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Catalytic ozonation process using MgO-PAC to degrade bisphenol A from aqueous solutions

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ABSTRACT

Endocrine-disrupting compounds are one of the most important pollutants around the environment which can have harmful effects on animals, humans, and the environment. Bisphenol A has been considered as a priority pollutant by the US Environmental Protection Agency and the National Pollutant Release Inventory. This compound, even at very low concentrations, has severe toxicity to human health. The general goal of the work was to evaluate the efficiency of the catalytic ozonation process to remove bisphenol A from aqueous solutions. In the study, accordingly, the capabilities of plain powder activated carbon (PAC) and PAC-MgO (impregnated with MgO as a catalyst) were studied on the removal of bisphenol A. In this study, three different methods were used to modify the catalyst and finally the best method was chosen. The variables considered effecting the process were initial bisphenol A concentration, contact time, pH, PAC dosage, and MgO catalyst. The amount of magnesium added in methods I, II, and III was 12.6%, 6.8%, and 1.1%, respectively. In addition, the field-emission scanning electron microscopy images indicate a better stabilization of magnesium oxide particles on the PAC. The MgO nanoparticles have been stabilized uniformly on the PAC surface, and the surface morphology of PAC has been substantially modified by the use of MgO nanoparticles. In the catalytic ozonation process with PAC and MgO-PAC, with increasing pH, the removal of bisphenol A increased. The findings of the use of the scavenger showed that the main mechanism involved in the decomposition of bisphenol A has been direct and indirect reactions. The GC-MS results showed that the highest mineralization rate in bisphenol A decomposition was related to O_3-MgO-PAC.

Keyword: Bisphenol A; Ozonation; Activated carbon; Mineralization; Magnesium oxide

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1. Introduction

Endocrine-disrupting compounds are one of the most important pollutants around the environment which can have harmful effects on animals, humans, and the environment [1,2]. The compounds can have harmful effects on human health even at very low concentrations [3–5]. Bisphenol A (BPA), or 2,2-bis(4-hydroxyphenyl) propane, is classified as one of the endocrine-disrupting compounds. Structurally, BPA or $C_{15}H_{16}O_2$ has two large groups of phenolic as well as two electrons rich $^{\bullet}OH$ group and two groups of methyl. BPA has been considered as a priority pollutant by the US Environmental Protection Agency (USEPA) and the National Pollutant Release Inventory (NPRI) of Canada [6]. BPA has a low vapor pressure, high melting point and medium solubility in water [7]. Many industries use these compounds, such as dental sealants, beverage containers, the lining of food [8]. This compound, even at very low concentrations (less than 0.05 mg/kg), has severe toxicity to human health. Acute toxicity of BPA in aquatic organisms was about 1–10 mg/L in fresh and marine species [9]. The production of these compounds in the US and China is 7.6×10^8 and 5.6×10^7 kg/y, respectively [10]. Therefore, BPA must be removed before entering the environment. So far, the various methods have been used to remove this pollutant from the environment, each of which has advantages and disadvantages. Among them, advanced oxidation processes are one of the most important processes for the removal of environmental pollutants especially BPA [11]. One of the new methods that have been considered to remove various organic pollutants, recently, is the catalytic ozonation process [12–14]. The processes can, also, enhance the decomposition rate of the target pollutants, as well as prevents secondary contamination [15]. According to previous studies, the most important factor in maximizing the removal efficiency of this process is the use of a suitable catalyst [16,17]. So far, various catalysts like marble powder, activated carbon, manganese oxide, have been used in conjunction with the ozonation process [18–20]. A review of the previous researches proposed that the use of MgO (magnesium oxide) catalyst is significantly associated with the ozonation process and has a significant effect on the degradation of pollutants especially organic compounds [15,21,22]. MgO is a heterogeneous catalyst which has well the catalytic potential for the degradation of organic pollutants [15,23]. This catalyst has a high destructive power [24]. Due to the high surface area and low costs of recovery and production, metal oxides have a high potential for application in water and wastewater treatment. Among the large category of metal oxides, MgO is a widely used material [25–27]. According to a literature review, so far, for various pollutants such as synthetic dyes, catechol, formaldehyde, VOCs, this process has been used, but no reports have yet been published on BPA removal [15,21]. So, the MgO catalyst shows great potential for combining with powder activated carbon (PAC) to develop a more efficient composite and degrade organic pollutants. Therefore, the main goal of the study was to evaluate the efficiency of the catalytic ozonation process to remove bisphenol A from aqueous solutions. In the present study, accordingly, the capabilities of plain PAC and PAC impregnated with MgO (MgO-PAC) as a catalyst were studied on the removal of BPA.

2. Materials and methods

2.1. Materials

All materials needed in this study were magnesium nitrate ($Mg(NO_3)_2$), sodium hydroxide, bisphenol A ($C_{15}H_{16}O_2$), sulfuric acid, PAC, acetic acid (CH_3COOH), acetonitrile (C_2H_3N), dichloromethane (CH_2Cl_2), and tert-butanol alcohol ($C_4H_{10}O$). Moreover, analytical grade chemicals (by Merck Co.) are used in his study.

