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Catalytic ozonation combined electroflocculation for the removal of Reactive Black 5 in aqueous solution using $CuMn_2O_4$/RGO coated zeolites

Amir Ikhlaq[a,*], Sidra Shabbir[a,*], Farhan Javed[b], Mosin Kazmi[c], Abdullah Yasir[d], Umair Yaqub Qazi[e], Mahrukh Zafar[a], Fei Qi[f]

[a]*Institute of Environmental Engineering, University of Engineering and Technology Lahore, Pakistan, emails: aamir.ikhlaq@uet.edu.pk (A. Ikhlaq), sidrashabbir106@gmail.com (S. Shabbir), gondal.mahrukh@gmail.com (M. Zafar)*
[b]*Department of Chemical Engineering, University of Engineering and Technology Lahore, Pakistan, email: Farhan.javed@uet.edu.pk*
[c]*University of Engineering and Technology Lahore KSK Campus, KSK, Pakistan, email: engrsmalikazma@gmail.com*
[d]*Sustainable Development Study Centre, Government College University Lahore, Pakistan, email: yasar.abdullah@gmail.com*
[e]*Department of Chemistry, College of Science, University of Hafr Al Batin, P.O. Box: 1803, Hafr Al Batin, 39524, Saudi Arabia, email: umairqazi@uhb.edu.sa*
[f]*Beijing Key Lab for Source Control Technology of Water Pollution, College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, P.R. China, email: qifei@bjfu.edu.cn*

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ABSTRACT

The treatment of Reactive Black 5 (RB5) was studied in this research by using the catalytic ozonation process. $CuMn_2O_4$/RGO along with zeolites was used first time in catalytic ozonation. A series of experiments were performed to understand the mechanism. These experiments involved ozonation, catalytic ozonation, electroflocculation, ozonation in combination with electroflocculation, electroflocculation with only catalyst, and catalytic ozonation in combination with electroflocculation. The effect of various parameters was studied such as pH, time, ozone dose, voltage, and hydroxyl radical scavenger on the removal of RB5. It was found that the removal efficiency was higher in catalytic ozonation in combination with electroflocculation as compared to the other processes. The order of decolorization efficiencies was: catalytic ozonation in combination with electroflocculation > catalytic ozonation > ozonation along with electroflocculation > ozonation > electroflocculation combined with catalyst > electroflocculation. The main role played in the decolorization was of catalytic ozonation. The maximum removal was achieved at pH 10 was up to 90% due to a higher rate of floc formation and rapid $OH^{\bullet}$ radicals generation leading to enhanced dye reduction. The active sites present on reduced graphene oxide played an important role in the removal of dyes due to their adsorption property. It can be concluded that the dye removal is more efficient by using catalytic ozonation along with electroflocculation.

Keywords: Ozonation; Catalytic ozonation; Electroflocculation; Zeolites; Decolorization; Reactive Black 5

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* Corresponding authors.

1. Introduction

Water is the most valuable resource present on the earth. It is required by all living organisms for their survival. Water is required by us for both domestic and industrial processes [1]. A major threat to the health of people is due to the contaminations present in waster. These contaminations are present both in groundwater and surface water [2]. The contaminants in water are due to human activities. Sewage is the primary source of contaminating freshwater when it mixes with the freshwater source. The other source of water contamination is the wastewater from different industries and industrial processes [3].

In the textile industry, Pakistan is one of the major exporters. Textile plays an important role in the economic growth of Pakistan. Almost 9% of Pakistan's economy depends on the textile industry [4]. The wastewater discharge of the textile industry has become a great challenge for the environment. The wastewater contains several contaminants which pollute our surface and subsurface sources of water [5]. In textile, the main source of water pollution is effluent-containing dyes. These dyes when present in high concentration in water bodies lead towards the deterioration of aquatic life. In high concentration, these limits and then ultimately stop the reoxygenation capacity by cutting off the light. It stops all the biological processes taking place underwater and can also prove toxic when present for a long time in the environment [6].

Reactive dyes are used in the textile dying due to their high reactivity and, these are easily soluble in water. Reactive Black 5 (RB5) is also a reactive azo dye. These dyes constitute about 60% of the commercial dyes used in textile [7]. Azo dyes contain double bonds and mostly these are found complex in nature. Dyes are carcinogenic and deleterious for soil as change its physical and chemical properties. Many microorganisms were died due to the toxic nature of these dyes. Because of these toxic properties, it is necessary to treat the wastewater containing dyes for the surveillance of the environment [8].

