Performance of photocatalytic ozonation process for pentachlorophenol (PCP) removal in aqueous solution using graphene-TiO₂ nanocomposite (UV/G-TiO₂/O₃)

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Abstract

The aim of this study was to evaluate the efficiency of photocatalytic ozonation process using graphene-dioxide titanium nanocomposite in removing Pentachlorophenol (PCP) from aqueous solutions. In this study, nanocomposites with graphene to TiO₂(G/T) ratios of 1:10 and 1:20 were synthesized by hydrothermal method, and its characteristics were assessed using various analyses, SEM, XRD, FTIR, TEM, BET and TGA. In this process, the effects of parameters including O₃ concentration (0.25–1.25 mg/L), nanocomposite concentration (50–500 mg/L), initial PCP concentration (10–100 mg/L), and time (10–60 min), were studied. The results showed that PCP removal efficiency was increased by decreasing solute concentration. Increasing nanocomposite dose to 100 mg/L was led to an increase in efficiency (99.1%), but then a decreasing trend was observed. Increasing the concentration of ozone, up to specific value, also enhanced the efficiency but then had a negative effect on process efficiency. Furthermore, the optimum ratio of the catalyst was determined to be 1:20. The highest efficiency of the process for initial pentachlorophenol concentration of 100 mg/L was obtained 98.82% in optimum conditions (catalyst dose of 100 mg/L and 60 min). It is concluded that the photocatalytic ozonation process using graphene-dioxide titanium nanocomposite had the highest efficiency in removal and mineralization of PCP.

Keywords Pentachlorophenol · Ozonation · Photocatalysis · Nanocomposite · Graphene · Titanium dioxide

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Introduction

The existence of non-biodegradable organic compounds in the chemical and petrochemical industries has become one of the major environmental challenges. The presence of such compounds in the environment and its entry into water resources have altered the chemical and physical quality of the water and have made it impossible to use [1]. Among the various types of organic matter, pentachlorophenol (PCP), which is a priority pollutant, is widely used in the manufacture of insecticides and herbicides, wood preservatives and reinforcement of wood bridges and fences, production of environmental antimicrobial agents and so on [2]. PCP is one of the derivatives of the phenol family that has found more attention than other phenol derivatives due to the higher chlorine content on the benzene ring. Discharging PCP-containing wastewater into receiving waters disrupts aquatic ecosystem balance, animal and plant species, and leads to killing the fish and other aquatic and contaminates the food chain. The contamination of the soil with this compound will also interrupt the chemical balance of the soil texture and cause

contamination of groundwater resources [3]. Short-term exposure to PCP may impair the function of the nervous system, circulatory system, and liver. Long-term exposure to this substance can also cause side effects such as reducing respiratory capacity and damaging to the circulatory system, liver, kidney, immune system, eyes and skin. Studies have also confirmed the association between cancer incidence and PCP exposure [4]. Several studies have confirmed that oral exposure to this compound causes several unknown liver tumors. The US Environmental Protection Agency (EPA) has classified PCP into group B2 [5]. This compound is found in drinking water and food in very small quantities. The EPA has stated a reference dose (RfD) of 0.03 mg/kg body weight for PCP and has also announced the maximum contaminant dose (MCL) of 0.001 mg/L and *Maximum Contaminant Level Goal* (MCLG) of zero for this chemical [5]. Due to the environmental and health implications of PCP, if the proper methods are not used to treat this material, PCP may be able to reach the receiving water and soil through the effluents of the industries and lead to adverse health and environmental effects. Therefore, removal of PCP from industrial wastewater is an important environmental issue.

Different methods such as adsorption [4, 6, 7], biodegradation [8–10], oxidation [2, 11, 12] photocatalytic degradation [13, 14], and electrochemical methods [15–17] have been used to remove PCP from the aquatic solutions.

The removal of contaminant by Advanced Oxidation Processes (AOPs) occurs based on the production of hydroxyl radicals with high oxidation potential ($E^0 = 2.7$ V), which convert many organic chemicals into minerals [18]. They are highly reactive and are produced by chemical, electrochemical and photochemical reactions in situ. Free radicals are very strong oxidants and rapidly attack to the molecules of organic matter and separate a hydrogen atom from its structure. Therefore, complete mineralization is possible if the treatment time and amount of free radicals to be sufficient [1, 18–20]. In recent years a new approach called the Catalytic Ozonation Process (COP) has considered [21–24].