2.2. Preparation of MgO-PAC composite

A catalyst coated on PAC was used, according to the previous studies [15,21,28]. In this study, three different methods were used to modify the catalyst and finally the best method was chosen. In the first method (I), 52.5 g of magnesium nitrate hexahydrate, purity ≥ 99%, was dissolved in distilled water (1L) and sodium hydroxide (3 mL, 1 N) was then added under constant stirring. To form a gelatinous suspension (homogeneous) of magnesium hydroxide, the BPA solution was stirred (for 5 min). In the following, 50 g of PAC was added and stirred (for 1 h). Then, the obtained suspension was allowed to settle (for 1 h) and the supernatant was separated. Finally, the PAC covered with magnesium hydroxide, $Mg(OH)_2$, the gel was dried (in an oven at 100°C for 3 h). To convert magnesium hydroxide to MgO nano-crystals, it was calcinated (in at 500°C for 2 h). In the second method (II), it was the same as the first one with the difference that 30 ml of sodium hydroxide (1 N) was added to the solution and placed in an oven (for 3 h) and then placed in a furnace (at 500°C for 2 h). In the third method (III), it was the same as the second one with the difference that the solution was placed in a furnace (at 500°C for 1 h). After preparation, the coated catalyst (MgO-PAC) for next use was placed in a polyethylene container.

2.3. Characterization of PAC and MgO-PAC composite

The characterizations of the PAC and MgO-PAC composite materials, after synthesis, were determined. For this purpose, X-ray diffraction (XRD) (Panalytical Company, X'Pert Pro model), field-emission scanning electron microscopy (FESEM) (Zeiss Company, Sigma VP500 model), Fourier transform infrared spectroscopy (FTIR) (PerkinElmer Company, Spectrum Two model) spectra, energy-dispersive X-ray spectroscopy (EDX) and Brunauer–Emmett–Teller (BET, BELSORP Mini model, Microtrac Bel Corp.) surface area and total pore volumes of the PAC and MgO-PAC were determined from N_2 adsorption isotherms at 77 K.

2.4. Experimental setup

The whole experiment was performed in batch conditions. The pilot used and its main components were similar to Moussavi et al. study [15]. It consisted of an air pump, a flow controller, an ozonation reactor, ozone generation and supply system, diffuser, glass reactor, catalyst particle, magnetic stirrer, magnet, ozone bubble, a destruction system of off-gas ozone, and KI solution flask. The only pilot difference used in this study with Moussavi et al. [15] was the volume of the reactor, which was used a volume of 1L.

The main variables that considered the effect of the process were initial BPA concentration (20–100 mg/L), pH (3–11), contact time, PAC dosage, and MgO catalyst (2–6 g). In this study, the dosage of O_3 injection was constant (5 g/h) [29].

2.5. Analytical methods

In addition, the mineralization of BPA was determined using total organic carbon (TOC) [30]. To determine the concentration of BPA, high-performance liquid chromatography (HPLC) was used. An HPLC system (Shimadzu Corp., Kyoto, Japan) consisting of UV-Vis detector (SPD-M10Avp), a quaternary pump (LC-10ATvp), vacuum degasser and a system controller (SCL-10Avp). A manual injector with a 10 µL sample loop was used for loading the sample. A Class VP-LC workstation was used to acquire and process chromatographic data. An RP cyano analytical column (150 mm × 4.6 mm, 5 µm, MZ-Analysentechnik GmbH, Germany) was used. Also, the effect of the radical scavengers (like tert-butanol, nitrate, and sulfate) on the performance of the process of oxidation of BPA was investigated. To specify the mechanism dominating the interaction of the ozonation process, in this study, with the MgO-PAC in the oxidation of BPA, the tert-butanol procedure was used as a radical scavenger [15,28]. This material, tert-butanol, was also used to investigate the effect of interceptive factors in the production of radical hydroxyl [31]. GC/MS was used to investigate the production of the intermediates during the decomposition process of BPA (GC2010 Plus, Shimadzu). After completion of the experiments, the removal efficiency of BPA and mineralization were estimated by Eqs. (1) and (2), respectively [15]:

$$\text{PBA removal},\% = \frac{\left(C_0 - C_t\right)}{C_0} \times 100 \tag{1}$$

$$\text{Mineralization},\% = \frac{\left(\text{TOC}_0 - \text{TOC}_t\right)}{\text{TOC}_0} \times 100 \tag{2}$$

3. Results and discussion

3.1. PAC and MgO-PAC characterization

The FESEM micrographs and EDX in Fig. 1 presents the surface morphology of PAC (a) and the MgO-PAC composites (b, c, and d). Based on EDX results (Fig. 1) in the second method, more MgO was added to the PAC. The amount of magnesium, Mg, added in methods I, II, and III was 12.6%, 6.8%, and 1.1%, respectively. These results indicated that magnesium coating on the surface of PAC was suitable. Due to the better stabilization of MgO particles on the PAC surface, method II was chosen to continue the work. In addition, the FESEM images indicated a better stabilization of magnesium oxide particles on the PAC surface. As shown in Fig. 1a, the PAC surface was heterogeneous and its tissue was granular [21], whereas the MgO-PAC surface was composed of porous MgO microagglomerates of irregular forms and sizes. These results are consistent with other researcher's findings [15,32,33]. The MgO nanoparticles have been stabilized uniformly on the PAC surface, and the surface morphology of PAC has been substantially modified by the use of MgO nanoparticles (MgO-PAC) [34].