Conventional treatment methods fail to treat completely wastewaters containing dyes. For this purpose, the world moves towards the advanced oxidation processes (AOP). It was a general observation that AOP is a reliable method for the removal of targeted components [9]. AOP, that is, ozonation alone is a strong oxidizing agent but in the presence of catalyst, it becomes more effective. For catalytic ozonation, different catalysts can be used to enhance the efficiency of the process [10]. Zeolites are used in various powdered forms or granular form as the catalyst. It is used as a catalyst as it eliminates the toxic and organic matters that are not easily biodegraded [11]. Nano carbons are used as a promising catalyst in the environmental field. The catalyst used in this research is reduced graphene oxide (RGO) which is a nanocarbon. They have the quality of activating ozone which is one of the fundamental elements of catalytic ozonation [12]. Graphene oxide has magnetic properties as an adsorbent. It is used in the treatment of wastewater due to this property for the removal of heavy metals and organics [13]. Manganese oxides are used as the catalyst as they are low in toxicity and catalyze peroxide to convert it into reactive oxygen species in AOP [14]. Previous research [15] reveals that RGO shows magnetic and paramagnetic behaviour at room temperature. RGO represents higher magnetism as compared to RO, due to density reduction [15]. This behaviour may help in the magnetic recovery of the catalyst.

Electroflocculation is used for the removal of organic pollutants from wastewater. Metal cations are formed when current passes through the anode to generate hydroxyl ions. These metallic hydroxides cause the pollutants to adsorb or precipitate [16]. In this study catalytic ozonation is utilized for the removal of RB5. All the above-mentioned catalyst was previously used individually for the treatment method but in this research zeolites coated with $CuMn_2O_4$/RGO were used for the first time.

Previous studies [17,18] have shown that zeolites are the highly effective catalysts in the presence of metal oxides when used in the catalytic ozonation process for dye degradation. Moreover, RGO supported $CuMn_2O_4$ acts as a modern catalyst that activates the ozonation process thereby promoting the generation of $OH^{\bullet}$ radicals in the solution for enhanced dye degradation rates as revealed by previous research works [12,19].

Since the real wastewater is a complex matrix containing multiple pollutants and radical scavengers thereby relying on a stand-alone treatment technology may not give effective treatment. Therefore, hybrid treatment technology such as catalytic ozonation in combination with electroflocculation in the presence of an advanced catalyst (zeolite modified with RGO supported $CuMn_2O_4$) may enhance the treatment efficiency. The present research is the first application of zeolite modified with RGO supported $CuMn_2O_4$ in catalytic ozonation – electrocoagulation hybrid treatment technology for the removal of RB5. Several experiments were performed for the optimization of ozone dose, voltage, pH, and time. For more understanding, different processes were compared in the research that includes electroflocculation, electroflocculation with catalyst, ozonation, catalytic ozonation, and ozonation in combination with electroflocculation

2. Materials

RB5 dye with molecular formula $C_{26}H_{21}N_5Na_4O_{19}S_6$, $CuMn_2O_4$/RGO catalyst, and zeolites were obtained from Sigma-Aldrich, UK. Aluminium electrodes, potassium oxide (KI) were obtained from Fisher Scientific, UK. Nitric acid, deionized water, hydrochloric acid (HCl), sodium hydroxide (NaOH) used were of analytical grade. Sodium bicarbonate ($NaHCO_3$) used for radical scavenger effect study was obtained from Fisher Scientific, UK.

2.1. Catalyst preparation

Catalyst preparation steps are shown in Fig. 1. $CuMn_2O_4$/RGO was prepared as per the standard method described elsewhere [20]. For the preparation of $CuMn_2O_4$/RGO-zeolite catalyst, the zeolites pellets (2 mm) were dipped in 0.1 M nitric acid solution for 1 d. Zeolites were then filtered and washed thoroughly with distilled water to obtain constant pH. Then it was placed in the oven for 24 h at 110°C. These zeolites were ready

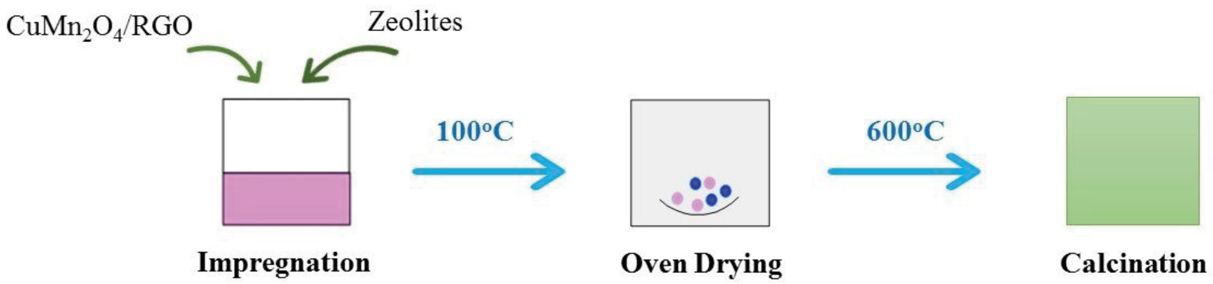

Fig. 1. Preparation of catalyst.