Ozonation and photocatalysis can be combined to attain a higher degree of pollutant degradation in a process called photocatalytic ozonation. Photocatalytic ozonation has following advantages: (1) ozone can scavenge conduction band electrons (e^-) and reduce charge carrier recombination and (2) ozone can react with the catalyst to produce additional Reactive Oxygen Species (ROS). These two factors increase the effectiveness of photocatalysis and ozonation. Furthermore, Ozone reacts with the conductive-band electron, thus preventing its return to the valence band, and forms ozonide radicals ($O_3^{\cdot-}$), an initial step towards the formation of more hydroxyl radicals in this system, shown by eqs. 1 and 2 [25, 26].

Currently, the photocatalytic process using Graphene-TiO₂ (G-TiO₂) nanocomposites has received much attention [27–31]. The benefits of the combination of graphene and TiO₂ are: increasing the adsorption capacity of catalyst, increasing the light absorption, and preventing the recombination of the charge [32]. Graphene-based TiO₂ composite has showed more photocatalytic activity than TiO₂ alone. Some reports have confirmed that graphene can act as a superior photocatalyst [33]. But so far, these nanocomposites have not been used in the photocatalytic ozonation process. Thus, the aim of this study was to evaluate the efficiency of photocatalytic ozonation process using G-TiO₂ nanocomposite in removing PCP from aqueous solutions.

Materials and methods

Chemicals and reagents

Pentachlorophenol (PCP, >99%) was provided from Sigma Aldrich, St. Louis, MO, USA). The characteristics of PCP are shown in Table 1. Potassium iodide (KI), sodium azide (NaN₃) and tert-butanol (t-BuOH) were provided from Sigma Aldrich. Double distilled water was utilized to prepare the solutions. All the chemicals used in the experiments were of analytical grade and were applied without further purification.

Nanocomposite synthesis

First, 100 mg/L of graphene oxide was sonicated in 250 mL of distilled water at room temperature for at least one hour to ensure complete distribution of graphene oxide in solution. Then a certain amount of titanium dioxide (1000 mg/L for ratio of 1:10 and 2000 mg/L for ratio of 1:20) nanoparticles was added to the above solution and mixed using a magnetic stirrer at 120 rpm. The weight ratios of graphene oxide added to TiO₂ were 1:10 and 1:20, respectively. After shaking for 2 h, the suspension was subjected to a hydrothermal process at 180 °C for 6 h in a 100 ml Teflon-coated autoclave. This hydrothermal process guarantees the reduction of graphene oxide to graphene. The obtained resultant was centrifuged at 10,000 rpm for 10 min. It was then rinsed with double distilled water until the pH of the supernatant was neutralized. The sediment samples were dried at 60 °C for 24 h in an electric oven and then fixed in the crucible [27].

Photocatalytic ozonation process

This experiments were carried out in a batch reactor made of glass with a useful volume of 250 mL. In the middle of the reactor, a UV lamp (UV-C 6 watt) was placed. The lamp was covered by quartz coating to avoid direct contact with water.

Table 1 Characteristics of Pentachlorophenol (PCP)

Component	Information/schematic/value
Molecular (chemical) formula	C_6HCl_5O
2D structure
Molar mass	266.34 g/mol
Melting point	190 to 191 °C (374 to 376 °F; 463 to 464 °K)
Boiling point	309–310 °C (588–590 °F; 582–583 °K)
Density	1.978 g/cm ³ at 22 °C

In addition, the aluminum foil was applied to cover the reactor for protecting against UV radiation. The mixing in the reactor was performed using magnetic stirrer and magnet. 0.1 N sulfuric acid (H_2SO_4) and 0.1 N sodium hydroxide (NaOH) were applied to regulate the pH of the solutions (Eutech, pH 5500model). To perform the photocatalytic ozonation process, the samples were placed in a reactor with a specific volume of PCP solution and the desired nanocomposite. The samples were then subjected to both ozonation and photocatalytic processes. Ozone generator (model: ODP) with an ozone generation capacity of 5 g/h (with oxygen feeding) was used for ozonation. To determine the ozonation capacity of the ozone generator, as well as the amount of ozone entered into the treatment system, the ozone gas produced by the ozone generator was measured using Method 2350E (potassium iodide) of Standard Methods [34]. The sample size consists of 268 samples of PCP and TOC which are the requirements of different parameters based on One factor at a time design of experiments.

