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RESEARCH PAPER

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The Using of Plain PAC and PAC Impregnated with MgO and Fe_2O_3 as Catalysts for the Degradation of Cationic Dyes: Homogenous and Heterogeneous Ozonation

Ali Akbar Mohammadi[1], Bahram Kamarehie[2], Ali Jafari[3], Nasrin Hosseingholizade[4], Mansour Ghaderpoori[2,*], Navid Alinejad[5], Muhammad Yousuf Jat Baloch[6], Mohammad Ahmadpour[7]

[1]Department of Environmental Health Engineering, Neyshabur University of Medical Sciences, Neyshabur, Iran
[2]Environmental Health Research Center, Lorestan University of Medical Sciences, Khorramabad, Iran
[3]School of Health, Kermanshah University of Medical Sciences, Kermanshah, Iran
[4]Public Health Promotion Association, Urmia University of Medical Sciences, Urmia, Iran
[5]Department of Public Health, School of Health, Fasa University of Medical Sciences, Fasa, Iran
[6]College of New Energy and Environment, Jilin University, Changchun, 130012, P.R. China
[7]Department of Public Health, Maragheh University of Medical Science, Maragheh, Iran

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Corresponding Author
E-mail: mghaderpoori@gmail.com

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Abstract

This study presented the removal of methylene blue in the batch system based on catalytic ozonation (heterogeneous and homogenous). The effect of variables such as initial MB (methylene blue)concentration, initial pH of solution (3-11), contact time (5-40 min), and catalyst dosage on homogeneous and heterogeneous ozonation systems was examined. The findings of the research showed that dye removal was better in alkaline conditions. The amount of dye removed in acidic conditions was slightly better than in neutral conditions (approximately 10% to 15%). In addition, the removal efficiency of dye was decreased by increasing of concentration. Besides, as the amount of catalyst (dosage) increased, the removal efficiency of MB had been increased by 40%. Due to the use of catalyst, the significant difference was between the use of two processes of single ozonation processes (SOP) and catalytic ozonation processes (COP_s). The results indicated thatMB degradation in COPs was several times faster (approximately 4.7 times). It was due to the numerous advantages of these processes in the removal of environmental pollutants, they can be widely used in the removal of various pollutants if their cost can be reduced.

Introduction

Water safety, as an important issue, can affect health and life quality (Iqbal et al., 2021). Advanced oxidation process (AOP) is one of the common methods applied to remove/degrade pollutants from different environments. Based on literatures, there are many different types of oxidation processes. AOP_s have various advantages and disadvantages that should be considered for final process selection. Single Ozonation Processes (SOP_s) is one of these processes that has been studied in some works (Schumacher et al., 2011; Kamarehie et al., 2018a; Kamarehie et al., 2018b). SOP_s have relatively low efficiencies in contaminants degradation and do not completely oxidize the contaminants (Asgari et al., 2015; Kamarehie et al., 2018a). There is another category of AOP_s called catalytic ozonation processes (COP_s). COP_s can considerably increase SOP_s efficiency (Asgari et al., 2015; Zhang et al., 2019). In COP_s a solid substance is added as a catalyst, which helps O_3 decomposition and creates active °OH radicals, finally increases the oxidation rate and further destruction of target pollutants. Based on the type of applied catalysts, two types of processes namely heterogeneous and homogenous has been defined (Abou-Gamra, 2013). Some of the advantages of heterogeneous catalyst over homogenous are lower cost, easy use, and resistance to interfering compounds (Moussavi et al., 2014). Various studies showed that some heavy metal oxides can enhance the performance. For this, various metals have been used as catalyst, such as Aluminum (Al), Iron (Fe), Chromium (Cr), Zinc (Zn), and Copper (Co) (Lai et al., 2013; Leili et al., 2013; Tiwari et al., 2015). Findings from other studies showed that catalyst type was a key factor in success in COP_s efficiency and performance (Yazdanbakhsh et al., 2018; Azarpira et al., 2019). Metal oxides as a catalyst have a high potential to remove/degrade pollutants from the environment due to low cost of production, high surface area and recovery. (Haldorai and Shim, 2014; Mohsenibandpei et al., 2016; Zhang et al., 2019).

Some benefits such as high catalytic potential, high reaction, and high surface area have been reported through using Fe as a catalyst, (An et al., 2005; Kamarehie et al., 2018a). Furthermore, in this process the used Fe can be easily separated from the solution using a magnet (Kakavandi et al., 2013; Fayazi et al., 2015). Some works showed that magnesium oxide (MgO), is support ozonation process. (Moussavi et al., 2013b; Moussavi et al., 2014; Moussavi et al., 2017). The main characteristic of MgO as a catalyst is the presence of active bases at the surface, which increases the efficiency of the process. In addition, MgO has destructive and adsorption properties, high surface reactivity, and high specific surface area (Moussavi et al., 2013b). Moussavi et al. and Nawrocki et al. reported significant effect of MgO as a heterogeneous catalyst on the removal of target pollutants from the environment (Nawrocki and Kasprzyk-Hordern, 2010; Moussavi et al., 2014). MgO is one of the main materials can be fixed on other media increases the thermal stability and chemical proprieties (Moussavi et al., 2010; Liu et al., 2013). When a catalyst is fixed on a base material, proper conditions are provided for mass and heat transfer, which affects the removal/degradation of contaminants. (Ma and gang Zhang, 2016). One of the most common materials used as base media is granular activated carbon (GAC) and powdered activated carbon (PAC). Furthermore MgO-PAC and PAC/γ-Fe_2O_3 nanocomposite have shown high destructive adsorption and high catalytic potential in degradation of different pollutants including bisphenol A (BPA) and Alizarene Red S (ARS) (Desalination-phenol; Kamarehie et al., 2018a; Kamarehie et al., 2018b; Kamarehie et al., 2018c). Our environment is exposing to various pollutants, and the amount of pollution is increasing, continuously. One of the common group of pollutants is organic dyes. Organic dyes are a large group of dyes that widely used in various industries (Santhi et al., 2016). Methylene blue (MB) as an organic dye may have various adverse effects on human health, animals and plants (Alinejad et al., 2019b). MB exposure can cause profuse sweating, nausea, mental confusion, vomiting, and methemoglobinemia (MetHb) in human (Rafatullah et al., 2010). Since MB is a polycyclic aromatic compound, its degradation in the environment is of concern.

Accordingly, this work investigated the viability of PAC and PAC impregnated with MgO and Fe_2O_3 as catalysts for degradation of MB. Nonetheless, to our knowledge, no report was found on the application of MgO and Fe_2O_3 for MB degradation from aqueous solutions. The aim of this study was to investigate MB degradation using PAC and PAC impregnated with MgO and Fe_2O_3 as catalysts.