Table 1
Surface characteristics of catalyst

Material	Surface area	Pore size
Zeolites	91.4 m^2/g	4 Å
$CuMn_2O_4$/RGO coated zeolites	110.17 m^2/g	0.5183 Å

for the impregnation of $CuMn_2O_4$/RGO. After that 5 g of $CuMn_2O_4$/RGO was dissolved in 150 mL of deionized water. 50 g of zeolites were added to this solution. It was placed on a water bath at 100°C until the water evaporated. At last, the prepared catalyst was placed in the oven at 100°C for 24 h and for calcination it was heated for 6 h at 600°C [21].

2.2. Catalyst characterization

Catalyst characterization is important for determining the activity of the catalyst. The catalyst was characterized by analytical methods including scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and BET. The scanning electron microscope is a tool for the investigation of elements and their structure. Whereas EDS is the technique for analyzing the elements and chemical composition of any material [22].

2.3. Experimental setup

A batch reactor was used for experimentation. In this batch reactor, Al electrodes were placed to supply the current. Also, a bubbler was used for the introduction of ozone. Then ozone was generated by using ordinary grade air using an ozone generator. The catalyst was also placed in the reactor. The aqueous solution of RB5 was added to the reactor. For 30 min the current was provided to the electrodes. At the same time, ozone was also introduced in the reactor. The reactor was covered with the help of a lid and 2% KI solution was used as a trap for excess ozone (Fig. 2). After regular intervals of 5 min the samples were drawn and were analyzed by using UV-Vis spectrophotometry.

2.4. Experimental procedure

Solutions of different ppm were made to determine the calibration curve by analyzing it on UV-Vis spectrophotometer (PerkinElmer Lambda 35, Shimadzu Japan). The effect of different parameters was studied like ozone dose, catalyst dose, voltage, pH, and radical scavenger. The ozone was generated from the ozone reactor and introduced into the semi-batch reactor containing aqueous solution and catalyst, that is, $CuMn_2O_4$/RGO with the help of a bubbler. For electroflocculation, the Al electrodes were used, and continuous agitation was provided for better mixing.

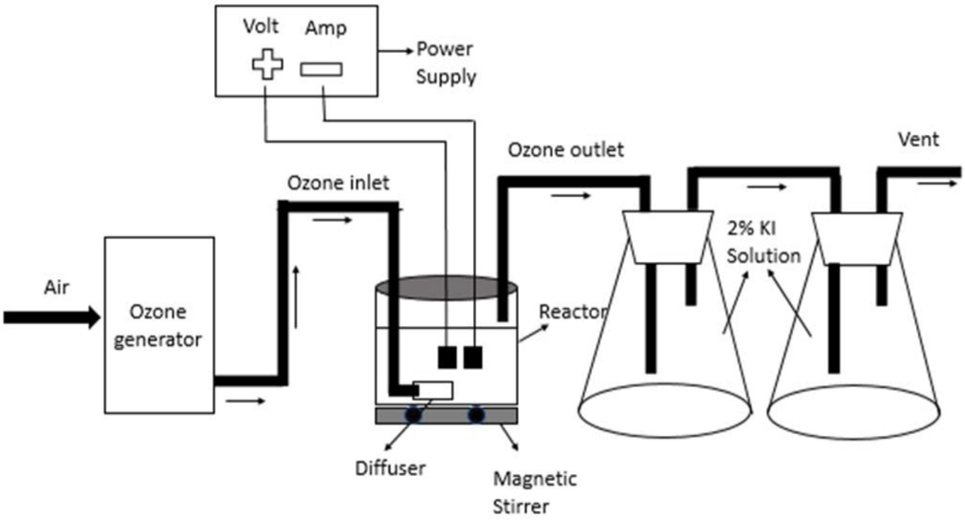

Fig. 2. Experimental set-up.

During the whole process, the reactor was covered with aluminium foil to prevent light penetration. Two traps of potassium iodide (KI) were attached to entrap the excess ozone leaving the reactor. The experimental setup is illustrated in Fig. 2. The samples were drawn at regular intervals of 5 min and 1N sodium carbonate (Na_2CO_3) was added into the samples to remove un-reacted ozone. These samples were then analyzed on the UV-Vis spectrophotometer [23]. It was done by comparing the absorbance of the standard solution at zero time and during treatment after different intervals of time.

