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Catalytic ozonation for the removal of reactive black 5 (RB-5) dye using zeolites modified with $CuMn_2O_4/gC_3N_4$ in a synergic electro flocculation-catalytic ozonation process

Amir Ikhlaq [a], Mahrukh Zafar [a], Farhan Javed [b,*], Abdullah Yasar [c], Asia Akram [d], Sidra Shabbir [a] and Fei Qi [e]

[a] Institute of Environmental Engineering and Research, University of Engineering and Technology, Lahore, Pakistan
[b] Department of Chemical Engineering, University of Engineering and Technology, Lahore, Pakistan
[c] Sustainable Development Study Centre, Government College University, Lahore, Pakistan
[d] Department of Chemistry, University of Management and Technology, Johar Town, Lahore, Pakistan
[e] School of Environmental Engineering and Science, Beijing Forestry University, Beijing, China
*Corresponding author. E-mail: farhan.javed@uet.edu.pk

AI, 0000-0002-3887-9562; MZ, 0000-0003-0174-0409; FJ, 0000-0002-2826-6439; FQ, 0000-0002-9938-941X

ABSTRACT

This study aims to investigate the decolourization efficiency of reactive black 5 (RB-5) dye by using $CuMn_2O_4/gC_3N_4$ coated zeolites (zeolite 4A) for the first time in a hybrid electro-flocculation-catalytic ozonation process. A comparison between various treatment options such as electro-flocculation, electro-flocculation in the presence of a catalyst, and catalytic ozonation in combination with electro-flocculation was explored. Moreover, the effect of different factors such as pH, time, catalyst dose, ozone dose, radical scavenger, and voltage has been studied in each treatment option mentioned earlier. The results indicated that the best treatment option was found to be catalytic ozonation in combination with electro-flocculation with removal efficiency (RE) of 90.31% at pH 10 after 30 min of the treatment process. The hydroxyl radical scavenger effect indicated that the synergistic catalytic process follows a radical mechanism. It is therefore concluded that $CuMn_2O_4/gC_3N_4$–zeolite catalysts in synergic electro-flocculation-catalytic ozonation process may be effectively used for the treatment of textile wastewaters.

Key words: catalyst, electro-flocculation, ozonation, reactive black 5, zeolites

HIGHLIGHTS

- The present research explores the $CuMn_2O_4/gC_3N_4$ coated Zeolites performance for the removal of RB5 in synergic processes.
- A comparison of synergic processes was studied.
- The synergic electro-flocculation catalytic ozonation process showed the highest RB5 removal efficiency of 90.31%.
- The work concludes the effective application of $CuMn_2O_4/gC_3N_4$ coated zeolites for the treatment of textile wastewater.

INTRODUCTION

Pakistan is ranked fourth in the world's largest textile producing countries and it contributes to about 60% of the country's exports (Memon *et al.* 2020). Although Pakistan's textile industry is flourishing continuously and is an integral part of the country's economy, the side impacts of this industry are problematic for the environment. A large quantity of water is used in the manufacturing processes such as resizing, bleaching, and dying. The textile industry is a major source of water pollution with the high discharge of dyes. Dyes are very toxic and recalcitrant in nature. These are persistent pollutants when discharged into the water and can be very harmful to aquatic life by reducing the penetration of sunlight and subsequently affecting the photosynthesis process. Moreover, some dyes have mutagenic and even carcinogenic effects on life. The release of these types of pollutants into the water bodies not only affects aquatic life but also the entire food web (Bilinska *et al.* 2020).

Wastewater containing dyes is very difficult to treat because these generally have a synthetic origin, complex structures, less biodegradability, and are relatively stable in water (Ali & El-Mohamedy 2010). Reactive black 5 (RB-5) dye is commonly used in the textile industry. RB-5 is an azo type dye that has a tendency to form a covalent bond between reactive groups present in the dye and the fabric. Even a small amount of these dyes is visible and very harmful. It is the utmost duty of textile industries to remove these types of pollutants from their discharge. As the concern for wastewater treatment is rapidly increasing,

industries want a more efficient and faster removal technology than the conventional treatment methods. Among these methods, catalytic ozonation is a relatively new and efficient technology for the effective removal of pollutants from wastewater originating from various industries. Photocatalysis based processes are also highly efficient for the degradation of dyes under solar radiations with composite catalysts (Guan *et al.* 2021). The removal efficiency of ozonation is very high because of its strong oxidation potential and the presence of a catalyst further increases the overall efficiency of the process (Rodríguez *et al.* 2018). Various factors such as pH, time, ozone dose, catalyst dose, and the presence of a radical scavenger can affect the decolorization efficiency of RB-5. The effect of pH is highly significant in the catalytic ozonation process. The efficiency of the ozonation process is less in an acidic medium as compared to that in the basic medium (Leitner & Fu 2005).

Some recent findings indicate that hybrid studies involving various processes such as electro-flocculation-catalytic ozonation were found to be highly efficient for wastewater treatment (Hernández-Ortega *et al.* 2010). Since it is difficult to treat the real wastewater matrix by applying a single technique due to the complex nature of wastewater. Using electro-flocculation with catalytic ozonation may enhance the overall efficiency in real conditions and may improve the applicability at a wider pH range due to the various mechanisms involved in hybrid processes (Daghrir *et al.* 2016). Electro-flocculation is also used in the textile industry to remove dyes from wastewater and is also a pH-dependent process. Furthermore, it depends upon the type, nature, and material of electrodes that may affect the overall efficiency of the process (Cerqueira *et al.* 2009).