Materials and Methods

Prepared Materials

All used materials were of high analytical grade, supplied by Merk and Sigma-Aldrich Chemicals Company. The used materials in this work were magnesium nitrate ($Mg(NO_3)_2$), sodium hydroxide (NaOH), Hydrochloric (HCl), sulfuric acid (H_2SO_4), powder activated carbon (PAC), Iron (II) sulfate ($FeSO_4.7H_2O$), Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), and tert-butanol alcohol ($C_4H_{10}O$).

Preparation of Activated Carbon Coating with Magnesium Oxide (PAC-MgO)

In our earlier study, the manganese oxide (MgO) was applied to enhance the capacities of activated carbon (Kamarehie et al., 2018c). Therefore, a 6.8%wt of MgO was used because of better MgO stabilization status on PAC. The method of preparation was as follow: Magnesium nitrate hexahydrate (52.5 g, purity≥99%) was dissolved in 1L distilled water. Next, under constant stirring, sodium hydroxide solution (30 mL, 1N) was added. Then, PAC (50 g) was mixed and stirred for three hours. The prepared suspension was then placed in a container for 1 h to settle and separate the suspension. After the settling the suspension, the remaining sediment (activated carbon coated with magnesium hydroxide) was dried in the oven (3 h at 100 ºC). After that, the calcination step was conducted using heating to high temperatures(2 h at 500 ºC), to convert magnesium hydroxide ($Mg(OH)_2$ to MgO (Moussavi et al., 2013b; Moussavi et al., 2014; Haidari et al., 2016). Finally, the prepared PAC-MgO was kept in a polyethylene container for further use.

Preparation of Activated Carbon Coating with Iron (III) Oxide (PAC-Fe2O3)

To prepare activated carbon coated iron oxide (III), ferric oxide was modified as in earlier studies (Kamarehie et al., 2018a; Kamarehie et al., 2018b). The steps were briefly as follows: 1) at first, PAC (20 g) was added to HNO_3 solution (150 mL, 5 M) and refluxed at 70°C for 1 h to achieve treated PAC. 2) Treated PAC (4.2 g), $FeCl_3$. $6H_2O$ (21.6 g) and 8 g of $FeCl_2$. $4H_2O$ (8 g) with more than 98 % purity was dissolved in 100 mL HCl solution (37%, 2 M). 3) 300 mL NH_4OH solution (30%, 2 M) was added to the solution followed by stirring for 2 h at 20°C. 4) The obtained dark brown precipitate was gathered by a magnet bar. 5) The final product was dried at 70°C for 24 h and washed several times with distilled water and ethanol. 6) Finally, the product (PAC-Fe_2O_3) was placed in a Polyethylene container for further use. (Darezereshki et al., 2013; Fayazi et al., 2015).

Characterization

The structure of the prepared PAC-MgO and PAC-Fe_2O_3 was verified by X-ray diffraction (Panalytical Company, X' Pert Pro model). The morphologic properties of the PAC and the prepared nanocomposites were examined by scanning electron microscope (SEM) (ZEISS Company, SIGMA VP500 model). Further characteristics of the final product, including Energy Dispersive X-Ray Spectroscopy (EDX), Brunauer-Emmett-Teller (BET, BElSORP Mini model, Microtrac Bel Corp), surface area (SA) and total pore volumes of the PAC-MgO and PAC-Fe_2O_3 were conducted.

Analytical Methods

The applied set up for catalytic removal of MB dye in this work was similar to that of previous studies (Moussavi et al., 2014; Kamarehie et al., 2018c). The components of the set up included 1) air pump, 2) a flow controller, 3) an O_3 generator and supply system, 4) an ozonation reactor, 5) an O_3 bubble, 6) a demolition system of off-gas ozone, 7) glass reactor, 8) diffuser, 9) catalyst particle, 10) magnetic stirrer, 11) magnet, and 12) flask of Potassium iodide (KI). Ozone (O_3) is organized by an Ozone generator. It can be fed through the glass diffuser to the basic reactor. The ozonation reaction was performed in a Pyrex glass reactor (1L). To create tiny bubbles during the experiments, a magnetic stirrer was used. To study the effect of variables on MB removal, following variables were examined: initial MB concentration (50-250 mg L^{-1}), solution pH (3-11), contact time, catalyst dosage (PAC, PAC-MgO, and PAC-Fe_2O_3). In this study, a dosing rate of O_3 was constant was kept (ARDA, AEGCOG-5S) as 5 g h^{-1}. The mineralization of MB dye, was studied using total organic carbon (TOC) (Eaton et al., 2012; Kamarehie et al., 2018a). The residual MB was determined by ultraviolet-visible spectroscopy at wavelength (λ) of 624 nm (R^2=0.9998) (Mohammadi et al., 2017). The structural formula of MB is shown in Figure 1. To assess the basic mechanism, which dominating the interplay of the COP$_s$, the tert-butanol procedure, as a radical scavenger, was used (Moussavi et al., 2014; Haidari et al., 2016). A radical scavenger, like tert-butanol, was also used to explore the impact of interceptive parameters in the generation of °OH radical in catalytic process (Asgari et al., 2015). At the end, the degradation yield/rate of MB dye and mineralization were calculated by Eq. 1 and Eq. 2, respectively (Moussavi et al., 2014):

$$\text{MB removal}, \% = \frac{(C_o - C_t)}{C_o} * 100 \tag{1}$$

$$\text{Mineralization}, \% = \frac{(TOC_o - TOC_t)}{TOC_o} * 100 \tag{2}$$

Where, C_o and C_t are the initial and final MB concentrations in dye solution (mg L^{-1}), respectively. TOC_o and TOC_t are the initial and final concentrations (mg L^{-1}), respectively. In terms of statistical validity, each test was repeated three times.