3. Results and discussion

3.1. Characterization of catalyst

Fig. 3 shows the results of SEM of the catalyst used, that is, $CuMn_2O_4$/RGO and $CuMn_2O_4$/RGO coated on zeolites. Fig. 3a shows the results of SEM for $CuMn_2O_4$/RGO only whereas Fig. 3b illustrates the results of SEM of $CuMn_2O_4$/RGO coated on zeolites. There is a clear difference between the two images. Fig. 3a represents the crevice type surface morphology of $CuMn_2O_4$/RGO which enhances the available surfaces when coated on zeolite granules as revealed by Fig. 3b. The results are supported by EDS Fig. 4, the change in the composition may lead to providing an enhanced platform for the ozone catalytic activity. The pore size indicates the microporous nature of the material (Table 1).

3.2. Effect of pH

pH is the dominant parameter that not only controls the surface charges of the catalyst but also the mechanism of radical generation in the ozonation process. Moreover, in the electroflocculation process, the floc formation and floc charges are driven by the prevailing pH. Decolorization efficiency of RB5 was studied by using zeolites coated with $CuMn_2O_4$/RGO as a catalyst in electroflocculation, ozonation, adsorption, electroflocculation with adsorption, catalytic ozonation, electroflocculation with ozonation, and catalytic ozonation along with electroflocculation at different pH values from 3 to 10. This range of pH was selected by considering the pH of textile wastewater. Fig. 5a–c reveal the removal efficiencies of RB5 due to different processes.

Electroflocculation shows decolorization of RB5 at pH 3 is about 49% and about 47% and 48% at pH 7.5 and pH 10 respectively. This shows that electroflocculation has no effect of pH on it. In the case of electroflocculation, the efficiency is slightly low at neutral pH whereas it is comparatively higher for acidic and basic pH. At low pH, there are no flocs of aluminium hydroxide. Whereas as the pH increases from neutral to basic the number of monomeric and polymeric aluminium hydroxide flocs form which then decreases as the pH increases from 8. Due to this floc formation the removal efficiency decreases [24].

Decolorization efficiency of RB5 due to ozonation at pH 3 is about 69% and about 77% and 84% at pH 7.5 and pH 10 respectively. Results indicate that with increasing pH decolorization efficiency also increases in the case of ozonation.

Fig. 5a–c show that the removal efficiency of RB5 due to electroflocculation with adsorption increases with the increase in pH. It indicates that at pH 3, 7.5, and 10 the decolorization efficiency is 52%, 59%, and 70% respectively. In the case of catalytic ozonation, the removal efficiency at pH 3 is about 80% and at pH 7.5 and 10 it is about 86% and 87%, respectively. Electroflocculation combination with ozonation shows that the decolorization efficiency is about 75% at pH 3, at pH 7.5 it is about 84% whereas removal efficiency is 86% at pH 4.

The overall combined process which includes catalytic ozonation and electroflocculation shows that the removal efficiency of RB5 at pH 3, 7.5, and 10 is about 78%, 86%, and 91%, respectively.

The pH used for further experimentation is 7.5 and 10. It was found that at pH 7.5 and 10 combined process shows better efficiency. Also, the pH is chosen on the basis that textile wastewater has a pH range between neutral to basic wastewater has a pH range from 7 to 9 [25].

Hossain et al. [26] studied the application of advanced GO/AFS composite for the treatment of dyes BB7 and AB 210 in tannery wastewater. Research showed high effectiveness of composite and 100% dye removal was achieved