In some recent studies, graphene-based materials such as gC_3N_4 were successfully studied as catalysts in catalytic ozonation processes. Ozone (O_3) itself is a very strong oxidizing agent but the presence of zeolites can enhance the catalytic activity because of their chemical and ion exchange abilities. When ozone is combined with an appropriate catalyst it will enhance the overall removal efficiency. Graphitic carbon nitride (gC_3N_4) has a very unique electronic structure, low density, and super endurance for chemical and thermal properties (Dong *et al.* 2014). The presence of active sites (that may interact with aqueous O_3 leading to the production of hydroxyl radicals) and surface properties make it an emerging candidate for catalysis (Zhu *et al.* 2014). Since the real wastewater contains various types of pollutants along with other constituents such as radical scavenges (bicarbonates, sulfates, and chlorides, etc.). Hence it is important to imply a combination of various kinds of catalysts that may operate via multiple mechanisms (radical based and non-radical based). Previous findings show that zeolites may operate through both radical and non-radical based mechanisms (Xu *et al.* 2019). In the current investigation, zeolites modified with $CuMn_2O_4/gC_3N_4$ were applied to the wastewater treatment for the first time. The previous finding (Liu *et al.* 2021) indicates that $CuMn_2O_4/gC_3N_4$ shows significant efficiency for various pollutants remediation in water when fabricated with membrane. $CuMn_2O_4$ showed acceptable performance for the degradation of micro pollutants. The gC_3N_4 was found to be excellent catalyst support (Liu *et al.* 2021). In real wastewater, due to the presence of radical scavengers, the catalyst following radical mechanism may not be effective. Moreover, due to the presence of various kinds of pollutants in real textile wastewater, it is indeed important to work on such catalysts that may perform better in various conditions. The zeolites were reported to follow both molecular ozone based and radical mechanisms (Ikhlaq & Kasprzyk-Hordern 2017). The zeolites may provide a platform on its surface to both pollutant and molecular ozone for pollutant degradation while $CuMn_2O_4$ will help to promote the generation of hydroxyl radicals leading to the degradation of pollutants inside the solution.

In the present study, $CuMn_2O_4/gC_3N_4$ modified zeolites (4A) were used to investigate the removal of RB-5 in the synergic electro flocculation- catalytic ozonation process. $CuMn_2O_4$-gC_3N_4 is a low-cost catalyst that can be used in the catalytic ozonation process (Cerqueira *et al.* 2009). Moreover, $CuMn_2O_4$-gC_3N_4 may provide active sites to promote the production of hydroxyl radicals. Besides, the application of the synergic process (electro-flocculation-catalytic ozonation) in real wastewater may further enhance the effectiveness of wastewater treatment. The electro-flocculation process not only removes dyes via the sweep flocs process (Ghernaout & Ghernaout 2012) but also the suspended particles in textile wastewater may be removed that hinder the dye removal via the oxidation process. This study is the continuation of the author's previous study implying synergic process (electro-flocculation-catalytic ozonation) on various kinds of wastewaters. In a previous findings, authors successfully studied the treatment of pharmaceutical polluted wastewater by the synergic process (Ikhlaq *et al.* 2020). In the current investigation, $CuMn_2O_4$-gC_3N_4 coated zeolite A was used for the first time to study the decolorization of RB-5. *The effectiveness of $CuMn_2O_4$-gC_3N_4 coated zeolite A in the synergic electro-flocculation-catalytic ozonation process was studied using the effect of variables like pH, ozone dose, voltage, RB5 concentration, and radical scavenger and mechanism was proposed.*

MATERIALS AND METHODS

Materials

In this study, zeolites (zeolite 4A) were used which were provided by Zeochem (Switzerland). The catalyst $CuMn_2O_4/gC_3N_4$ was used as supplied. Reactive black dye was obtained from Sigma Aldrich. All the other chemicals employed in the experimental stage were of analytical grade and used without further purification. Ultrapure deionized water was used to perform all types of experiments.

Catalyst preparation

The $CuMn_2O_4$/g-C_3N_4 was synthesized by method as described elsewhere (Liu *et al.* 2021). It involves a two-step method where urea (10.0 g) was mixed with obtained $CuMn_2O_4$ (0.2 g), as prepared by the method described by Liu *et al.* (2021), The material was evenly grinded and was placed in a quartz crucible. It was then placed in a muffle furnace and calcined at 350 °C for 2.0 h (heating rate = 10 °C/min).

Zeolites (zeolite 4A) were added to the 0.1 M nitric acid solution for 24 h. Zeolites were then filtered. Distilled water was used to thoroughly wash the sample to obtain a constant pH (Ersöz 2014). After this step, the sample was placed in the oven overnight. The temperature of the oven was set at 110 °C. The catalyst was prepared by impregnating $CuMn_2O_4/gC_3N_4$ on zeolites as shown in Figure 1. About 40 g of $CuMn_2O_4/gC_3N_4$ along with 50 g of zeolites were dissolved in a beaker containing approximately 180 mL of deionized water. It was heated in a water bath to evaporate water at 102 °C. Finally, a wet catalyst was placed in the furnace for 6 h at 600 °C to regenerate active sites (Figure 1).

Catalyst characterization

The surface morphological characteristics of the $CuMn_2O/gC_3N_4$ coated zeolites were analyzed by scanning electron microscope (SEM) while the elemental investigation was studied using energy-dispersive X-ray spectroscopy (EDS) using JSM-6060A analyzer. The surface characteristics were determined by the Brunauer–Emmett–Teller (BET) technique using Micro metrics (USA, ASAP 2020) (Preocanin & Kallay 2006).