Figure 1. Methylene blue (MB) dye and its structural formula**.**

Results and Discussion

Characterization of PAC, PAC-Fe2O3, and PAC-MgO

Figure 2 showed the SEM image of PAC (a), PAC-Fe_2O_3 nanocomposite (b), and PAC-MgO nanocomposite (C). Based on Figure 2(b), it can be seen that iron oxide particles, e.g. Fe_2O_3, were well stabilized on PAC. The results show that the distribution of Fe_2O_3 was uniform. Also, based on the findings, the structure was spherical. The stabilization process of Fe_2O_3 particles on PAC was because of the chemical reaction (Kamarehie et al., 2018a; Kamarehie et al., 2018b). If Figure 2(a) and Fig 2(b) are compared to each other, it can be seen that the SA of PAC particles is much smoother and more uniform than that of PAC-Fe_2O_3. Therefore, it can be concluded that Fe_2O_3 particles are well stabilized on PAC. The result of Fayazi and Darezereshki et al. studies have almost shown the same (Darezereshki et al., 2013; Fayazi et al., 2015). The findings reported in Figure 2(c) show that MgO particlesa are well stabilized on the surface of PAC. According to Figure 2(a) and Fig 2(c), it can be seen that the surface of PAC is heterogeneous and it has a regular and granular structure, but in magnesium oxide fixed on carbon, the surface is more irregular. (Mohandes et al., 2010; Moussavi et al., 2013a; Moussavi et al., 2013b; Moussavi et al., 2014). So, the MgO nanocomposite has been uniformly fixed on the surface of carbon, and the surface morphology of carbon has been considerably impregnated by application of MgO nanocomposite (PAC-MgO) (Moussavi and Mahmoudi, 2009; Kamarehie et al., 2018c). EDX authenticated the stabilization of iron and magnesium on the PAC. Elements such as iron, carbon, and oxygen were found in the EDX for PAC-Fe_2O_3, which confirms the stabilization of iron on the PAC. Fayazi et al. 2015 reported that the percentage of iron oxide stabilizied on carbon was 51.3% (Fayazi et al., 2015). Kamerehie et al. 2019 reported that iron oxide stabilized on PAC was 48.7% (Kamarehie et al., 2018a). In the present study, the amount of iron oxide stabilized on activated carbon was 50.1%, which is an acceptable amount. The finding of this study also confirmed that the amount of magnesium oxide coated on PAC was 12%, which is an acceptable amount. Kamerehie et al. 2019 reported that magnesium oxide coating on PAC was 12.6% (Kamarehie et al., 2018c). In general, the results of XRD confirmed the stabilization of iron oxide and magnesium oxide on the PAC. Figure 3 presents XRD patterns of PAC (A), PAC-Fe_2O_3 (b), and PAC-MgO (C) respectively. The peak observed in the raw and

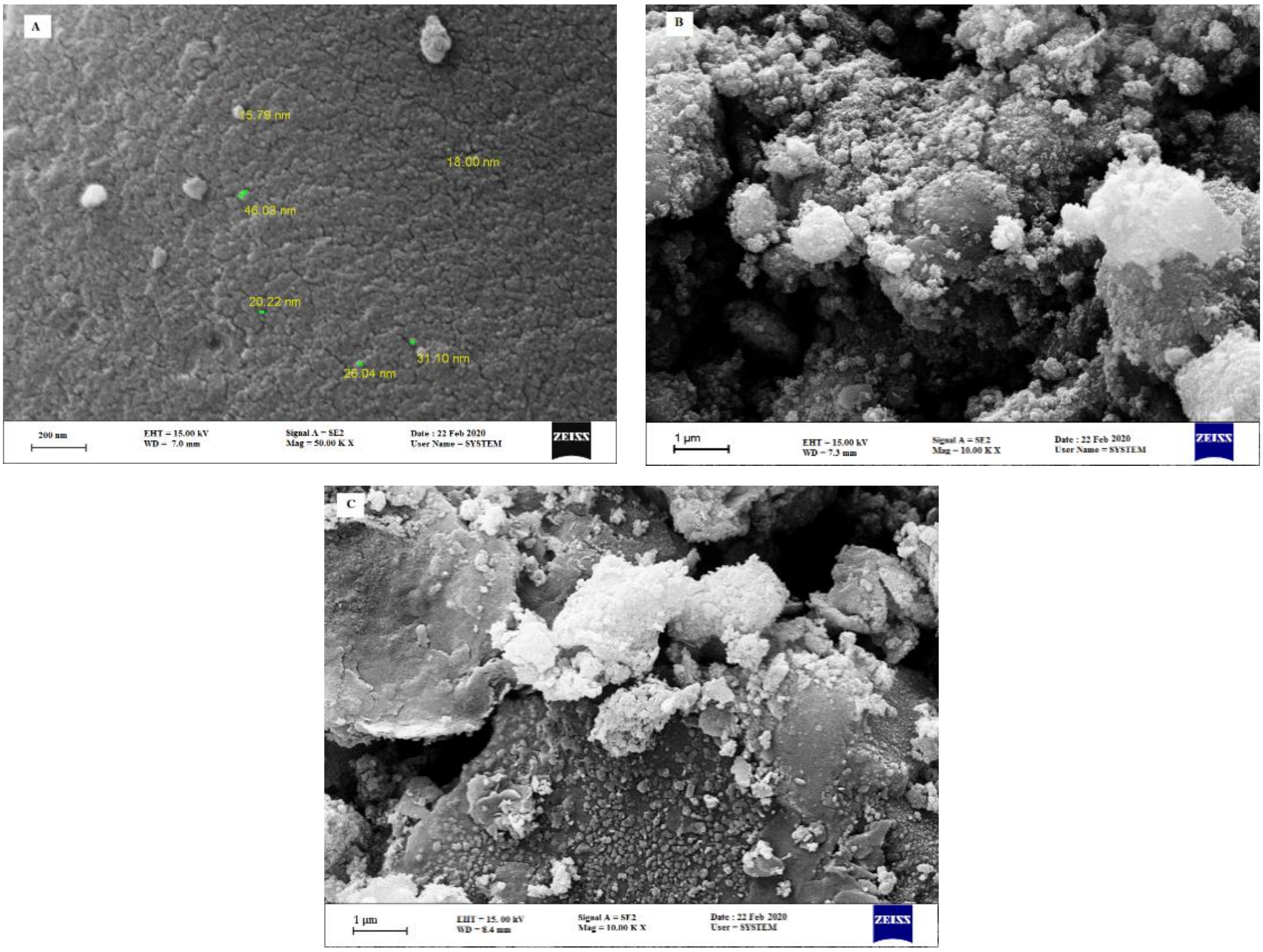

Figure 2. The SEM image of PAC (A), PAC-Fe_2O_3 nanocomposite (b), and PAC-MgO nanocomposite (C).

improved catalyst, are very similar to previous published studies (Derakhshan et al., 2013; Fayazi et al., 2015; Kamarehie et al., 2018a; Kamarehie et al., 2018c). BET of the catalysts was performed to show the SA and pore volume. The results showed that the SA of PAC, PAC-Fe_2O_3, and PAC-MgO were 750 m^{2}g^{-1}, 480 m^2 g^{-1}, and 550 m^2 g^{-1}, respectively. The pore volume of PAC, PAC-Fe_2O_3, and PAC-MgO were 0.54 cm^3 g^{-1} and 0.45 cm^3 g^{-1}, and 0.45 cm^3 g^{-1}, respectively. As can be seen, the SA and pore volume in the catalyst modified with Fe_2O_3 and MgO decreased, compared to the plain type, which also confirms the successful coating. Depci et al. 2012 reported that decrease in SA and pore volume during the modification is related to the formation of iron oxide and magnesium oxide within the base material (Depci, 2012). Darezereshki et al. reported that characteristics of pore volume and SA, after the modification, had decreased in the modified adsorbent (maghemite/activated carbon) (Darezereshki et al., 2013). The SA and pore volume in maghemite/activated carbon were 356 m^{2}g^{-1} and 361 m^3 g^{-1}, while in the initial type it was 597 m^2 g^{-1} and 0.46 m^3 g^{-1}, respectively. The decrease in characteristics of total-pore volume, specific SA, and average-pore diameter in a catalyst or absorbent can be related to the dispersion of composites, i.e. PAC-Fe_2O_3, and PAC-MgO, into the pores on the base material, i.e. PAC, and blocking the pores (Moussavi et al., 2014).