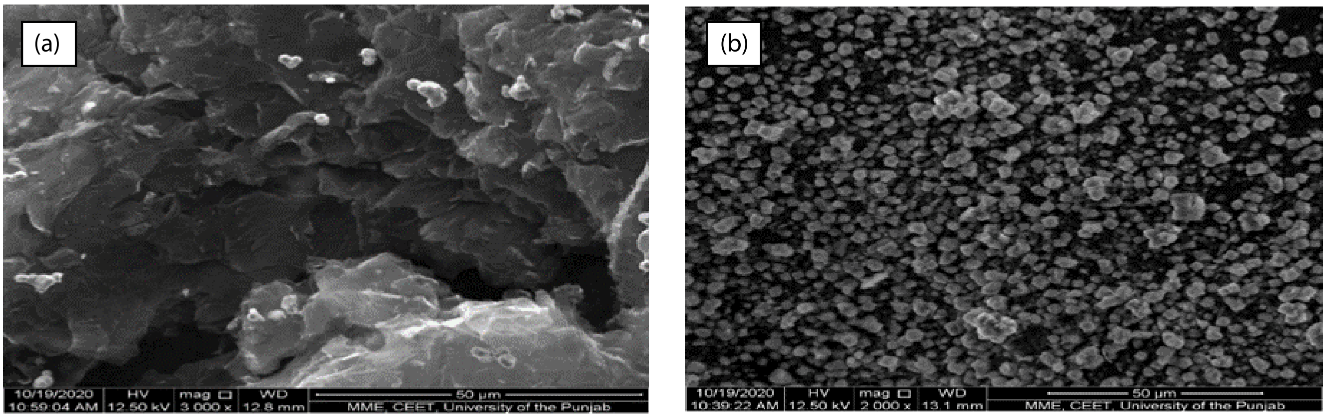

Fig. 3. SEM of (a) $CuMn_2O_4$/RGO and (b) $CuMn_2O_4$/RGO coated zeolites.

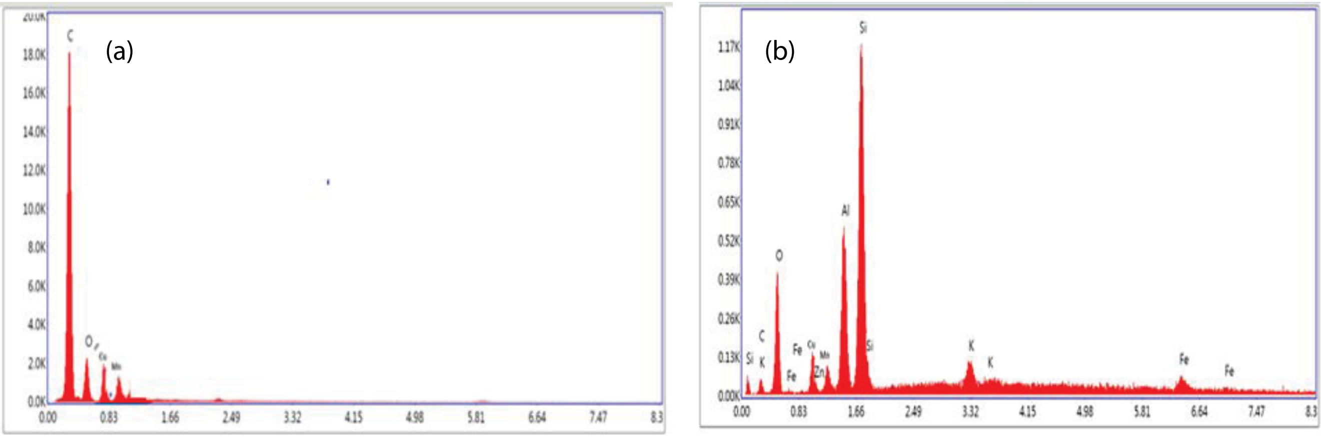

Fig. 4. EDS results for (a) $CuMn_2O_4$/RGO and (b) $CuMn_2O_4$/RGO coated on zeolites.

within 2 min at pH 7 which is comparable to RGO performance in present work achieved at pH 7.5. Liu et al. [27] studied the removal of Rhodamine B dye by GO/4A composite. A high adsorption capacity of GO composite was achieved. The highest removal of dye was reported at pH 2, which may be due to the cationic dye nature. The results are comparable to present work with RB5 removal at pH 7.5 due to the anionic nature of the dye.

3.3. ozonation effect

The speed of the dye degradation depends on the availability of ozone in the aqueous solution. Furthermore, the catalyst enhances the radical generation which leads to rapid dye degradation. The ozone dose effect was studied to determine the optimum dose. The efficiency of ozonation basically depends on the hydroxyl radicals. At pH 3 most of the ozone coming from the ozone generator is the form of O_2. O_2 has an oxidation potential of 2.07 eV. At pH 7.5 the O_3 existed both in the form of O_2 and O_3. This O_3 have the oxidation potential of 2.8 eV and it also reacts with water to form hydroxyl radicals. These hydroxyl radicals react to destroy the pollutant in the water. Similarly, at pH 10, there will be more hydroxyl radicals present so there will be even more removal efficiency [28].

Fig. 6a and b show the effect of ozone dose on decolorization percentage at pH 7.5 and 10. Fig. 6 reveals that at pH 7.5 the removal efficiency is 73%, 87% and 81% at ozone flowrate of 0.6, 0.9 and 1.4 mg/min respectively.