Experimental setup

The experimental setup of the present research is shown in Figure 2. A pyrex glass reactor of capacity 1,500 mL was used to carry out the treatment process. Two spiral-shaped aluminium electrodes with a surface area of approximately 18 in^2 connected with the DC power supply, were placed in the reactor. For each experimental run, 1 L of wastewater was taken in the reactor, where after adjusting the pH value ozone was introduced into the reactor through ceramic sparger from the ozone generator. The samples were drawn at regular intervals for further analysis.

Experimental procedure

All the experimental runs were performed in a semi-batch mode at the temperature of 25 °C. For each run, 1,000 mL wastewater was taken in the glass reactor. After adjusting pHs, a specific amount of catalyst was added, and the voltage and ozone rate were adjusted. The Indigo method was used to find out the ozone concentration present in the aqueous phase (Ersöz 2014). Two sets of ozone traps were filled with 200 mL of 2% potassium iodide KI solution. A ceramic sparger continuously

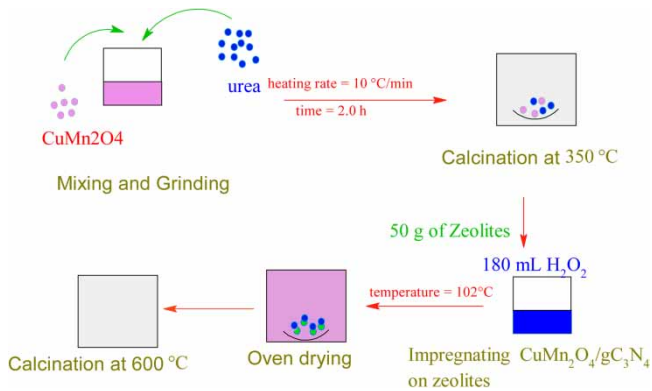

Figure 1 | Schematic illustration for the preparation of $CuMn_2O_4/gC_3N_4$-zeolite catalyst.

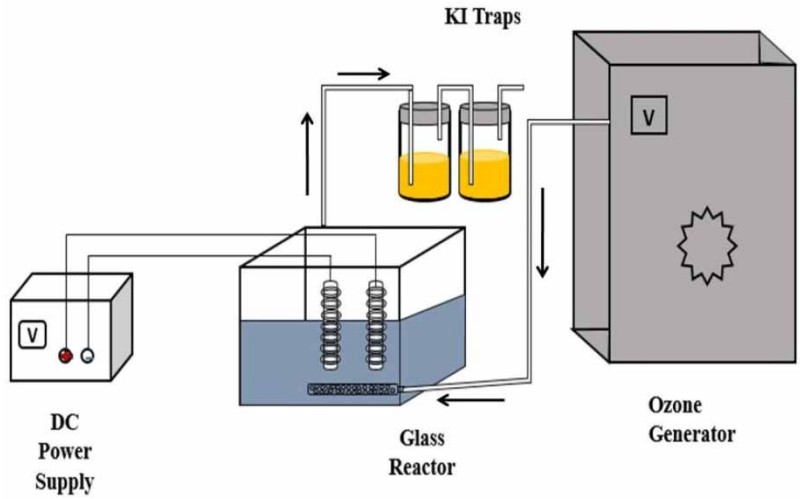

Figure 2 | Experimental assembly.

introduced gaseous ozone into the experimental assembly shown in Figure 1. Removal of RB-5 was analyzed during electro-flocculation, electro-flocculation in the presence of the catalyst, and catalytic ozonation in combination with electro-flocculation.

1,000 ppm stock solution of RB-5 dye was prepared from which a working solution was taken. The maximum absorption value was found at 596 nm. Before performing the experiment, the calibration curve was prepared. Each experiment was performed three times to ensure accuracy and the RSD value was found to be less than 5%. Samples were taken after every 5 min over a half-hour time span for electro-flocculation, electro-flocculation in the presence of a catalyst, and catalytic ozonation in combination with ozonation. pH during experiments was thoroughly maintained using 1N HCL and 1N NaOH. The samples were then analyzed on Perkin Elmer Lambda 35 double beam UV-VIS spectrophotometer.

The removal efficiency of RB-5 was determined:

$$\text{Removal efficiency } (R.E) = \frac{A_o - A_t}{A_o} \times 100$$

A_o = initial absorbance at time zero
A_t = absorbance at time t

RESULTS AND DISCUSSION

Characterization of catalyst

The SEM images of $CuMn_2O_4/gC_3N_4$ and $CuMn_2O_4/gC_3N_4$ coated zeolites are shown in Figure 3(a) and 3(b) respectively which indicate a crevice type structure of the surface of the catalyst. The EDS graphs of $CuMn_2O_4/gC_3N_4$ and $CuMn_2O_4/gC_3N_4$ coated zeolites are shown in Figure 3(c) and 3(d) respectively. The EDS spectra of $CuMn_2O_4/gC_3N_4$ and synthesized catalyst $CuMn_2O_4/gC_3N_4$-zeolite was shown in Figure 3(c) and 3(d) respectively. The EDS results clearly show the impregnation of $CuMn_2O_4/gC_3N_4$ on zeolites which is indicated by peaks of Cu, Mn and C (Figure 3(d)). The zeolites exhibited a BET surface area of 89.5 m^2/g, which was reduced to 86.32 m^2/g after gC_3N_4 coating which may be due to surface coverage by the molecules. The surface characteristics of the catalyst are given in Table 1.