Effect of Different Operation Parameters on Process Efficiency in Methylene Blue Removal (pH, Initial MB Concentration, and Catalyst Dosage)

According to the previous studies, one of the most influential variables on the efficiency of processes such as advanced oxidation processes, adsorption, and etc. is the changes of solution pH. Changing of pH can affect the degradation of oxidizing agents (like O_3), surface catalyst properties, the degree of ionization of the target pollutants, and, finally, the rate of degradation materials (Kamarehie et al., 2018a; Alinejad et al., 2019a; Kamarehie et al., 2020). The pH of the solution is the most important factor studied in the degradation process due to its effect on the structure of the degradable substance and the applied catalyst. This study was performed to determine the best effect of pH (3 to 11) on MB removal using SOP_s and COP_s. (Figure 4). The first step was to determine pH_{ZPC}. The pH of zero point of charge (pH_{ZPC}) is the point of pH in which electrical charges of the positive and negative on the catalyst surface are balanced (Kamarehie et al., 2018a). The pH_{ZPC} is a key factor to determine the mechanism of contaminants removal via COP_s (Lan et al., 2013). The interpretation of the pH_{ZPC} can vary depending on its value. If pH_{ZPC} is more than, less than and equal to pH, the electric charge of the catalyst surface will be positive, negative and neutral, respectively. (Lan et al., 2013; Kamarehie et al., 2018a). According to Figure 4, with increasing pH from acidic to alkaline conditions, from 3 to 11, the removal or degradation of the dye was significantly reduced. In pH of 3 and 11, the removal MB efficiency was 40% and 90%, respectively. As can be seen from Fig 4, the MB concentration has decreased significantly at the pH 11, while there was no significant decrease in other investigated pH. The proper efficiency of the catalytic ozonation system in alkaline conditions can have various reasons. One of the leading reasons for increasing the degradation of the MB removal process is to increase O_3 transfer from the gas phase to liquid phase and the reduction ozone reactions (Akbari et al., 2017). According to Akbari et al, the degradation potential of MB is transferred to negative values with increasing pH, because the increase in solution pH causes to increase in O_3 reduction from oxidation pathways of direct and indirect reactions (Akbari et al., 2017). In acidic conditions, the charge on the MB is positive, while due to the production of H^+ protons and its binding (induction) to the surface of the catalyst, the catalyst also acquires a positive charge. The repulsive force created between the positive charge of the catalyst and the positive charge of the MB will cause electrostatic repulsion and subsequently reduce the removal efficiency. In alkaline conditions, the production of hydroxyl ions (OH^-) will significantly increase (Kamarehie et al., 2018a; Alinejad et al., 2019b). The contact and collision of hydroxyl ion with a catalyst surface causes the production of hydroxyl radicals, °OH, which will increase the MB degradation ability. Therefore, the findings of this research showed that pH=11 was the best pH for degradation of MB. In

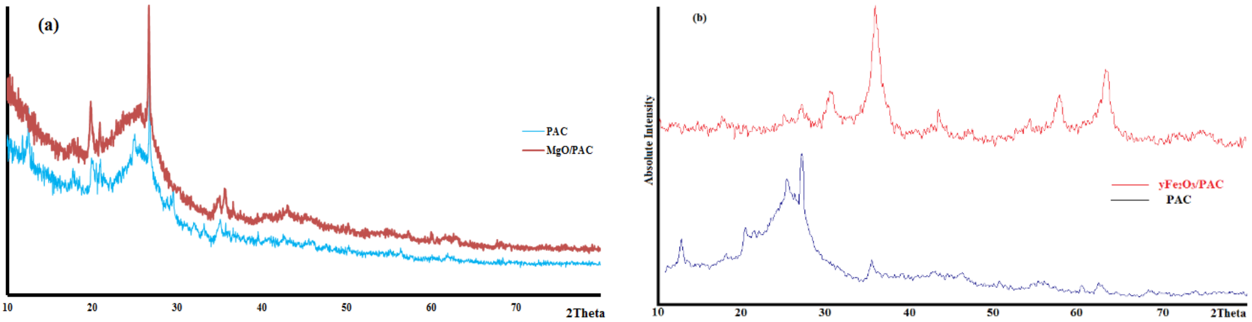

Figure 3. XRD spectrum for the nanocomposite of PAC-MgO (a) and (b) PAC-Fe_2O_3.

alkaline pH, the amount of °OH (hydroxyl radicals) is increased. Since the oxidation strength of °OH is higher than O_3, at higher pH, as degradation of O_3 increases and generation of °OH radicals ($E_{°OH}$=2.33V) increases due to the high oxidative power of °OH compared to O_3 (E_{O3}=2.07V), therefore enhances the MB degradation (Khan and Jung, 2008; Garoma and Matsumoto, 2009). Hence, alkaline conditions indirectly enhances the removal efficiency compared to acidic conditions (S and A, 2008). The finding of Bahrami-asl et al. proved that the best pH for removing reactive red 120 via COPs, using MgO as a catalyst, is 10 (Bahrami-asl et al., 2017). In COP$_s$, increasing pH, also, affects both O_3 gas transfer rate and degradation rate (Akbari et al., 2017; Kamarehie et al., 2018a). Because of intermediate direct and indirect oxidation at neutral pH, the MB degradation efficiency was less than acidic and alkaline pH. In other words, removing the lower MB in COP$_s$ under acidic conditions is due to the lack of °OH radicals for O_3 degradation. Based on Figure 4, the COP$_s$ were more efficient than the SOP$_s$. The main reason for this increase is most likely due to the use of the efficient catalysts. Among catalytic processes, the best MB removal efficiency dependent on O_3-PAC-Fe_2O_3. By producing various radicals, in COPs, pH changes can use in the oxidation of MB dye (Staehelin and Hoigne, 1982; Kamarehie et al., 2018a). The nature of metal oxides affects the amount and properties of the hydroxide group (Valdes et al., 2008). Without the protonated (Eq. 3) and deprotonated (Eq. 4) surface functional groups, the catalyst can act as an acid and base Lewis (Erol and Özbelge, 2008):

$$S-OH+H^{+} \Leftrightarrow S-OH_2^{+} \quad (3)$$

$$S-OH+OH^{-} \Leftrightarrow S-O^{-}+H_2O \quad (4)$$

These chain reactions can cause the production of highly reactive radicals of °OH, HO_2, and HO_3 that finally can enhance MB degradation. As shown in Figure 4, the amount of MB removed in acidic conditions is slightly better than neutral conditions (approximately 10% to 15%). The main reason for this increase in efficiency is related to the low degradation rate of O_3 at low pH (Kamarehie et al., 2020). The results of Kamarehie et al., showed that catalytic processes can effectively be used to remove/degrade pollutants (Kamarehie et al., 2018a).