Whereas Fig. 6b shows that at pH 10 the decolorization efficiency at 0.6 mg/min is 78% and efficiency is 86% and 87% for 0.9 and 1.4 mg/min respectively. It shows that with increasing ozone dose the removal efficiency also increases, but there is a negligible increase in the efficiency from 0.6 to 1.4 mg/min.

3.4. Voltage effect

The voltage is the key parameter that influences the rate of electrochemical reactions in the electroflocculation process. The voltage effect was studied at pH 7.5 and 10 for the decolorization of RB5. Fig. 7a and b show the results of decolorization efficiency at pH 7.5 and 10 at different voltages of 5, 10, and 15 V. Fig. 7 reveals that with the increase in volts the removal efficiency also increases. As for 5 V, the decolorization efficiency is 43% and that is 47% and 49% for 10 and 15 V, respectively.

The effect of different voltages of 5, 10, and 15 V at pH 10 is shown in Fig. 7b. It shows that at pH 10 the removal efficiency is maximum at 10 V which is 70%. Whereas the decolorization efficiency for 5 and 15 V is 43% and 50% respectively.

At high pH, the decolorization efficiency decreases. This is because at high pH when the voltage is more the flocs of aluminium hydroxide produced are negatively charged. The dye used in this research is also negatively charged. Because of the same charges, there was repulsion between the dye and flocs of aluminium hydroxide. That's why the decolorization efficiency decreases at high volts as at high volts more flocs are produced and there will be more repulsion [29]. So, the voltage used in the experimentation was 10 V rather than 15 V.

3.5. Effect of high concentration of dye

The bar graph shows the effect of high concentration on the removal efficiency at different processes including ozonation, catalytic ozonation, electroflocculation with ozonation, and the combined process of catalytic ozonation with electroflocculation. Fig. 8 shows that with the increase in the concentration of pollutants the removal efficiency also increases at the same dose of catalyst. The process which shows the actual increase in the decolorization percentage is catalytic ozonation.

The removal efficiency at 30, 60 and 90 ppm dye concentration in ozonation was 84%, 77% and 83% respectively. In the catalytic ozonation process, the removal efficiency was 87%, 91%, and 94% at pollutant concentrations of 30, 60, and 90 ppm respectively.

Bar graph of electroflocculation with ozonation shows that at RB5 concentration 30, 60 and 90 ppm shows the decolorization efficiency of 86%, 90%, and 91%, respectively. The decolorization efficiency in the combined process of catalytic ozonation and electroflocculation was 92%, 93%, and 96% at RB5 concentration 30, 60, and 90 ppm respectively.

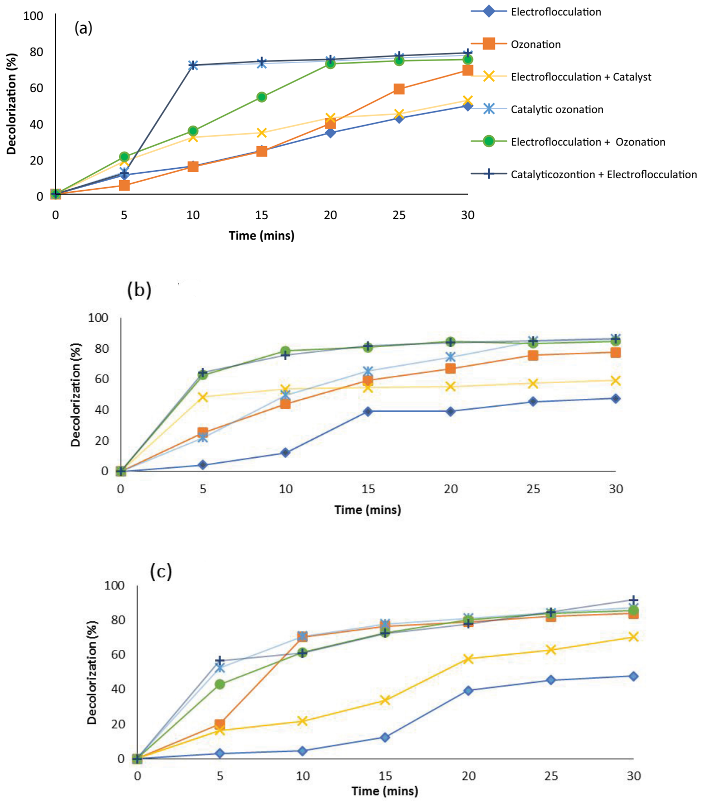

Fig. 5. Effect of pH on percentage removal of RB5 during the adsorption, electroflocculation, ozonation, catalytic ozonation, electroflocculation with adsorption, electroflocculation with ozonation and catalytic ozonation with electroflocculation (Amount of catalyst = 5 mg/L; O_3 = 0.98 mg/min; Time = 30 min; Temp. = 25°C; *V* = 10 V) (a) pH 3, (b) pH 7.5, and (c) pH 10.