The FTIR spectrum of the PAC and MgO-PAC composite (II) are shown in Fig. 2. As it is seen, the main peaks at 3,412.52 and 3,426.78 cm^{-1} in PAC and MgO-PAC corresponded to O–H bending, respectively. The spectra of 1,618.61 and 1,620 cm^{-1} in MgO-PAC and PAC have represented a weak binding of C=C, respectively. The 1,384 cm^{-1} spectrum was in both MgO-PAC and PAC associated with the CH_3 functional group. The spectra of 1,029.7; 1,036.6; 620.76; 535.5; 480.55; and 472.67 cm^{-1} for MgO-PAC and PAC were related to C=S, C–I, and Si–O–Si bonds, respectively. With a comparison to the FTIR spectrum of PAC and MgO-PAC, it can be seen that the number of functional groups in MgO-PAC has increased [21]. The XRD patterns for PAC and MgO-PAC composites are shown in Fig. 3. A comparison of XRD patterns showed that peak positions of 37.1, 43, and 62.4 in the XRD spectrum of the MgO-PAC were obtained after MgO stabilization on the PAC surface [35]. As indicated in the XRD pattern of the MgO-PAC, the intensity of the peaks was reduced after the MgO coated on the PAC surface. Based on the XRD spectrum and Scherrer equation, the size of the MgO-PAC nano-composite was 50.51 nm. Based on BET, the specific surface area, total pore volume, and average pore diameter of the PAC were 750.3 m^2/g, 0.553 cm^3/g, and 5.067 nm, respectively. Also, the specific surface area, total pore volume, and average pore diameter of MgO-PAC were 678.21 m^2/g, 0.455 cm^3/g, and 4.649 nm, respectively. The reduction in the specific surface area, total pore volume, and average pore diameter of the MgO-PAC can be related to the dispersion of MgO into the pores on the PAC and blocking its pores [15].

3.2. Impact of various variables on process efficiency

3.2.1. Influence of pH

The solution pH is an important factor in the removal of organic matter during the catalytic ozonation process, which affects the state of degradation materials, ozone decomposition and surface catalyst properties [29,36]. To better investigate the effect of pH on the removal of BPA using a catalytic ozonation process, in this study, the effect of this parameter on O_3 alone, O_3-PAC, and O_3-MgO-PAC processes were studied. Fig. 4 presents the effect of the solution pH on the BPA degradation in the various processes. In acidic and alkaline pH, the removal of BPA showed a higher increase in O_3 alone process than neutral pH. The reason for increasing the removal efficiency in acid pH can be attributed to the very slow decomposition of ozone in such conditions and ozone is the main radical of the reaction to the pollutant that reacts selectively. At higher pH, alkaline conditions, ozone decomposition increases and leads to the production of $^{\bullet}$OH radicals, E = 2.33 V, which due to the high oxidative power of this radical compared with ozone, E = 2.07 V, increased the decomposition of BPA [37,38]. Also, the BPA-related pK_a is 9.9 to 10.2, which causes the substance to be in an anionic state at higher pH and to a lower cationic state [39,40]. This result showed which ozonation alone process is not the only process responsible for BPA decomposition and the contribution of $^{\bullet}$OH radicals increases with increasing pH giving