Figure 5 shows the effects of different initial concentration of MB at contact time of 10 min by SOP$_s$ and COP$_s$. As seen in Figure 5, by increasing the concentration, MB degradation increased. Therefore, degradation of MB dye decreased with increase in concentration. With increasing the initial concentration of the dye, the number of MB molecules increase in the solution, but due to the low hydroxide radical produced from Ozone degradation, the degradation is carried out slowly at high MB concentrations. According to Figure 5, in all processes, the amount of dye removal has decreased (Jiang et al., 2002). Among the other factors that cause a decrease in MB removal, it is important to pay attention to the by-products formed during MB degradation, because these products occupy the desired surface sites and prevent the removal of pollutants (Liu et al., 2013). In COPs using O_3-PAC-Fe_2O_3 and O_3-PAC-MgO, by enhancing the dosages up to 150 mg L^{-1}, the degradation efficiency was increased by a sharp slope. In the following, the removal efficiency increased and then decreased with a gentle slope, dropped.

The amount of required catalyst is one of the key factors in COP$_s$. Based on the previous studies, catalysts dosage can enhance surface area and active sites for more O_3 removal. (Asgari et al., 2015). In lower concentrations of MB, the molecules are rapidly adsorbed on the catalyst surface, but with the increasing

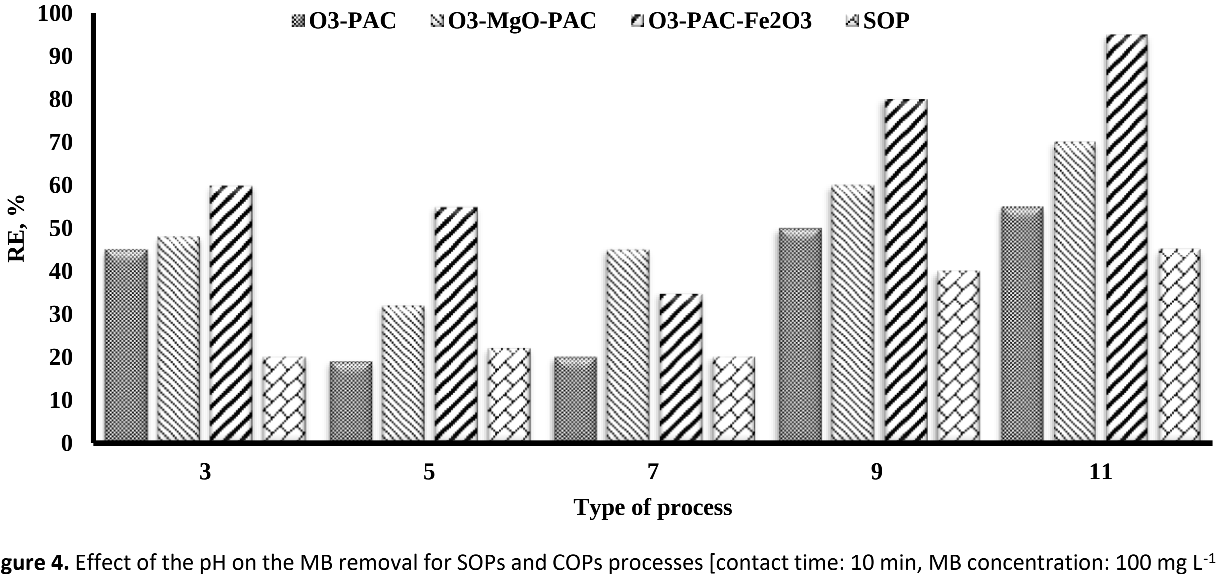

Figure 4. Effect of the pH on the MB removal for SOPs and COPs processes [contact time: 10 min, MB concentration: 100 mg L^{-1}, O_3 concentration: 5 g h^{-1}]

the concentration, it is gradually saturated. Finally, the MB degradation rate decreased due to the repulsions among dye molecules (García et al., 2014).

Increasing the catalyst dose leads to an increase in active sites and subsequently improves the production of active free radicals. Also, with the increase of the catalyst, the possibility of the pollutant encountering the slag-destroying agent will increase significantly (Rashidi et al., 2019; Sadani et al., 2020). To determine the optimal dosage of the catalyst, COPs were performed in the range of 0.5 to 3 g L^{-1}. Because catalyst dose has a great effect on production of °OH radicals, it plays an important role for better efficiency of COP_s. According to Figure 6, by increasing the catalyst dosage, the efficiency of the COP_s increased. Several reasons can be mentioned for increasing the removal efficiency of MB by increasing the catalyst dosage. Increasing the number of active sites, increasing the catalyst surface for the pollutant oxidation and the oxidizer, e.g O_3.

But by increasing the dosage more than the optimum value (150 mg L^{-1}), the synthesized catalyst becomes a ball (clot) state and the activity of free radicals producer level decreases. In simpler terms, pelletizing or catalyst aggregation deactivates the active surfaces which are responsible for the production of various free radicals. A study on diazinon removal with nanocatalyst showed that, with increasing the catalyst concentration, the efficiency of the process firstly increased and then decreased (Shokrzadeh, 2016). According to the results, with increasing the amount of catalyst, the removal MB efficiency increased by 40%. The reason for this is the increase in the number of free °OH radicals in the solution. As the catalyst increased, the degradation of O_3 and the production of intermediate species such as HO_o^-, HO_2^-, O_3^-, O_2^-, and HO_o^- increased too. These can react with each other and O_3, consequently more hydroxide radicals can be produced. As a result, the MB removal efficiency, also, increase (Asgari et al., 2014). Figure 6 presents the effect of the catalyst dosage on MB degradation for COPs processes. According to Figure 6, there is a significant difference between the application of SOPs and COP_s