Effect of pH

Studies have shown that the pH of solution significantly affects the efficiency of ozonation and electro-flocculation processes (Ersöz 2014). Electro-flocculation, electro-flocculation in the presence of the catalyst, and catalytic ozonation in combination

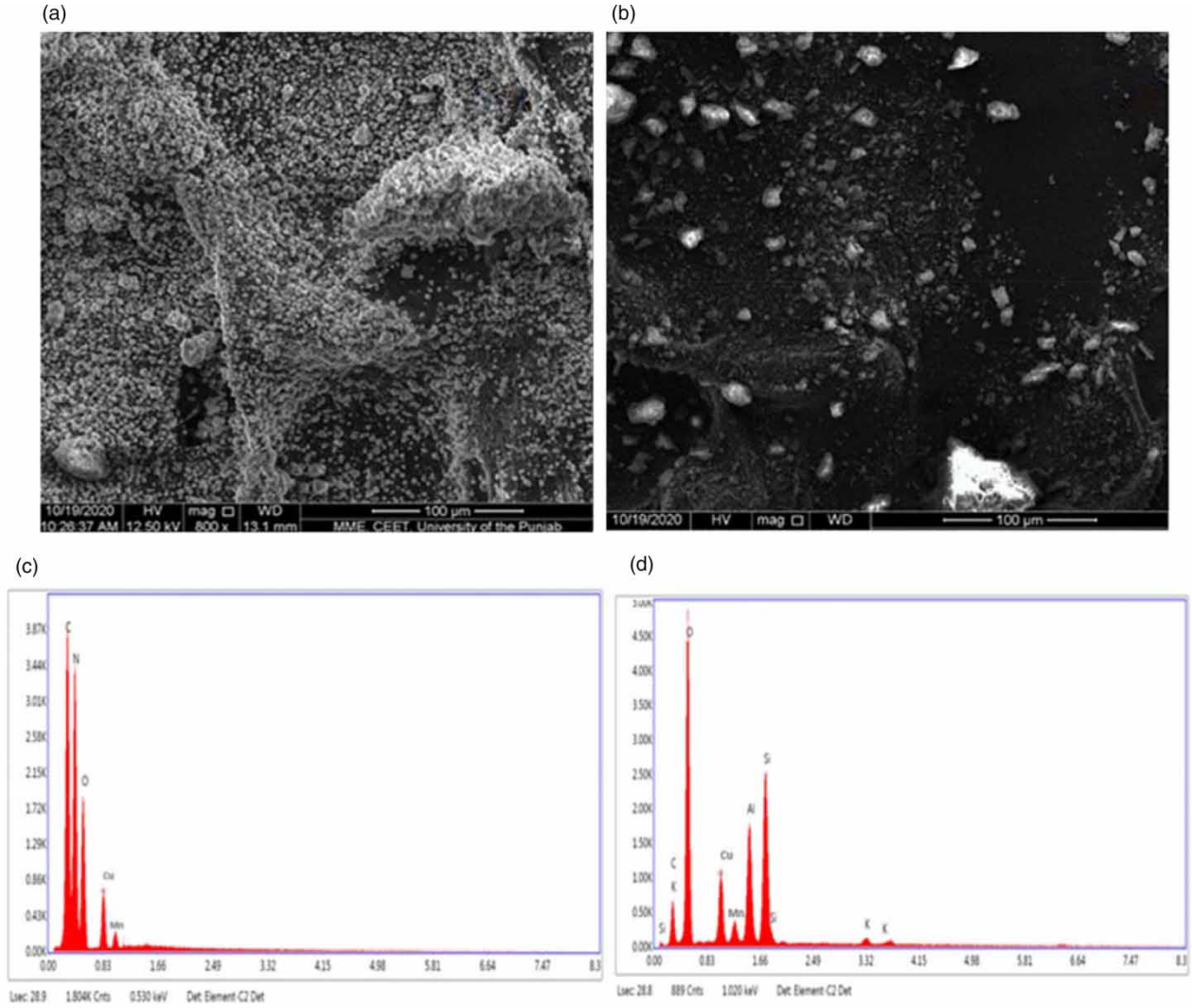

Figure 3 | (a) SEM for $CuMn_2O_4/gC_3N_4$, (b) $CuMn_2O_4/gC_3N_4$ coated on zeolites, (c) EDX for $CuMn_2O_4/gC_3N_4$ (d) $CuMn_2O_4/gC_3N_4$ coated on zeolites.

Table 1 | Characteristics of catalyst

BET area (m^2/g)	BET area after coating (m^2/g)	Pore size (^oA)	Point of zero charge
89.50	76.32	5.33	6.1 ± 0.03

with electro-flocculation experiments were performed at pH = 3, 7.5, and 10. The pH of the experiments was adjusted using 0.1 M HCl and 0.1 M NaOH. Ozonation reactions follow different mechanisms at different pH values. During the ozonation process, hydroxyl radicals (˙OH) are produced depending on the pH of the water and are found to be significant at alkaline pH values.

At pH 3 the decolorization efficiency of RB-5 for electro-flocculation and electro-flocculation in the presence of the catalyst and catalytic ozonation in combination with electro-flocculation was 45.4%, 50.77%, and 56.79% respectively after 30 min (Figure 4(a)).