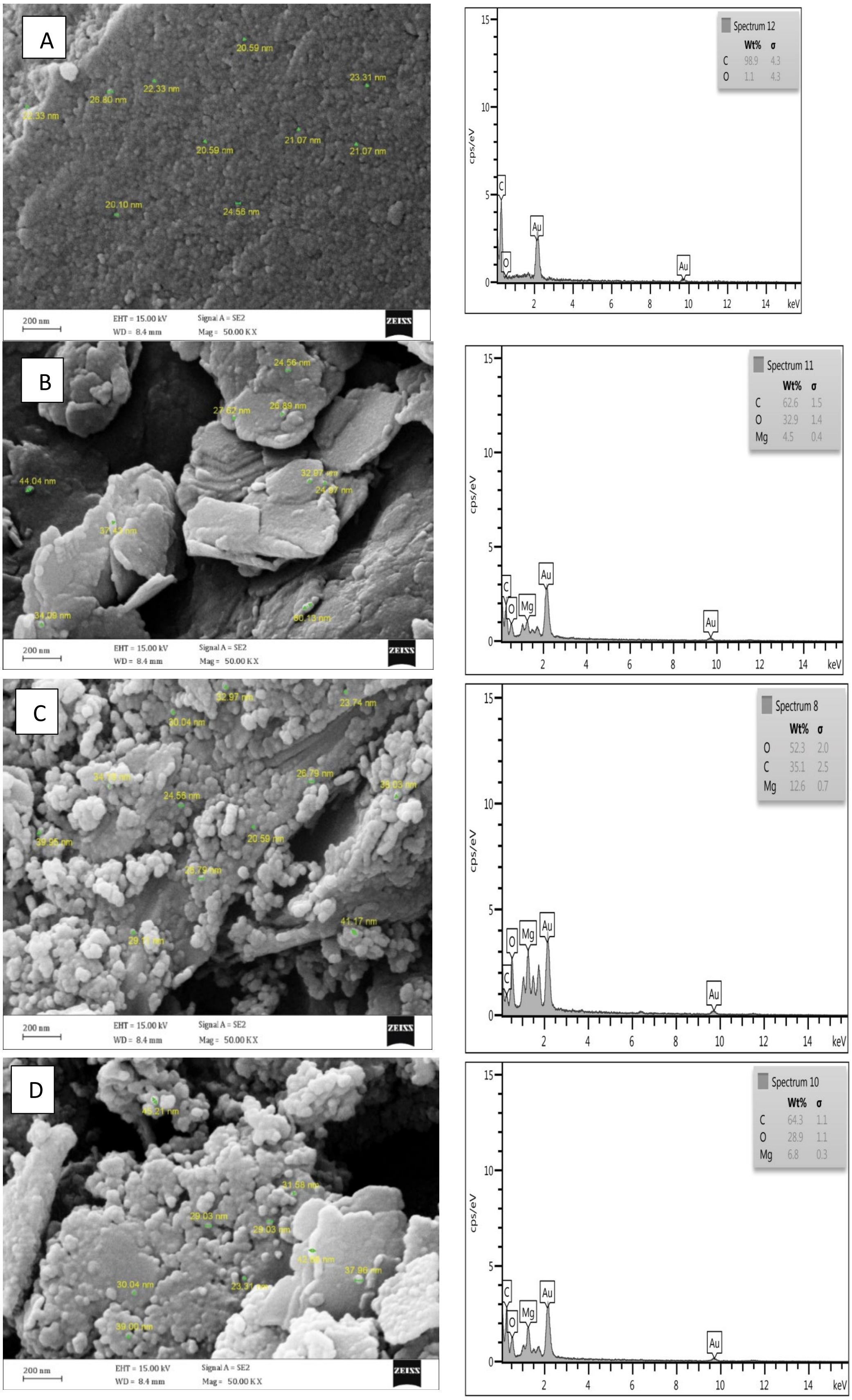

Fig. 1. FESEM micrographs of PAC (a), MgO-PAC composites (b,c, and d for methods of I, II, and III, respectively).

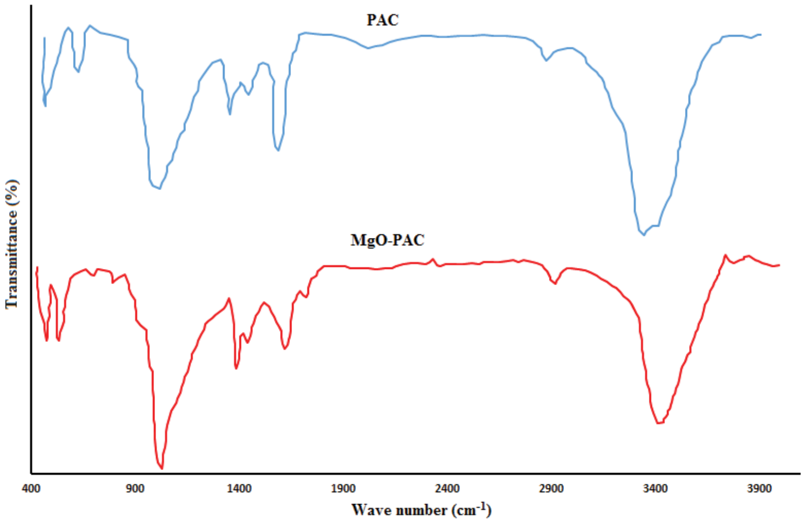

Fig. 2. FTIR spectrum of the composites of PAC (a) and MgO-PAC (b).

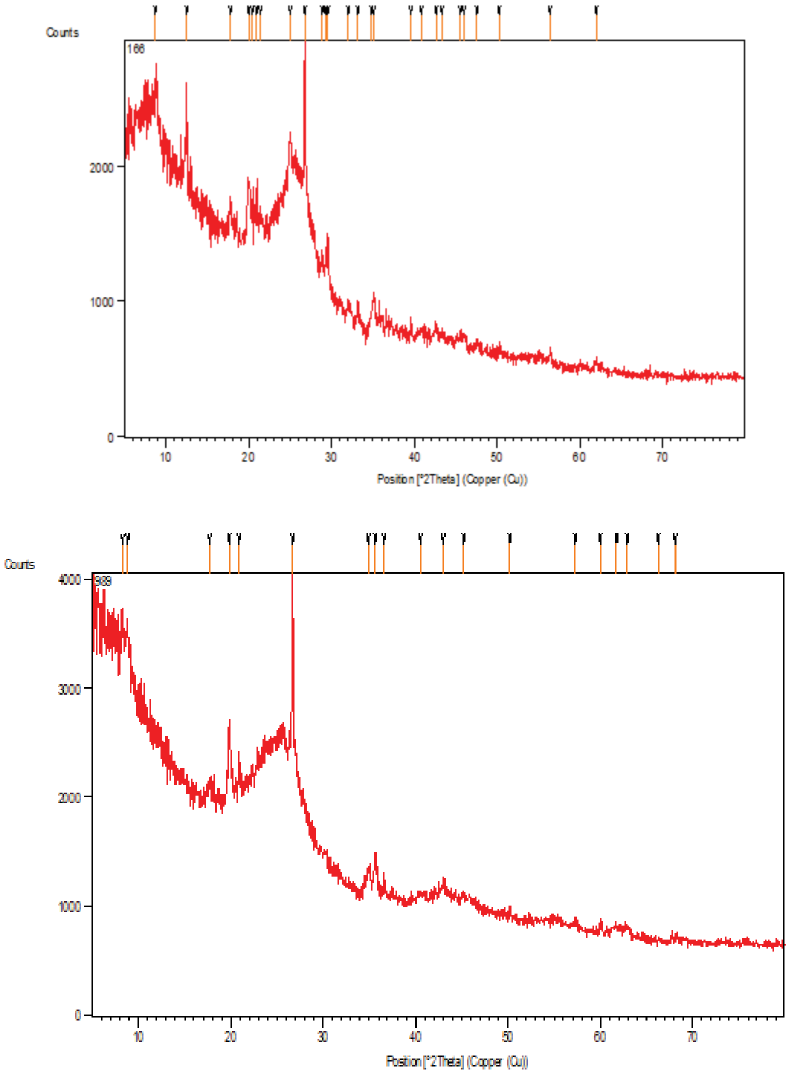

Fig. 3. XRD spectrum of the composite of PAC and MgO-PAC.