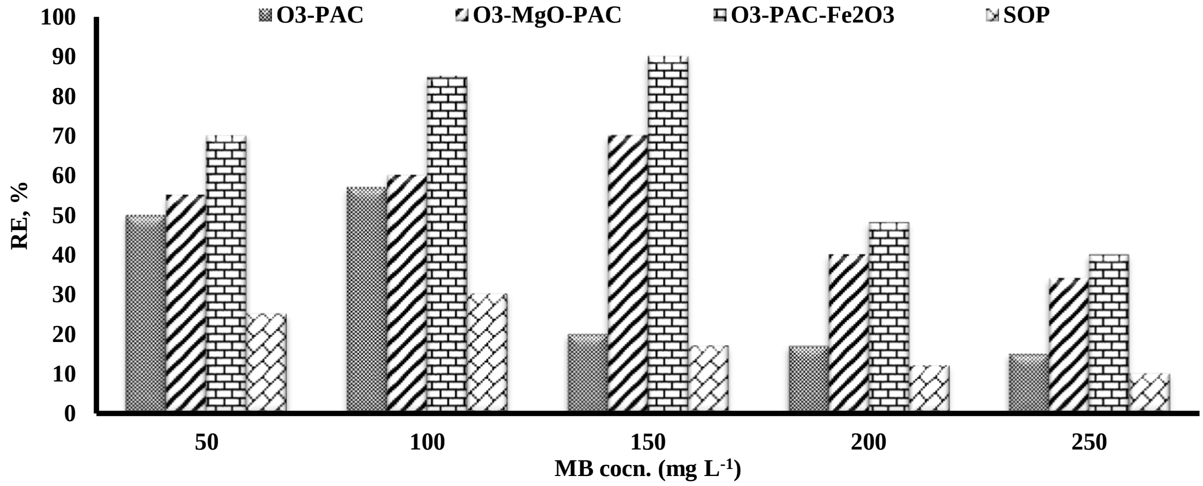

Figure 5. The effect of the initial BPA concentration on the MB degradation for SOPs and COPs processes [contact time: 10 min, O_3 concentration: 5 g h^{-1}]

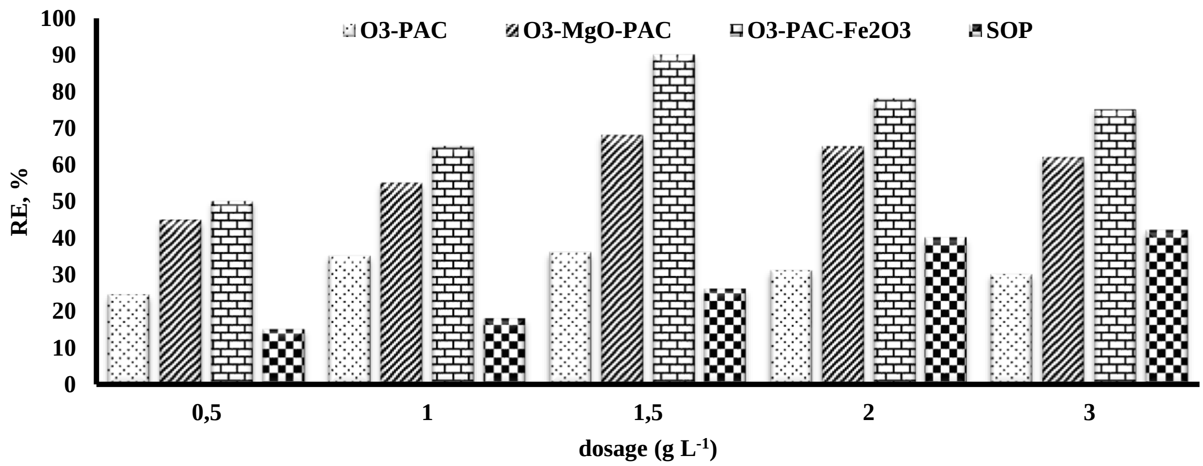

Figure 6. The effect of the catalyst dosage changes on the MB degradation for COPs processes [contact time: 10 min, O_3 concentration: 5 g h^{-1}].

due to the use of catalysts. The best catalyst dosage (based on the highest removal efficiency) for O_3-PAC, O_3-PAC-Fe_2O_3, and O_3-PAC-MgO were 1.5 g L^{-1}, 2 g L^{-1}, and 1.5 g L^{-1}, respectively.

Determining the optimal catalyst dosage is mainly depends on to various parameters such as surface area, reaction conditions, the type of catalyst, and target pollutant composition. As shown in Figure 6, the initial dosage of catalyst harmed the removal efficiency of MB, so by increasing the catalyst from 2 to 3 g l^{-1}, the removal efficiency decreases from 78% to 75%. According to the results, there is no significant change in the removal efficiency with the increase in catalyst dosage. In this work, the adsorption capacity of the catalysts for MB removal was measured. The results showed that the catalyst is a weak adsorbent for MB dye and the catalytic properties are not affected by adsorption. Therefore, according to the results, the strengthening effects and ozone-catalyst composition in COPs can be recognized. Therefore, in the process of removing MB by catalytic process, catalytic reactions predominate over oxidation and adsorption reactions. As mentioned earlier, due to the presence of surface-active sites at the catalyst level and the reaction between O_3 and active sites, O_3 change into active oxygen atoms and reactive oxygen atoms that consequently attack the bonds between carbon atoms or the bonds between H-C atoms and benzene rings (Roshani et al., 2014).

Effect of Contact Time and the Mechanism of the Catalytic Process

Compared to SOP_s, COP_s is more efficient and faster to remove/degrade dyes. In other words, reaction rate and contact time are important factors in removing a dye. Reaction time is one of the parameters affecting advanced oxidation processes (Massoudinejad et al., 2020). An important factor in catalytic process is to provide sufficient contact time under specific conditions, because the required high contact time increases the cost of energy and the reactors volume (Rashidi et al., 2019). As the reaction time increases, the oxidizing agent such as O_3 and °OH radicals have the opportunity to be in contact with the dye for a longer time, removing a higher percentage of the pollutant (Lutterbeck et al., 2015; Trojanowicz et al., 2018). The use of a good catalyst has beneficial strengthening (or synergistic) effects and makes the removal process faster (Moussavi et al., 2009; Rahmani et al., 2015; Abdoli et al., 2016). According to Figure 7, it can be said that by increasing the contact time from 5 to 40 min, the removal efficiency increases, therefore, increasing the contact time has a positive effect on removal of MB in both SOP_s and COP_s. In general, due to the presence of catalysts (regardless of the type of catalyst) in COP_s compared to SOP_s, the removal efficiency was higher and faster. In all processes, to understand the process reaction of dye removal, the study of reaction kinetics is performed. This part of the study will help to better model and execute the process for an application scale. In this study, three models of zero-degree, first-degree, and second-degree kinetics were applied to study the reaction kinetics for MB degradation. The results related to the kinetics for MB degradation in SOP_s and COP_s are presented in Table 1. According to Table 1, the kinetics of the reaction in the process under study follows the first-order kinetics. Based on the results, the reaction rate (K_1) for SOP, O_3-PAC, O_3-PAC-MgO, and O_3-PAC-