At pH 7.5, removal of RB-5 in case of electro-flocculation, electro-flocculation in the presence of the catalyst and catalytic ozonation in combination with electro-flocculation was 35.65%, 44.97%, and 87.48%, respectively (Figure 4(b)). At pH 10 removals of RB-5 were 31.18%, 39.27%, and 90.31%, respectively (Figure 4(c)). Results have clearly shown that with the

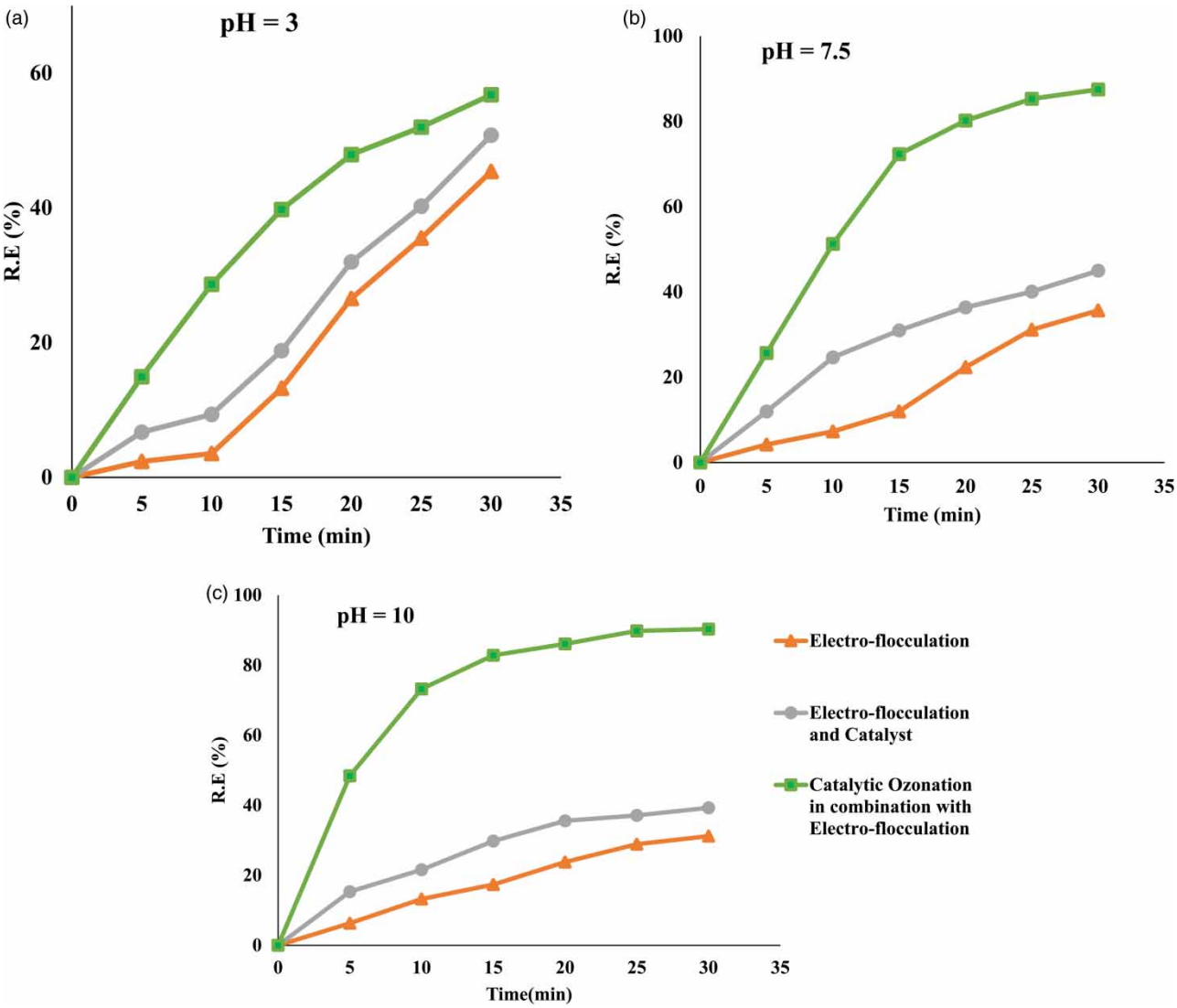

Figure 4 | pH effect along with process comparison (amount of catalyst = 1 mg, amount of RB-5 = 30 ppm, O_3 = 1 mg/min, time = 30 min, pH = 3, temp = 25 °C, vol = 1,000 mL).

increase in pH, the decolorization of RB-5 increased substantially for catalytic ozonation in combination with electro-flocculation. This may be due to the availability of active sites on catalysts at various pH values (Ikhlaq *et al.* 2012). In addition, the combined process involves various pH-dependent processes that lead to the removal of dyes faster than a single process. For example, sweep floc, ozonation, catalytic ozonation, and electro-oxidation (Ersöz 2014).

pH also played a vital role during the electro-flocculation process. It affects the color removal efficiency in the electro-flocculation process (Cerqueira *et al.* 2009). The maximum efficiency was achieved in acidic pH for electro-flocculation in the presence of the catalyst and simple electro-flocculation. At lower pH, positively charged species of aluminium hydroxide was present while RB-5 is a negatively charged dye so the neutralization of dye through positively charged aluminium hydroxide took place at lower pH, hence increasing the removal efficiency. Insoluble $Al(OH)_3$ were present at neutral pH due to which removal through sweep flocculation mechanism was increased rather than by radical method. The hydroxide radical present in water helped in the removal of dye to some extent but the overall efficiency decreased at neutral pH as compared to acidic pH (Ensano *et al.* 2018). The generation of $Al(OH)_4^-$ became the most dominant species at alkaline pH which was not as capable of oxidizing RB-5 as compared to positively charged aluminium hydroxide ion which further decreased the removal efficiency in the acidic range (Giwa *et al.* 2018).