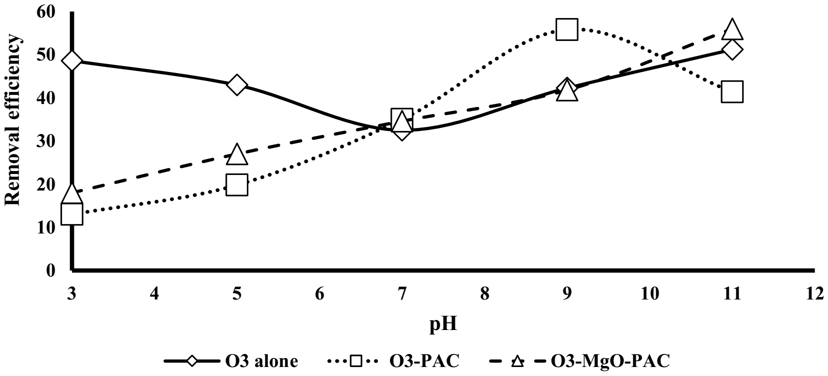

Fig. 4. Effect of the solution pH (3 to 11) on the BPA degradation for O_3 alone, O_3-MgO-PAC, and O_3-MgO-PAC processes (contact time: 10 min, BPA concentration: 100 mg/L, and O_3 concentration: 5 g/h).

higher BPA removal [38]. In the catalytic ozonation process with PAC and MgO-PAC, the BPA removal efficiency increased with increasing pH. The reason for this is ozone acts as an electrophile and can attack the high-electron density centers of the molecules. Because, as mentioned above, at pH higher than pk_a, it contaminates the anionic material, and thus the ozone reacts to it [38]. Other reasons for increasing the removal efficiency of BPA in alkaline pH in O_3-PAC and O_3-MgO-PAC processes can increase the production of $^{\bullet}$OH radicals in alkaline pH compared with the ozone process alone.

3.2.2. Influence of BPA concentration

Pollutants are found in different concentrations in the environment, and the efficiency of the different processes for removing them can also be significantly influenced by the initial concentration. Consequently, in this work, BPA concentrations in the range of 20–100 mg/L were studied. The effect of the initial BPA concentration (20–100 mg/L) on the removal efficiency for O_3 alone, O_3-MgO-PAC, and O_3-MgO-PAC processes is presented in Fig. 5. As Fig. 5 shows, the removal efficiency increased with increasing BPA concentration from 20 to 50 mg/L, then decreased from 50 to 100 mg/L. Reducing the removal efficiency of BPA due to the increase in concentration can be attributed to the competition of the reaction with hydroxyl radicals ($^{\bullet}$OH) at high concentrations [41]. One of the reasons for reducing the removal efficiency of BPA can be the production of intermediates that are formed during BPA decomposition. The intermediates can occupy active sites on the catalyst surface and, finally, reduce the reaction sites for BPA molecules [42]. In COPs, by increasing the BPA concentration up to 30 mg/L, the removal efficiency was increased with a sharp slope. In the following, the removal efficiency increased and then decreased with a gentle slope for O_3-PAC (50 mg/L) and O_3-MgO-PAC (70 mg/L), then dropped.

3.2.3. Influence of scavenger

As shown in Fig. 6, the presence of tert-butanol scavenger in the solution reduced the removal efficiency of BPA. The reduction rate of BPA for single O_3, O_3-PAC, and MgO-PAC was 11.8%, 11.09%, and 6.47%, respectively. The findings of the use of tert-butanol determined that the main mechanism involved in the decomposition of BPA has been an indirect

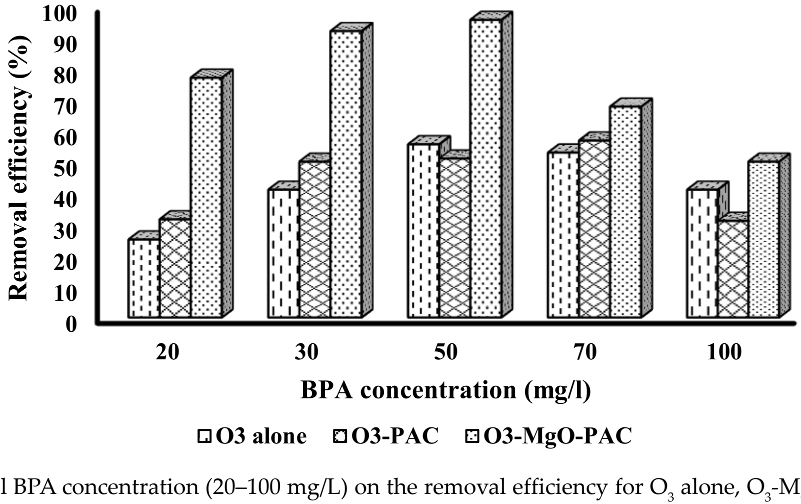

Fig. 5. Effect of the initial BPA concentration (20–100 mg/L) on the removal efficiency for O_3 alone, O_3-MgO-PAC, and O_3-MgO-PAC processes (contact time: 10 min and O_3 concentration: 5 g/h).

