cm^2)	% R_{CR} = 99.50	[20]
HCOP-EC	Real textile wastewater	(Electrode material: Al, pH: 9.0, Time = 30 min, j = 15.7 mA/cm^2, ozone dose = 0.3 mg/min, catalyst dose = 50 mg/L, Catalyst: ZIF 67)	% R_{cod} = 73.30, % R_{CR} = 79.60	Current study

[a] % R_{CR} – the Color removal (CR) removal efficiency, % R_{COD} – the chemical oxygen demand (COD) removal efficiency.

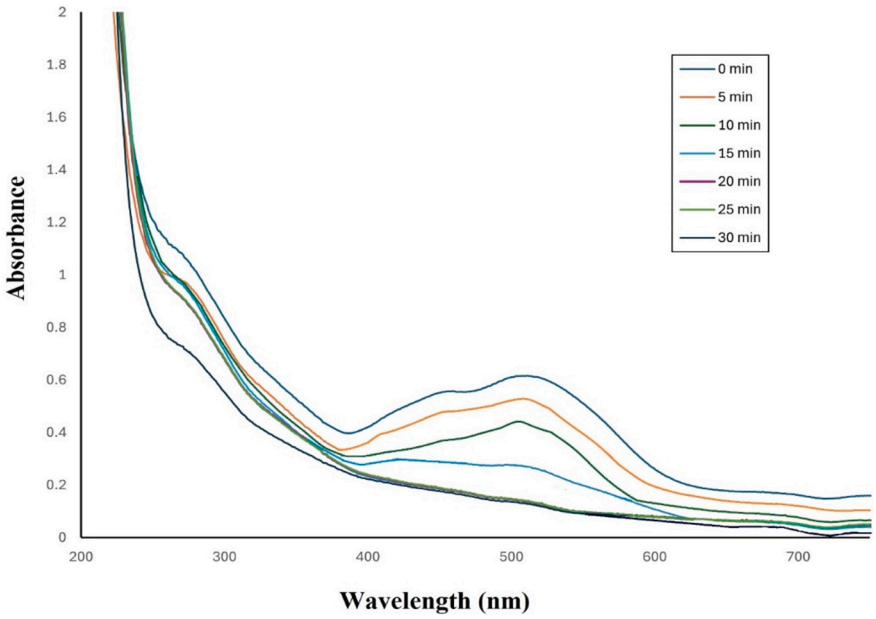

Fig. 7. UV spectrum of real textile wastewater.

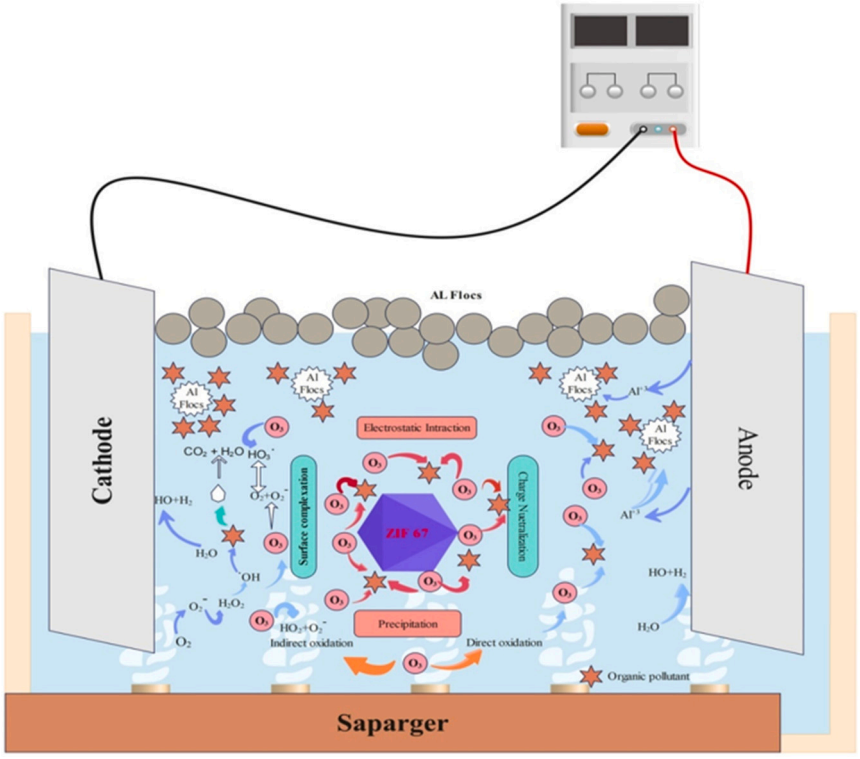

Fig. 8. Proposed mechanism for hybrid process.

organic pollutants in textile wastewater.