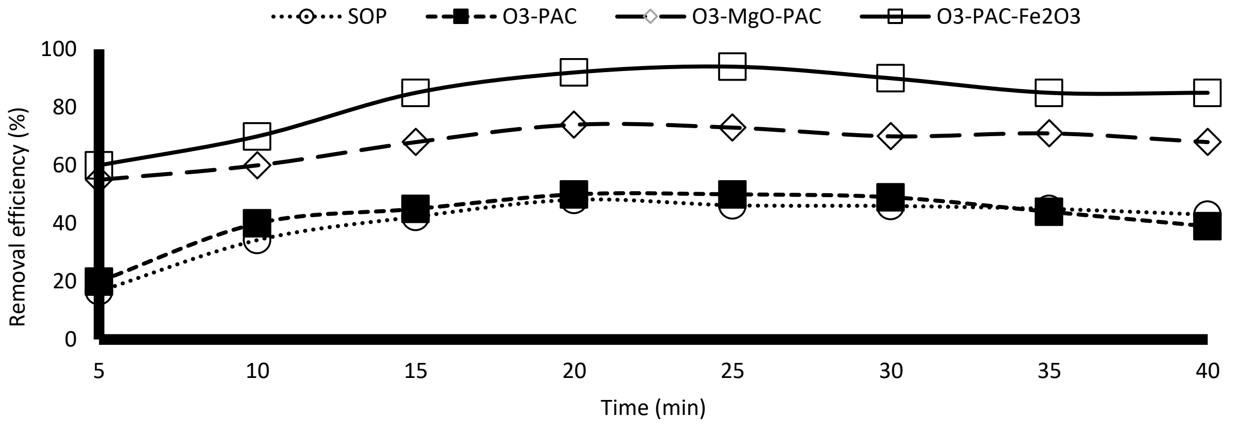

Figure 7. The effect of the reaction time on the MB degradation for COPs processes [concentration: 100 mg L^{-1}, O_3 concentration: 5 g h^{-1}].

Table 1. Kinetic data (R^2) for degradation of methylene blue in SOP_s and COP_s.

Type of process	Zero order reaction	first-order reaction	second-order reaction
SOP_s	0.785	0.985	0.908
O_3-PAC	0.669	0.929	0.88
O_3-PAC-MgO	0.831	0.891	0.863
O_3- PAC-Fe_2O_3	0.744	0.944	0.879

Fe_2O_3 were 0.0187, 0.0298, 0.0536, and 0.0879 min^{-1}, respectively. Therefore, the results of this study proved that MB degradation in COP_s was several times faster than SOP. The reaction rate of dye degradation in O_3-PAC, O_3-PAC-MgO, and O_3-PAC-Fe_2O_3 was 1.59, 287, and 4.7 times faster than SOP, respectively.

Figure 7 displays the effect of the contact time on the MB degradation for various COP_s. According to Figure 7, the best reaction time for COP_s was 15 min. As can be seen in Figure 7, after this reaction time, the MB removal efficiency increases, but this increase was slight and can be ignored. The MB removal experiments lasted for 40 min, the amount of dye removal changed slightly after 15 min. The mechanism of O_3 action is a function of pH. O_3 reacts with organic matter in both direct and indirect ways (mainly °OH radicals). In the direct reaction, O_3 is selectively reacted with cyclic compounds, such as MB (Eq. 5), whereas in the indirect reaction method, O_3 is converted to secondary oxidants (mainly hydroxyl radicals) through chain reactions (Eq. 6), which has the potential of the O_3 molecule (Hsu et al., 2003; Moussavi et al., 2017).

$$\mathrm{PAC-MgO\ or\ Fe_2O_3}^{-O_3} + \mathrm{MB} \rightarrow \mathrm{PAC-\gamma\ Fe_2O_3\ or\ MgO + CO_2 + H_2O + intermediates} \quad 5$$
$$\mathrm{PAC-MgO\ or\ \gamma\ Fe_2O_3}^{-MB} + \mathrm{O_3} \rightarrow \mathrm{PAC-MgO\ or\ \gamma\ Fe_2O_3 + CO_2 + H_2O + intermediates}$$
$$\mathrm{O_3 + MB \rightarrow CO_2 + H_2O + intermediates}$$

$$\mathrm{PAC-MgO\ or\ \gamma\ Fe_2O_3}^{-OH} + \mathrm{MB} \rightarrow \mathrm{PAC-MgO\ or\ \gamma\ Fe_2O_3 + CO_2 + H_2O + intermediates} \quad 6$$
$$\mathrm{PAC-MgO\ or\ \gamma\ Fe_2O_3}^{-MB} + {}^{\circ}\mathrm{OH} \rightarrow \mathrm{PAC-MgO\ or\ \gamma\ Fe_2O_3 + CO_2 + H_2O + intermediates}$$
$${}^{\circ}\mathrm{OH + MB \rightarrow CO_2 + H_2O + intermediates}$$

Effect of Tert-butanol Scavenger (TBS) and Mineralization (TOC) on the MB Degradation

The most important mechanism in AOPs, such as the ozonation process, is the production of active °OH radicals with high oxidation potential. In aqueous media, the degradation of the O_3 molecule due to the presence of °OH radical scavengers can be significantly reduced. Different compounds have been studied by various researchers such as carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), tert-butanol ($C_4H_{10}O$), etc. can control the reaction of radical chains. In this study, tert-butanol scavenger (TBS) was selected. TBS is a very strong consumer of oxidizing radicals which reacts more rapidly than other radical scavengers. The constant rate of the reaction for TBS with °OH radicals ($K_{OH}=6\times10^8$ M^{-1} S^{-1}) is much higher than O_3 molecule ($K_{O3} < 3\times10^8$ M^{-1} S^{-1}). For this reason, this compound is widely used in AOPs as a radical trapper to determine the role of °OH radicals (Zhang et al., 2019). Figure 8(a) demonstrates the presence of TBS in the MB removal process has a reducing effect. The decrease rate of MB for SOP, O_3-PAC, O_3-PAC-MgO, and O_3-PAC-Fe_2O_3 was 24%, 37%, 40%, and 58%, respectively. Reduction of removal efficiency in the presence of TBS proved the dominance of indirect oxidation system under optimal pH, which was stronger and more desirable than direct oxidation. In COP_s, the produced radicals, except °OH, do not react with TBS and these