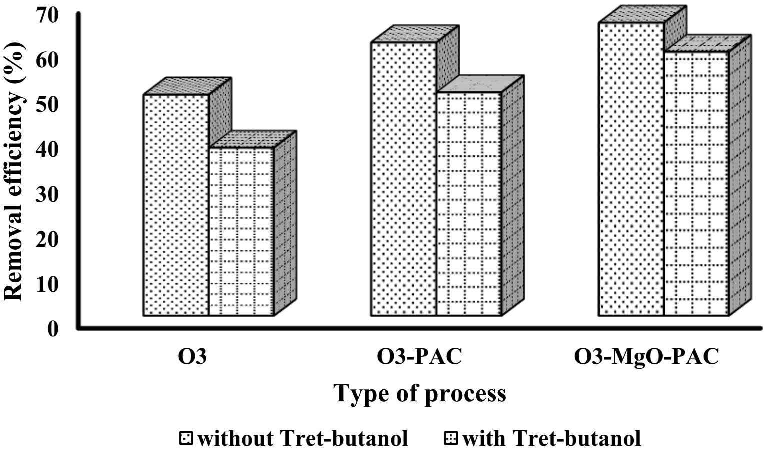

Fig. 6. Effect of tert-butanol on degradation and mineralization of BPA with O_3 only, O_3-PAC, and MgO-PAC processes (contact time: 10 min, BPA concentration: 300 mg/L, and O_3 concentration: 5 g/h).

reaction with $HO^\bullet$ radical [15]. Similar studies have reported similar results in this work [43,44]. The results of Dong et al. [43] showed that the conversion of ozone molecule to hydroxyl radical in the COPs was reduced in comparison with the single ozonation process (SOP). This shows that the $HO^\bullet$ radical was not the main oxidant in the COPs [43].

3.3. Study of the mechanism of the catalytic ozonation process

Based on the theory of ozonation and the findings of this work, the catalytic ozonation of BPA in the presence of MgO-PAC, ozone molecule, and pollutant was absorbed on the catalyst surface and then the BPA was oxidized using ozone. Adsorption by the catalyst increased the probability of contact between the ozone and the pollutant, So, the decomposition of pollutants increased [45]. In addition to the direct reactions of the BPA with the molecule of O_3, the indirect reactions of the produced radicals at the catalyst surface and in the solution can also be involved in the removal BPA mechanism. According to Mousavi et al. [15], the three proposed paths are as follows (the reactions of direct and indirect):

Direct reactions:

$$\mathrm{PAC-MgO^{-O_3}+C_6H_5OH \Rightarrow PAC-MgO+CO_2+H_2O+intermediates} \tag{3}$$

$$\mathrm{PAC-MgO^{-C_6H_5OH}+O_3 \Rightarrow PAC-MgO+CO_2+H_2O+intermediates} \tag{4}$$

$$\mathrm{O_3+C_6H_5OH \Rightarrow CO_2+H_2O+intermediates} \tag{5}$$

Indirect reactions:

$$\mathrm{PAC-MgO^{-OH}+C_6H_5OH \Rightarrow PAC-MgO+CO_2+H_2O+intermediates} \tag{6}$$

$$\mathrm{PAC-MgO^{-C_6H_5OH}+{}^\bullet OH \Rightarrow PAC-MgO+CO_2+H_2O+intermediates} \tag{7}$$

$$\mathrm{{}^\bullet OH+C_6H_5OH \Rightarrow CO_2+H_2O+intermediates} \tag{8}$$

3.4. Mineralization of BPA

To determine the amount of mineralization of BPA during ozonation processes, the TOC analyzer was studied. The effect of mineralization of BPA with single O_3, O_3-PAC, and MgO-PAC based on TOC is presented in Fig. 7. The findings showed that the highest mineralization rate in BPA decomposition was related to O_3-MgO-PAC. The rate of mineralization in the single O_3, O_3-PAC, and O_3-MgO-PAC was 10.26%, 21.1%, and 32.6%, respectively. The results of the mineralization of BPA using the single O_3 process reflected the low power of the ozonation process for the mineralization of pollutants. In the ozonation process, in a shorter time, ozone is attacked by aromatic bonds and produces linear intermediates. Also, increasing the mineralization by combining processes reflects increasing the power of the COP to react with the intermediate produced and converting them into H_2O and CO_2 [10]. Kusvuran et al. [10] reported that after 25 min of ozonation, the TOC value decreased by 30%, which the initial BPA concentration in 25 min was finished [10]. According to the findings of Rivas et al. [46], BPA mineralization has been reported as follows:

$$-\frac{dC_{\mathrm{TOC}}}{dt}=k_{\mathrm{TOC1}}C_{\mathrm{TOC}}\alpha C_{\mathrm{O_3}},\ \alpha=\frac{C_{{}^\bullet\mathrm{OH}}}{C_{\mathrm{O_3}}} \tag{9}$$

$$-\frac{dC_{\mathrm{TOC}}}{C_{\mathrm{TOC}}}=k'_{\mathrm{TOC}}C_{\mathrm{O_3}}dt \tag{10}$$

$$\int_{C_{\mathrm{TOC}_0}}^{C_{\mathrm{TOC}_t}}\ln\left(C_{\mathrm{TOC}}\right)=\int_0^t k'_{\mathrm{TOC}}C_{\mathrm{O_3}}dt=-\ln\frac{C_{\mathrm{TOC}_t}}{C_{\mathrm{TOC}_0}}=k'_{\mathrm{TOC}}C_{\mathrm{O_3}}t \tag{11}$$