To determine the effect of ozone concentration on the photocatalytic ozonation process, ozone concentrations of 0.25, 0.5, 1 and 1.25 mg/L was selected. In order to determine the effect of nanocomposite ratio on pentachlorophenol removal in photocatalytic ozonation process, 1:10 and 1:20 nanocomposite ratios were synthesized. In addition, investigation of the effect of nanocomposite dosage on the photocatalytic ozonation process was carried out using the nanocomposite dosages of 50, 100, 250 and 500 mg/L. Also, to determine the amount of pentachlorophenol mineralization, TOC and COD removal

rates by different processes (including ozone alone, UV alone, nanocomposite alone, UV/ozone, conventional photocatalyst, photocatalyst with nanocomposite, photocatalytic ozonation with nanocomposite) were evaluated at contact times of 10, 20, 40 and 60 min using the optimum conditions obtained at the previous steps mentioned.

Analytical procedure

After conducting the related experiments, the samples were collected at predetermined time intervals and were filtered through 0.45 μm membrane filter, and the concentration of PCP was measured using High-performance liquid chromatography (HPLC) at a wavelength of 254 nm. HPLC (Knuver model) equipped with a UV-Vis detector (UV-K2600KNAUER). AC18 column (250 mm $\times$ 4.6 mm, with 5 μm particle size) was used as the stationary phase. The mobile phase was a mixture of sodium acetate and methanol (20:80 v/v, HPLC grade, Merck) with a flow rate of 1 mL/min at 25 °C.

The total organic carbon (TOC) content of the PCP was determined by TOC analyzer (TOC-L Shimdzu). The chemical oxygen demand (COD) was estimated by COD ampoules (HACH Chemical) using a spectrophotometer (DR 5000, HACH, USA).

The efficiency of photocatalytic ozonation by graphene-TiO₂ nanocomposite process in removing PCP, COD and TOC was calculated using Eq. (3).

$$\text{Removal (\%)} = \frac{[C]_0 - [C]_t}{[C]_0} \times 100 \quad (3)$$

where C_0 is initial concentration (mg/L) and C_t is concentration of pollutant at t time (mg/L).

All experiments were conducted at least three times and the mean value was reported as the result with standard deviation of $\pm 4\%$.

Quality Control criteria include a correlation coefficient greater than 0.999 for the calibration curve, relative standard deviation (RSD) of standard replicates of $< 2\%$ for both TOC and PCP. It should be noted that KHP (potassium hydrogen phthalate) was applied for accuracy of TOC measurements.

Characterization of Nanocomposite

The structure and physicochemical characteristics of titanium dioxide, graphene oxide, graphene, G-TiO₂ nanocomposites with ratio of G/T = 1/10 and G/T = 1/20 were assessed using the analyses, e.g., Scanning Electron Microscopy (SEM), X-ray diffraction (XRD pattern) by X'Pert Pro diffractometer, Fourier-Transform Infrared Spectroscopy (FTIR), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) theory and thermogravimetric analysis (TGA).

Results and discussion

Characterization of synthesized nanocomposites

Scanning electron microscopy analysis

Scanning electron microscopy (SEM) technique was used to evaluate the microstructures of the graphene oxide, graphene-titanium dioxide (G-TiO₂) nanocomposites substrate at magnifications (5 and 1 μm , respectively) has been shown in Fig. 1. According to Fig. 1, G-TiO₂ nanocomposites did not mix with graphene easily and it seems that they were trapped between the graphene plates. SEM nanocomposites images showed its porous structure. It also seems that the nanocomposites with TiO₂ have a relatively uniform structure.