Effect of ozone dose

Ozone is an effective oxidant that readily oxidizes the pollutants present in wastewater. Different values of ozone doses were studied on RB-5 removal. The results show that as the ozone dose was increased, the removal efficiency of the treatment process also increased. The results (Figure 5(a)) show that for ozone value 0.75 mg/min, 1 mg/min and 1.25 mg/min, the achieved RE was 77.69%, 85.47% and 90.55%, respectively. The increase in ozone dose accelerates the radical-based reactions taking place on the catalyst surface which significantly increases the RB-5 removal (Ikhlaq *et al.* 2020).

Effect of voltage

Voltage is one of the main factors that can have a potential effect on the performance of the electro-flocculation process. For analysis 5, 10 and 15 V were selected at pH 10. Theoretically, by increasing the voltage the oxidation capacity of the process increases hence, increasing the overall efficiency. The RE results obtained for 5 V, 10 V, and 15 V were 35.78%, 37.74%, and 32.78%, respectively, shown in Figure 5(b). There is no significant difference at 5 and 10 volts but at 15 V there was a considerable deviation from the expected trend. The increase in voltage causes a fast dissolution of electrodes to produce ions in the solution, giving more metal hydroxide flocs which readily neutralizes the RB-5 molecules (Ikhlaq *et al.* 2020). However, the decline in efficiency at 15 V may be due to the dissipation of electric energy into heat energy in the solution.

Effect of higher concentration of RB-5 dye

Results shown in Figure 6 indicate that by increasing the concentration of dye, the amount of dye removed during catalytic ozonation in combination with electro-flocculation at pH 10 also increased. This phenomenon indicates the oxidation ability of the process. For 30 ppm, 60 ppm, and 90 ppm, the amount of dye oxidized was 27.09 mg/L, 47.12 mg/L, and 66.43 mg/L, respectively.

Effect of hydroxyl radical scavenger

45 mL of $NaHCO_3$ solution was added into the wastewater as a scavenger to analyze the mechanism of the radical-based removal process. In the absence of hydroxyl radical scavenger, the efficiency for the catalytic ozonation in combination with electro-flocculation was 90.21% at pH 10, as shown in Figure 7. While in the presence of hydroxyl radical scavenger, the efficiency of the same process with the same experimental condition decreased to 76.51%. It confirms that the radical scavenger effect is significant and the removal of RB-5 in the process operates through the radical-based mechanism.

Proposed mechanism

The proposed mechanism for the removal of RB-5 dye from wastewater is explained in Figure 8. It is a very complex mechanism consisting of multiple sub-mechanisms

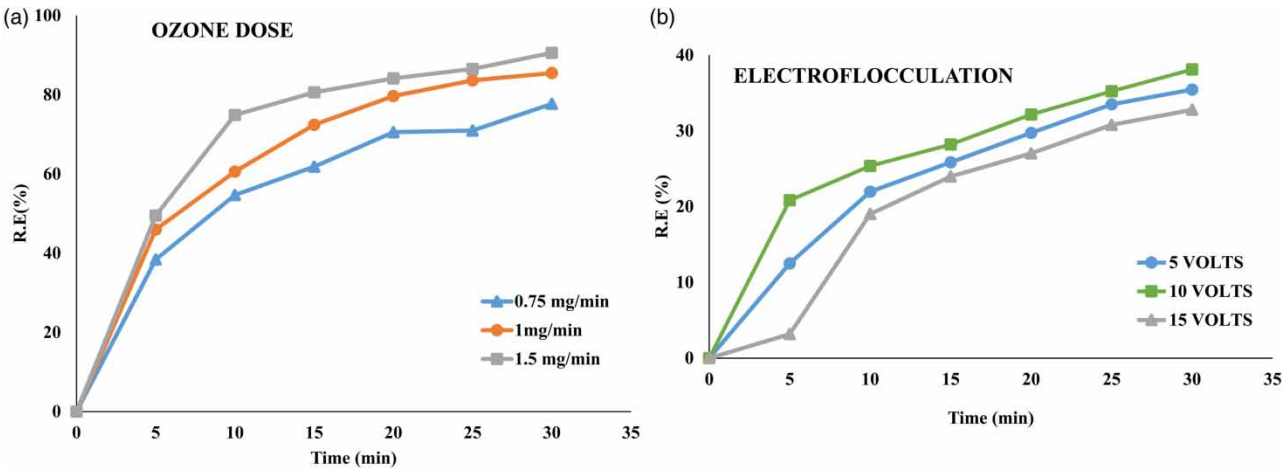

Figure 5 | (a) Effect of ozone dose in synergic process (amount of catalyst = 1 mg, amount of RB-5 = 30 ppm, time = 30 min, pH = 10, temp = 25 °C, vol = 1,000 mL); (b) effect of voltage in electro-flocculation.