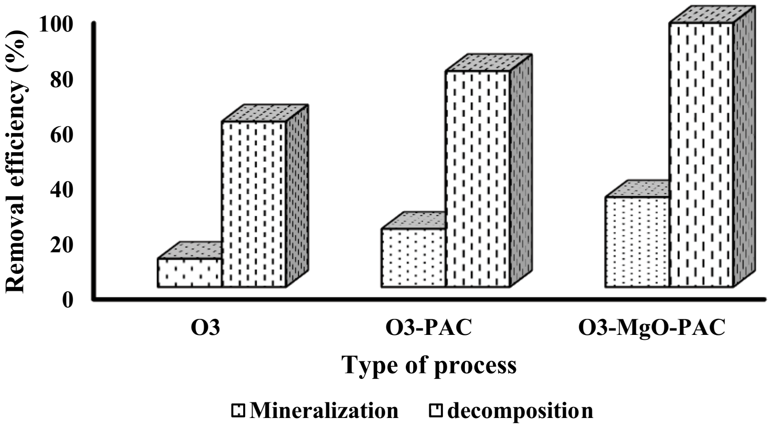

Fig. 7. Effect of mineralization of BPA with single O_3, O_3-PAC, and MgO-PAC processes based on TOC (contact time: 10 min, BPA concentration: 300 mg/L, and O_3 concentration: 5 g/h).

The difference in the results can be due to differences in catalyst type, ozone dose, or other test conditions.

Fig. 8 shows intermediates produced after decomposition of BPA in a catalyst ozonation process. As shown in Fig. 8, there were several peaks in the BPA spectrum after the reaction in the catalytic ozonation process. BPA has a phenol ring in its structure, so it can be expected that the intermediates associated with the decomposition are similar to phenols. In the study of Deborde et al. [47], in the degradation of phenol, five main compounds were observed. These compounds were benzoquinone, muconic acid derivatives of BPA, 2-(4-hydroxyphenyl)-propan-2-ol, orthoquinone, and catechol. In addition to the main compounds, other compounds were also observed. In the study of the ozonation of phenol, the intermediates like catechol, hydroquinone, orthoquinone, and muconic acid derivatives have been reported by Yamamoto et al [48]. Also, the intermediates like resorcinol, acetone, formaldehyde, acetic, formic, the organic acids, malic and oxalic acid as additional reaction intermediates during the ozonation of BPA have also been reported by Garoma et al. [49]. The intermediates of BPA decomposition with catalyst ozonation observed in this study were similar to the compounds found in previous studies.

3.5. Effect of reaction time and kinetics of BPA degradation in catalyst ozonation processes

To better describe the catalytic ability of the modified composite, O_3-MgO-PAC, compared with the O_3 and O_3-PAC, decomposition of the BPA was studied as a function of contact

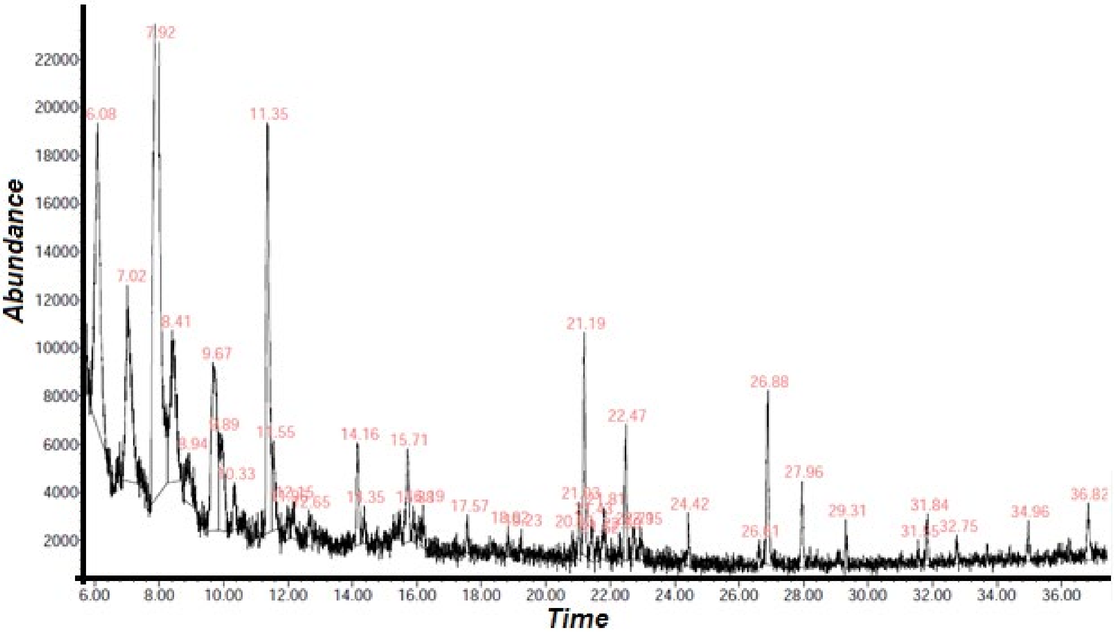

Fig. 8. Intermediates produced after decomposition of BPA with COPs.