Table 3 presents the comparison of the catalyst performance of various catalysts studied in HCOP processes. Results in Table 4 reveal that the ZIF 67 hybrid system exhibited excellent COD removal compared to previous studies in which COD removal ranged from 51 % to 89 %. There was also 69.06 % removal of BOD by the ZIF 67 compared to 72.5 % by the Fe/AC catalyst, but it required a longer treatment time of 180 min, 6 times more than the ZIF 67 catalyst. The lowest color removal by ZIF 67, 79.6 %, probably stemmed from the shorter treatment time compared to previous studies. Overall, the removal of COD/BOD and color by the ZIF 67 catalyst in this study was comparable to or even better than that of previous ones, considering the faster processing time that did not exceed 30 min to achieve these results.

4. Conclusions

This research presented the first-ever application of MOF ZIF-67 in a catalytic ozonation-electrocoagulation (HCOP-EC) hybrid process for the treatment of real textile effluent. The results revealed the potential of ZIF 67 in a hybrid process and productive performance. At optimum

Table 4
Performance comparison of various catalysts.

Catalyst	Process	%COD removal	%BOD removal	Treatment time	%Color removal	Reference
$O@gC_3N_4/Al_2O_3$	HCOP	77	–	60 min	99	[70]
Fe/AC	HCOP	66.3	72.5	180 min	96.7	[72]
Fe-DLA	HCOP	76.44	–	40 min	98.76	[58]
Fe^{2+} nZVI	HCOP	73.5	–	50 min	92	[65]
($BiNiO_3$/RHAC)	EC-CWAO	37.1	–	90 min	76.2	[73]
Cu doped ZnO	HCOP	89	–	30 min	–	[74]
MgO-SCCA-Zn	HCOP	51.12	–	60 min	–	[75]
ZIF 67	Hybrid	73.3	69.06	30 min	79.6	This study

conditions, 79.6 % decolorization, 73.3 % COD, and 69.05 % BOD removal were achieved after 30 min of treatment at pH 9, ozone dose 0.3 mg/min, current density (j) 15.2 mA/cm^2, and catalyst dose 50 mg/L. When compared with previous research works reported [61,62] for textile wastewater treatment, this research offers an applicable approach for textile wastewater treatment at prevailing pH, lower current density, and reduced treatment time. Thereby, this process may cause realistic cost reductions when applied on a large scale for wastewater remediation. Process comparison showed a significant enhancement in the degradation of organics in the wastewater by the HCOP-EC process compared to standalone technology. The order of process efficiency was as HCOP-EC > O_3 > EC > MOF. ZIF 67 also exhibited an efficient reuse performance with up to 55.80 % removal after the third cycle. Hence, The HCOP-EC process is a suitable and efficient method for treating textile effluent in a hybrid reactor. The findings of this study exhibit the effectiveness of catalyst (ZIF 67) in the HCOP-EC process for demineralizing pollutants with high color removal, COD removal, and BOD removal for the treatment of textile wastewater. The results showed significant reductions in color, COD, BOD, TDS, and turbidity of the wastewater, and the quality of parameters were well within the limits of NEQ standards. There are some future recommendations, such as more research that may be performed focusing on examining the detailed mechanism of catalytic ozonation-electrocoagulation. Future studies should examine the relationship between catalyst structure and performance and the catalytic degradation process.

CRediT authorship contribution statement

Farhan Javed: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Muhammad Fahad Tariq:** Writing – original draft, Validation, Methodology, Data curation, Conceptualization. **Amir Ikhlaq:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Hafiz Muhammad Shahzad Munir:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Ali Altaee:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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