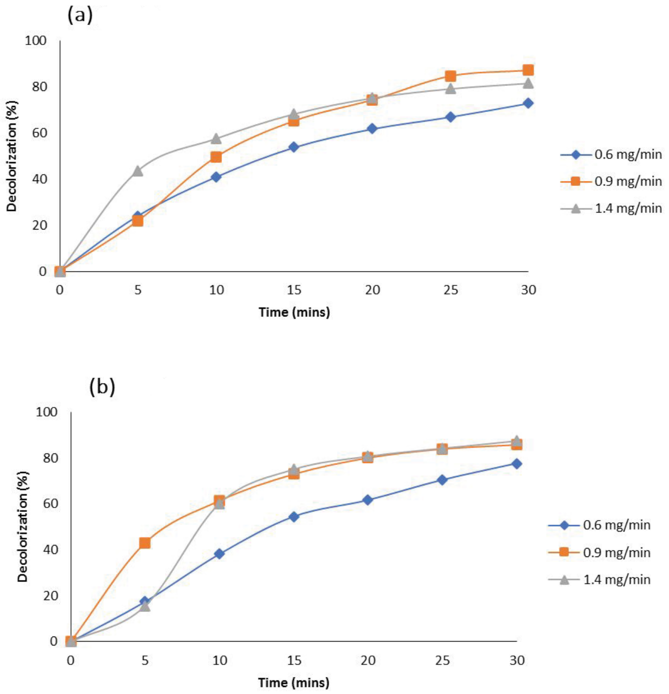

Fig. 6. Effect of ozonation on percentage removal of RB5 during the single ozonation (Time = 30 min; pH = 10; Temp. = 25°C) (a) pH 7.5 and (b) pH 10.

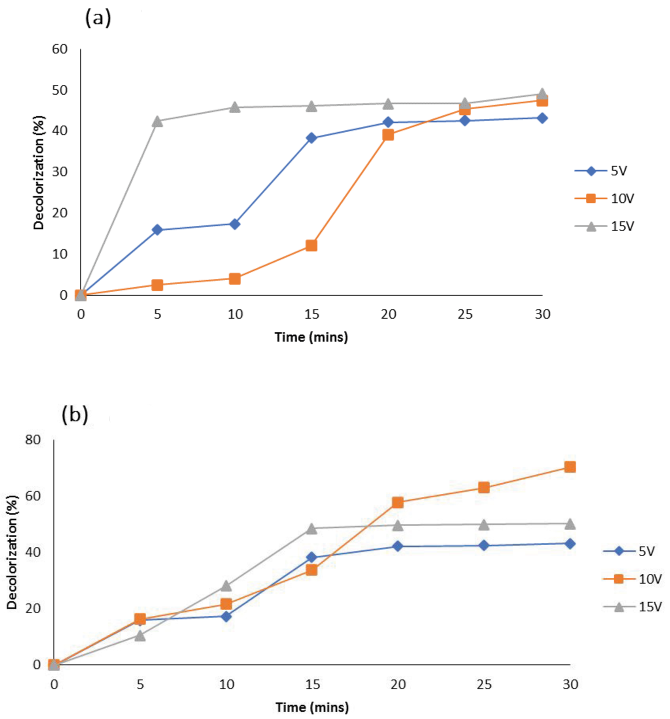

Fig. 7. Effect of voltage on percentage removal of RB5 during the single electroflocculation (Time = 30 min; pH = 10; Temp. = 25°C) (a) pH 7.5 and (b) pH 10.

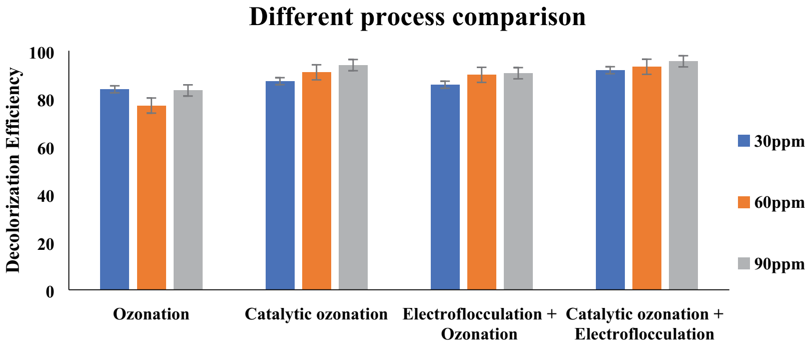

Fig. 8. Effect of high concentration of pollutant on percentage removal of RB5 during the ozonation, catalytic ozonation, electroflocculation with ozonation and catalytic ozonation with electroflocculation (O_3 = 9.8 mg, Catalyst dose = 5 mg; V = 10 V; Time = 30 min; pH = 10; Temp. = 25°C).