time. The kinetic models of the pseudo-first reaction order, first-order reaction, and second-order reaction were calculated in optimal conditions of the variables. Table 1 shows kinetic information for BPA degradation and mineralization in catalyst ozonation processes. The basis for choosing the most suitable kinetic models to show the data obtained for PBA decomposition, based on the higher determination coefficient (R^2) [29]. According to Table 1, the kinetic models describing the data obtained by the processes O_3, O_3-PAC, and O_3-MgO-PAC were following the order: first-order reaction, second-order reaction, and first-order reaction, respectively. Based on the results of Moussavi et al. [15] in the catechol degradation, the first-order reaction was obtained for the single ozonation and the COP, with GAC and MgO-GAC, with the reaction rate constant of 0.124, 0.036, and 0.08839 min^{-1}, respectively. In the present research, the reaction rate constant for the SOP, O_3-PAC, and O_3-PAC-MgO were 0.1, 0.184 and 0.1233 min^{-1}, respectively. In the processes of ozonation with PAC and MgO-PAC, after 10 min of contact time, the highest removal efficiency was obtained. Fig. 9 shows the effect of the reaction time on the removal efficiency of BPA with O_3 alone, O_3-MgO-PAC, and O_3-MgO-PAC. Compared to the ozonation process alone, catalytic processes, O_3-PAC and O_3-MgO-PAC, had a higher removal efficiency over a shorter time. Also, the removal efficiency of O_3-MgO-PAC was more than O_3-PAC. In all processes, the amount of BPA removal was initially high and then increased with a slight slope. The rapid decomposition of the BPA in the first minutes of the reaction indicates the ability of ozone to attack binary bonds of ring compounds, but the ability to react with linear bonds for ozone is low. Therefore, increasing the removal percentage at the beginning of ozonation and then reducing the slope is justifiable because BPA is an aromatic combination that is converted to linear compounds by reaction with ozone [10]. The results of this study were consistent with results from other researchers [42,50,51]

4. Conclusion

This work examined the removal efficiency of the COPs in the removal of BPA. In this study, MgO was used as a good catalyst in the COPs. All experiments were performed in batch conditions. The main variables considered the effect of the process were initial BPA concentration, contact time, solution pH, MgO catalyst, and PAC dosage. Also, the dosage of ozone injection was constant (5 g/h). In this study, three different methods were used to modify the catalyst and finally the best method was chosen. According to the results in the single O_3 process, the efficiency of BPA removal in acid and alkaline conditions was better. But, in the COP with PAC and MgO-PAC, the removal efficiency of BPA increased with increasing pH. The findings of the use of powerful scavenger (tret-butanol) showed that the main mechanism involved in the degrading of BPA has been an indirect reaction with OH$^{\bullet}$ radical. In addition to the direct reactions, the indirect reactions of the radicals produced at the catalyst (MgO) and in the solution can also be involved in the removal mechanism of BPA. According to the study results, the kinetic models

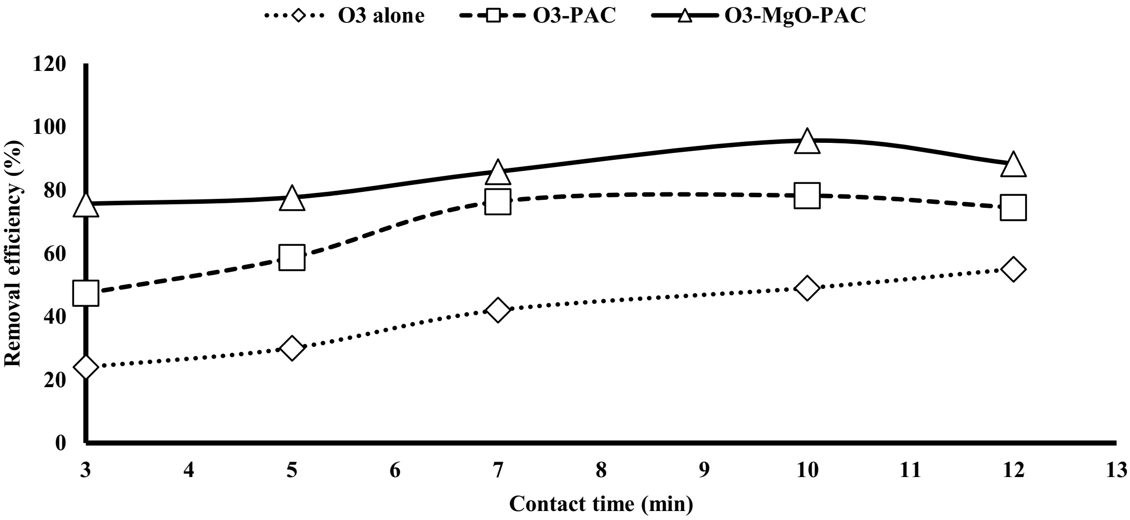

Fig. 9. Effect of the reaction time on the removal efficiency of BPA with single O_3, O_3-MgO-PAC, and O_3-MgO-PAC (concentration: 100 mg/L and O_3 concentration: 5 g/h).

Table 1
Kinetic information (R^2) for mineralization and degradation of BPA in COPs

Type of process	Pseudo-first-order reaction	First-order reaction	Second-order reaction
O_3	0.935	0.958	0.908
O_3-PAC	0.869	0.887	0.88
O_3-MgO-PAC	0.931	0.954	0.863

describing the data obtained by the processes O_3, O_3-PAC, and O_3-MgO-PAC were following the order: first-order reaction, second-order reaction, and first-order reaction, respectively.

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