XRD patterns

The X-ray diffraction patterns (XRD) images obtained from the TiO₂, graphene oxide, graphene and G-TiO₂ nanocomposites has presented in Fig. 2. According to Fig. 2, the main peaks are observed at 2θ of 25.3° , 37.8° , 48.0° , 53.9° , 55.0° , and 62.7° for G-TiO₂ nanocomposites, which can be

Fig. 1 SEM images of (a) graphene oxide, b G-TiO₂ nanocomposites with a ratio of G/T = 1/10 and c G-TiO₂ nanocomposites with a ratio of G/T = 1/20

Fig. 2 XRD images of **(a)** TiO₂, **(b)** I) graphene oxide and II) graphene, **(c)** G-TiO₂ nanocomposites with a ratio of G/T = 1/10 and **(d)** G-TiO₂ nanocomposites with a ratio of G/T = 1/20

attributed to the (101), (004), (200), (211) and (204) crystal-line surface of anatase titanium dioxide, respectively.

The main peak of graphene is at 25.3° but in the Fig related to nanocomposite, no peak of graphene is observed; this may be due to the overlap of the main of graphene peak at 25.3° with a strong peak of anatase [27, 35]. The main peak of graphene oxide is also at 12.6°, which has completely disappeared in the graphs of the nanocomposites. Therefore, XRD of the samples shows that graphene oxide is reduced to graphene and G-TiO₂ nanocomposites are well synthesized under hydrothermal conditions. Also, according to the calculations based on Bragg and Debye-Scherrer equations (Eqs. 4 and 5), the size of the crystals in nanocomposites with ratios of 1:10 and 1:20 were 36.85 and 36.49 nm, respectively. The size of nanocomposites with different ratios had no significant difference.

$$D = \frac{K \lambda}{B \cos \theta} \quad (4)$$

$$\lambda = 2d \sin \theta \quad (5)$$

where D , λ and θ , B are the size of crystals, the peak width at mid-height of the highest peak (in radians), the angle of highest peak, and the x-ray wavelength, respectively. $K = 0.9$ is a constant that depends on the morphology of the crystals.

Transmission electron microscopy

The TEM images of anatase titanium dioxide and graphene-titanium dioxide nanocomposites synthesized with two ratios of 1:10 and 1:20 (G: T) are shown in Fig. 3. The particle size of the synthesized nanocomposite is about 25 to 35 nm. With the placement of TiO₂ particles on the graphene plates, in some points, some agglomerates were observed, which they were more numerous in nanocomposites with higher titanium dioxide. The TEM images of the synthesized nanocomposites (Fig. 3) show the heterogeneous dispersion of TiO₂ particles in graphene networks. Particles were accumulated between graphene plates. This accumulation limits the surface contact between TiO₂ and graphene resulting in inadequate use of excellent electrical conductivity of graphene [36]. The particle size of TiO₂ nanoparticles is in range of 10 to 25 nm. The

Fig. 3 TEM images of (a) TiO_2 , b Graphen oxide, c G- TiO_2 nanocomposites with a ratio of G/T = 1/10 and d G- TiO_2 nanocomposites with a ratio of G/T = 1/20

TEM of the samples shows that the particles of the synthesized nanocomposites are in the range of 25 to 35 nm. Therefore, the addition of graphene to TiO_2 and their synthesis together have increased the particle size. But the TEM comparison of the two synthesized nanocomposites indicates that the particle sizes of these two nanocomposites were not significantly different.

BET surface areas and pore distributions

BET method was used to measure the porosity and effective surfaces of synthesized nanocomposites. Since this method is based on nitrogen adsorption-desorption, the nitrogen adsorption-desorption graphs related to titanium dioxide, graphene, graphene-titanium dioxide

Table 2 BET surface area, total pore volume, and mean pore diameter of synthesized nanocomposites