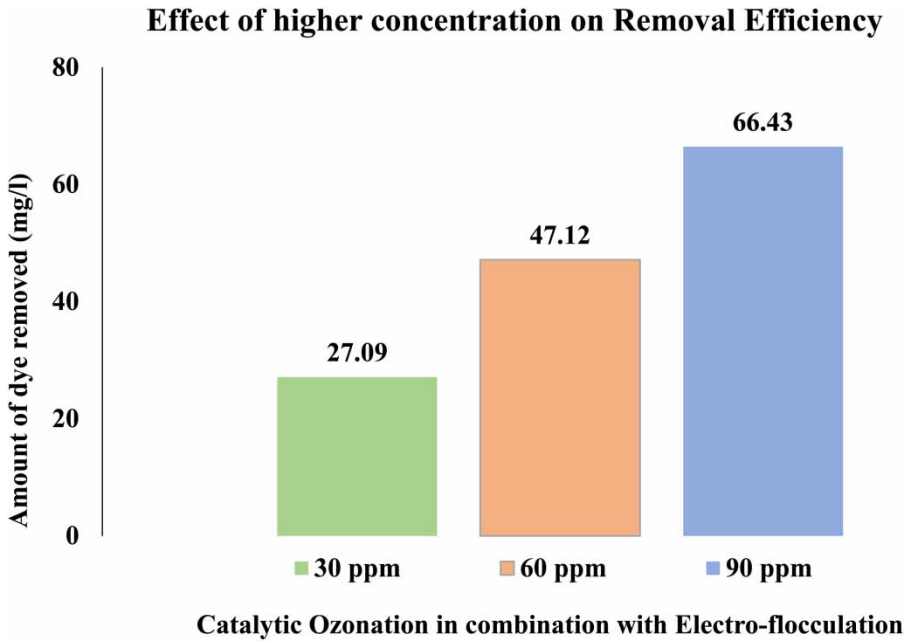

Figure 6 | Effect of higher doses of pollutant, catalytic ozonation in combination with electro-flocculation (amount of catalyst = 1 mg, O_3 = 1 mg/min, time = 30 min, pH = 10, temp = 25 °C, vol = 1,000 mL).

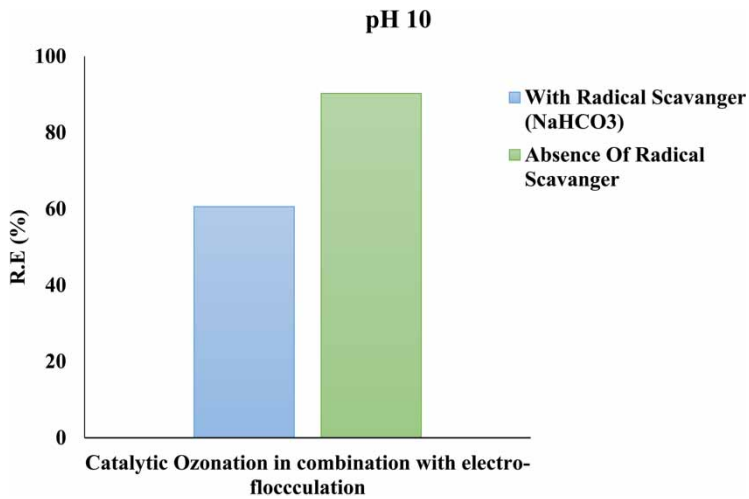

Figure 7 | Effect of radical scavenger (sodium bicarbonate), catalytic ozonation in combination with electro-flocculation (amount of catalyst = 1 mg, amount of RB-5 = 30 ppm, O_3 = 1 mg/min, time = 30 min, pH = 10, temp = 25 °C, vol = 1,000 mL, amount of $NaHCO_3$ = 45 mL).

(i) Radical-based mechanism: The interaction of catalyst active sites such as surface hydroxyl groups may lead to the production of hydroxyl radicals in the synergic process. Since hydroxyl radical is a stronger oxidant and has more electron affinity; the removal efficiency increases significantly. Hydroxyl radicals will react with pollutants and convert into less toxic compounds efficiently (Ikhlaq *et al.* 2020). The results presented in Figure 8 clearly indicate that hydroxyl radicals may involve in the synergic process leading to the decolorization of dyes (Ikhlaq *et al.* 2020). In addition, the direct ozone attack on the adsorbed pollutants on the catalyst surface may also contribute as indicated in some previous findings (Ikhlaq *et al.* 2020).

(ii) Sweep flocculation: One of the major factors on which electro-flocculation process depends is the type of electrodes used. In this study, Al-electrodes were used. Aluminium has the property to form monomeric or multimeric flocculated species of aluminium hydroxide. These flocculated species acted as adsorbents to carry out the removal process of RB-5 (Bensadok *et al.* 2008).