The whole result indicates that there are still active sites present on the catalyst that can be utilized for decolorization even at higher concentrations.

3.6. Proposed mechanism

The mechanisms involved in the experimentation are direct mechanism, radical based mechanism, sweep flocculation, and catalytic decomposition of H_2O_2 as shown in Fig. 9. All the mechanisms are discussed in detail below.

3.6.1. Direct mechanism

It is one in which molecules of O_3 directly react with the pollutant. The ozone molecules by directly reacting with pollutants convert them into the less toxic compounds. These fewer toxic compounds may include water and CO_2. This direct mechanism of converting pollutants into less toxic compounds is effective at the acidic pH range. This is the reason that the efficiency of ozonation is less at low pH.

3.6.2. Radical-based mechanism

In the process of ozonation when the pH of the solution is basic then most of the ozone in the reactor exists in the form of hydroxyl radical. $^{\bullet}$OH is the strong oxidant having more electron affinity. When the electron affinity is more it will react more with the pollutants by converting them into less toxic compounds. In this way, it also increases the

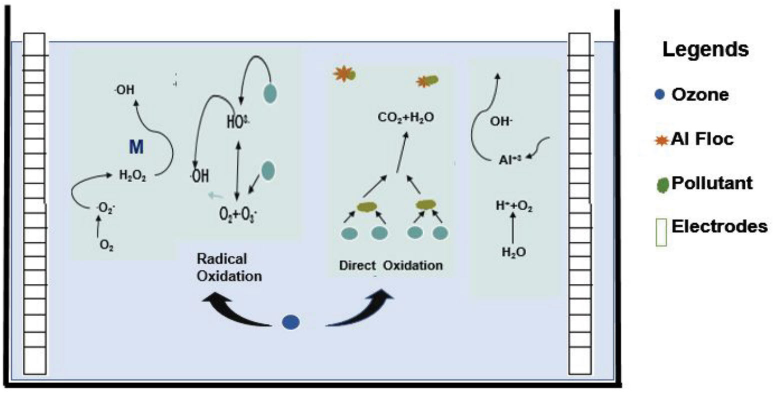

Fig. 9. Proposed mechanism.

decolorization efficiency by reacting with more pollutants and by converting them.

3.6.3. Sweep flocculation

Electrodes are involved in the sweep flocculation mechanism. Also, these electrodes are the major component of electroflocculation. In this study, the electrodes used are of aluminium. Aluminium metal can form monomeric and multimeric flocculated species. These monomeric and multimeric species are of aluminium hydroxide. The flocculated species formed then acted as adsorbents and with the help of these adsorbents the removal of RB5 takes place.

3.6.4. Catalytic decomposition of H_2O_2

During the process of ozonation, hydroxyl radicals are generated. These hydroxyl radicals are very reactive, and these result in the formation of hydrogen peroxide when they react with each other. Oxidation potential of hydrogen peroxide is 1.7 eV [30]. Oxidation potential of hydroxyl radical is 2.8 eV [31]. It indicates that H_2O_2 is also an oxidant, but it is not strong whereas hydrogen peroxide is a strong oxidant. The production of hydrogen peroxide results in the decrease in decolorization efficiency. In the catalyst metals like Cu and Mn are present. These metals then react with the hydrogen peroxide to again form the hydroxyl radicals [32].

4. Conclusions

The overall research shows that removal of RB5 by modified catalyst, that is, $CuMn_2O_4$/RGO is very effective within the pH range of real textile water. This pH range lies between 7.5 to 10 pH. The use of different catalyst combinations enhances the effect by supporting each other. From all the processes combined process, that is, catalytic ozonation with. electroflocculation works best as its efficiency is above 90%. This efficiency is achieved at 10 V, 30 min, and 1 mg/min dose of ozone. The efficiency of ozonation and catalytic ozonation also increases as pH increases. Also, when the same amount of catalyst is used for the removal of pollutants at high concentration it is even more effective than the pollutants at low concentration.

The removal process is carried out by active sites present on RGO as these active sites played an important role in the removal of dye high concentration. This process will take less time for decolorization as compared to other conventional treatment methods.

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