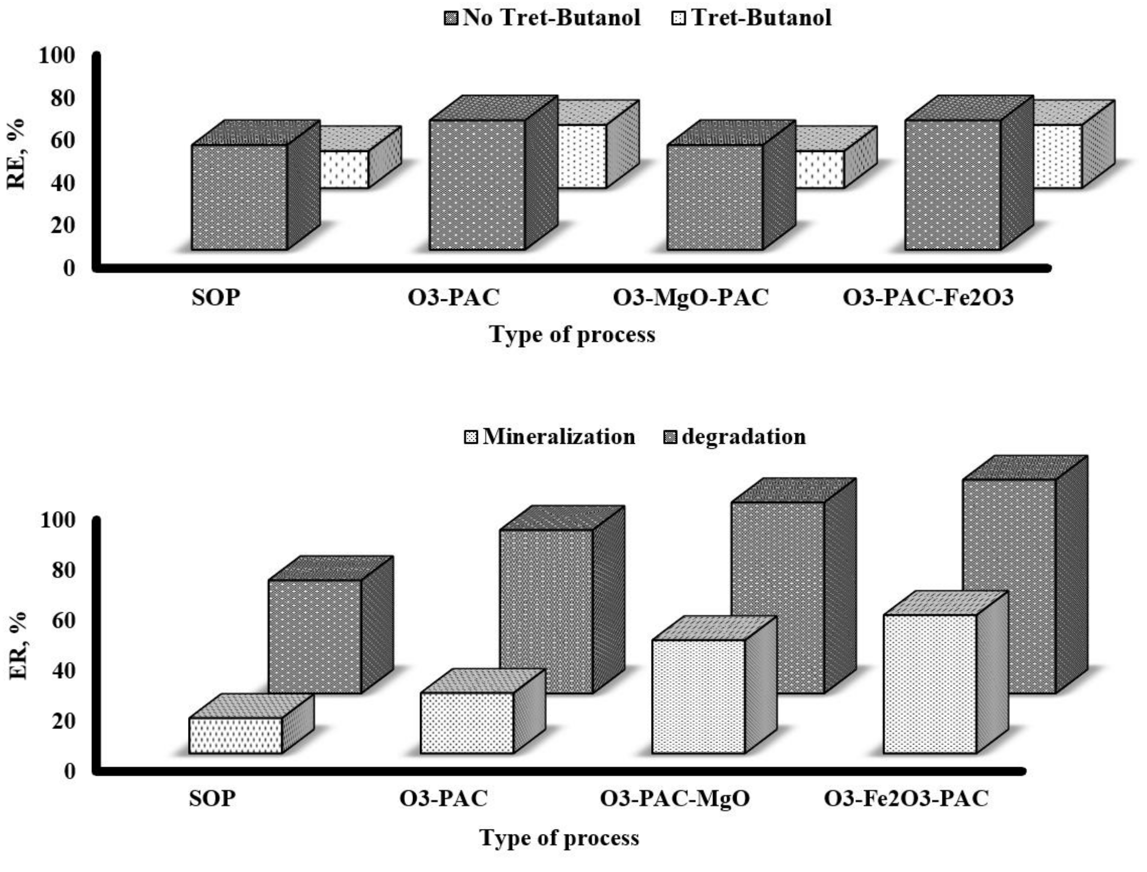

Figure 8. (a) The effect of TBS on the degradation of MB with SOPs and COPs, (b) the effect of mineralization of MB by SOP and COP_s based on TOC [contact time: 15 min, MB concentration: 100 mg L^{-1}, O_3 concentration: 5 g h^{-1}].

reactions may occur on the catalyst surface which are not affected by radical consuming factors and increase the efficiency of the COPs compared to SOP. Figure 8(b) presents the effect of mineralization of MB by SOP and COPs, according to total organic test. In this section, first, the TOC created by MB dye with a concentration of 100 mg L^{-1} was measured and, then, the amount of mineralization was investigated for SOP and COPs via TOC as a simple, low-cost, yet fast method. Also, chemical oxygen demand (COD) was used to determine the removal efficiency of the process. According to the studied structure and the presence of aromatic rings in MB structure causes the process speed to decrease and, decrease in the efficiency. The findings of this research confirmed that the maximum mineralization value for MB dye was related to O_3-PAC-MgO and O_3-PAC-Fe_2O_3. The mineralization in the SOP, O_3-PAC, O_3-PAC-MgO, and O_3-PAC-Fe_2O_3 was 14%, 24%, 45%, and 55%, respectively. As the results showed, the amount of mineralization for COP_s was much higher than for SOP_s. In this process, O_3 firstly attacks the aromatic bonds in a shorter contact time and converts into intermediate and linear compounds. Therefore, the enhancement in mineralization in COP_s indicates the increase in the potency of the COP_s to react with the produced intermediate compounds and finally transform into H_2O and CO_2 (Kusvuran and Yildirim, 2013).

Conclusion

COP_s, as a AOP_s due to the use of high-efficiency direct and indirect oxidation mechanisms and the lack of by-products was applied to degrade MB. Important and effective variables were examined to remove/degrade MB. The structural and microscopic characteristics of the prepared catalysts, also, were examined. Based on the findings of this study, the surface area of PAC was much smoother and more uniform than that of iron-stabilized type, PAC-Fe_2O_3 nanocomposite. The EDX confirmed the stabilization of iron as Fe_2O_3, and magnesium as MgO on the PAC. With increasing the solution pH from acidic to alkaline, from 3 to 11, MB removal increased. The MB concentration is one of the issues that should be considered. With the increase of initial concentration, the removal efficiency significantly decreases. As the contact time increases, the removal efficiency increases in both SOP_s and COP_s. Due to the presence of catalysts in COP_s compared to SOP, their removal efficiency was higher and faster. The reaction rates of dye degradation in O_3-PAC, O_3-PAC-MgO, and O_3-PAC-Fe_2O_3 were 1.59, 287, and 4.7 times faster than SOP_s, respectively. It also needs more time to remove TOC. Energy costs and relatively specialized guidance should be set for this process. It also requires real-scale studies for industrial use. In addition as a complete and separate treatment system, this system can be used as a pre-treatment system for biological systems in industries that are no longer capable of treatment.

Ethical Statement

Not applicable.

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Author Contribution

Writing—original draft; Ali Akbar Mohammadi and Mansour Ghaderpoori; Conceptualization; Mansour Ghaderpoori; methodology; Mohammad Ahmadpour.; formal analysis; Mansour Ghaderpoori.; resources; Mansour Ghaderpoori and Arefeh Sepahvand; data curation; Nasrin Hosseingholizade.; review and editing; Nasrin Hosseingholizade and Shahabaldin Rezania, Mohammad Ahmadpour; visualization; supervision; Mansour Ghaderpoori. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest

The author declares that they have no competing interests.

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