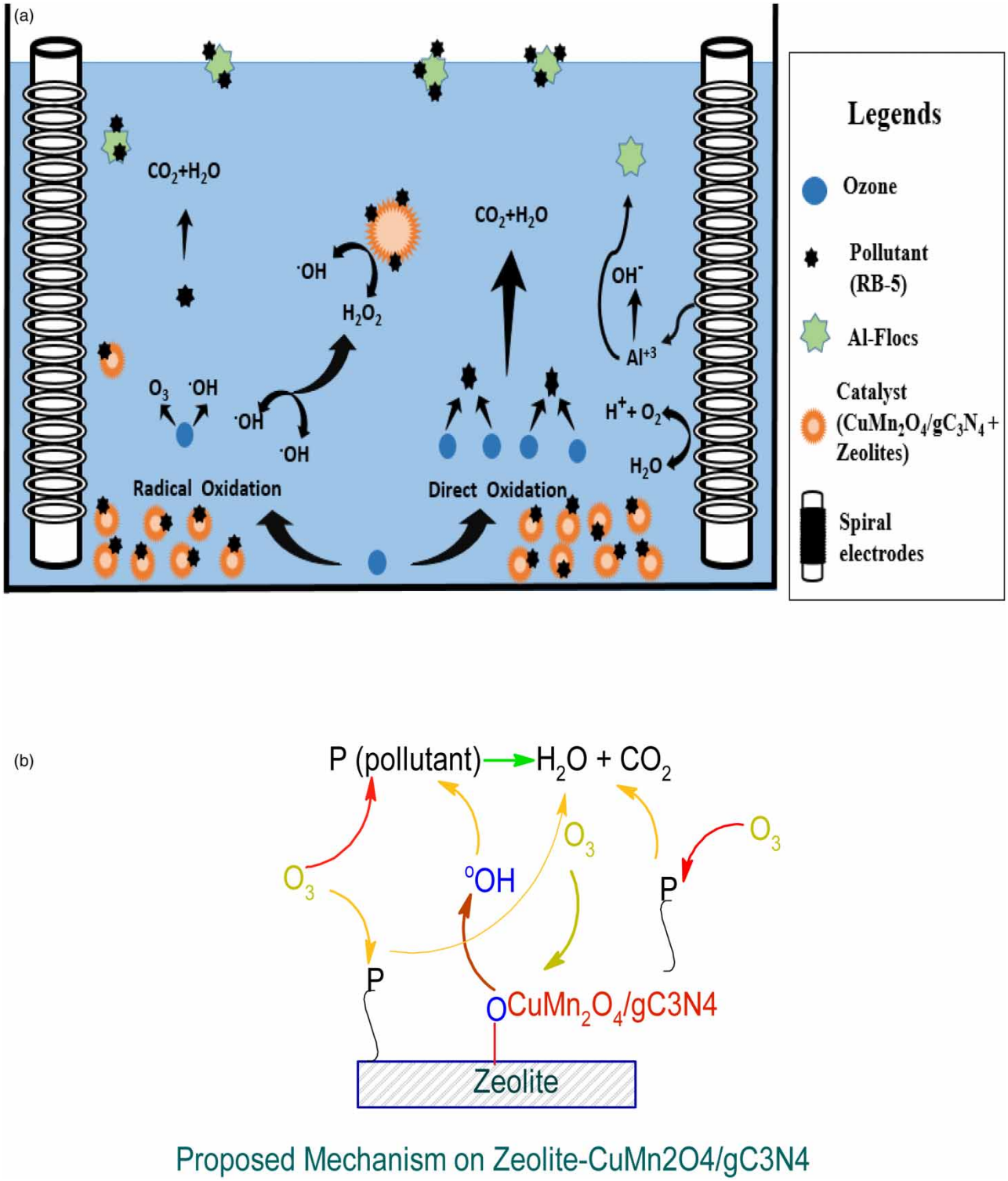

Figure 8 | Proposed mechanism.

(iii) Catalytic decomposition of H_2O_2 or activation of H_2O_2: During the ozonation process, hydroxyl radicals are generated. Hydroxide radicals are very reactive species that can react with each other to form hydrogen peroxide. Hydrogen peroxide has oxidation potential of ($E^0 = 1.7$ eV) while hydroxide radical has oxidation potential of ($E^0 = 2.8$ eV). Hydrogen peroxide is also an oxidant but not as strong as hydroxide radical so the continuous generation of hydrogen

peroxide can decrease the removal efficiency of the overall process; however, the metal present in the catalyst (Cu and Mn) will react with hydrogen peroxide and regenerate hydroxyl radicals (Shen *et al.* 2021) through the following reactions.

$$OH + {}^{\cdot}OH \rightarrow H_2O_2 \quad (1)$$

$$O_2 + 2H^+ + e^- \rightarrow H_2O_2 \quad (2)$$

$$M^{+2} + H_2O_2 \rightarrow M^{+3} + OH^- + {}^{\cdot}OH \quad (3)$$

Figure 8(b) further elaborates the mechanism on zeolites modified with $CuMn_2O_4/gC_3N_4$. The removal of pollutant may be due to the production of hydroxyl radicals as a result of the interaction of ozone with the active sites (metals) on the catalyst (Yuan *et al.* 2019). The effect of hydroxyl radical scavenger (Figure 6) confirmed the involvement of hydroxyl radicals in the studied process. Moreover, the molecular ozone reactions on the surface of zeolite (Ikhlaq *et al.* 2012), also leads to the removal of pollutants. It is further hypothesized that the adsorption of dye on the surface of zeolite and gC_3N_4 may also play an important role in dye removal. The adsorbed dye may be removed by the molecular ozone attack (Figure 8(b)). The comparison of results for electro-flocculation and combined electro-flocculation with catalyst (Figure 3(c)) indicate the adsorption of dye on the catalyst. The previous findings indicate that gC_3N_4 and zeolites were found to be good adsorbents for organic pollutants (Ikhlaq *et al.* 2012; Fronczak 2020).

CONCLUSIONS

The present research has shown that catalytic ozonation in combination with electro-flocculation for the removal of RB-5 dye is a promising treatment technique for textile wastewater treatment. This study also encourages the use of $CuMn_2O_4/gC_3N_4$ modified zeolites as a catalyst in ozonation and electro-flocculation. $CuMn_2O_4/gC_3N_4$ was used in a very fine powdery form for which zeolites provided a perfect base. So, the use of multiple catalysts with different physical and chemical properties can have a positive effect on the treatment process.

At optimal conditions of voltage 10 V, ozone dose 1 mg/min, and at pH 10 more than 90% removal efficiency was achieved in 30 min. The results reveal that $CuMn_2O_4/gC_3N_4$ modified zeolites may be effectively used in the textile industry to meet effluent quality standards in relatively less time and decrease the footprint as compared to conventional treatment technologies.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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