Parameters	(m^2/g) BET surface area	Total pore volume (mL/g)	(nm)pore diameter
Titanium dioxide	68.726	0.5058	29.439
GT 1:10	76.385	0.2821	14.773
GT 1:20	84.019	0.2845	13.542

nanocomposite synthesized with a ratio of 1:10 (titanium dioxide: graphene) and the ratio of 1:20 (titanium dioxide: graphene) are shown in Fig. 4. Also, the BET surface area, total pore volume and mean pore diameter of graphene, titanium dioxide and synthesized nanocomposites are presented in Table 2. The mean pore diameters for titanium dioxide, graphene, 1:10 graphene-titanium dioxide and 1:20 graphene-titanium dioxide were 29.439, 136.12, 14.773 and 13.542 nm, respectively. According to IUPAC classification, nanocomposite in both ratios were corresponding to mesoporous materials (2–50 nm) [37, 38]. Therefore, the nanocomposites with greater graphene have a relatively higher pore diameter. Moreover, the surface area of anatase titanium dioxide was obtained to be 68.77 m²/g, which was lower than the synthesized nanocomposites (76.3 and 84 m²/g, respectively). Therefore, the results showed that with increasing the graphene, the surface of the synthesized nanocomposite was increased. So that the surface area of nanocomposites was much lower than the graphene (2600 m²/g). This may be due to the minimal amount of graphene. Therefore, of the main responsible of surface area and porosity in nanocomposites is titanium dioxide [39].

FTIR spectra

The FTIR images obtained from the Anatase titanium dioxide, Graphene oxide, G-TiO₂ nanocomposites with a ratio of G/T = 1/10 and G-TiO₂ nanocomposites with a ratio of G/T = 1/20 has presented in Fig. 5.

The presence of strong absorption bands in the range 400 to 1000 cm⁻¹ in this Fig is due to the presence of Ti-O-Ti and Ti-O-C bands, indicating the chemical interaction between the hydroxyl groups on the surface of TiO₂ and functional groups of the graphene oxide. The C-O vibration peak at 1051 cm⁻¹ and the C=O and -COOH vibration peak at 1730 cm⁻¹ observed in graphene oxide were completely eliminated in the synthesized nanocomposites. Therefore, oxygen-containing functional groups were completely eliminated during the thermal reaction [40].

TGA spectra

TGA analysis was used to show the exact ratios of the synthesized nanocomposites. The results of TGA experiments of titanium dioxide, graphene oxide, nanocomposite with a ratio of 1:10 and nanocomposite with a ratio of 1:20 are shown in

Fig. 4 Nitrogen adsorption and desorption graphs of (a) Anatase titanium dioxide, b Graphen oxide, c G-TiO₂ nanocomposites with a ratio of G/T = 1/10 and d G-TiO₂ nanocomposites with a ratio of G/T = 1/20

Fig. 5 FTIR images of TiO₂, Anatase titanium dioxide, Graphen oxide, G-TiO₂ nanocomposites with a ratio of G/T = 1/10 and G-TiO₂ nanocomposites with a ratio of G/T = 1/20

Fig. 6. As shown in Fig. 6, the TGA analysis of the samples was carried out at 1200 °C. The graphs of graphene show that this substance has been completely decomposed. But with increasing temperatures, titanium dioxide has been almost constant. So, in fact, the reduction rate of substance reflects the amount of graphene in the nanocomposite. In the graph of 1:10 nanocomposite, about 10% decrease in substance is observed which indicates the presence of 10% graphene in this composition, so the ratio of synthesized nanocomposite is confirmed. Also, in the graph of nanocomposite with a ratio of 1:20, about 5% reduction was observed, confirming the 1:20 ratio of graphene to titanium dioxide [41, 42].

The effect of synthesized nanocomposite ratio

Investigation of the effect of nanocomposite ratio on the efficiency of photocatalytic ozonation process in PCP removal showed that the removal efficiency of PCP by graphene/dioxide titanium nanocomposite with a ratio of 1:10 at 5, 10, 20, 40 and 60 min were 41.57, 74.06, 83.49, 93.98 and 97.3%, respectively. But removal percentages for nanocomposites with a 1:20 ratio at the mentioned interval times were obtained to be 58.48, 83.09, 88.11, 95.77 and 99.27%, respectively. According to Fig. 7 (a), the efficiency of nanocomposite with a ratio of 1:20 was higher; it is in accordance with Zhang et al. (2014) [27]. In their study, graphene and P25 titanium dioxide were used to remove sodium pentachlorophenol in the

photocatalytic process. The nanocomposites were synthesized with 4 ratios of 1:10, 1:20, 1:50 and 1:100, which the highest performance was observed for the highest ratio, i.e., 1:100. Considering the results, by reducing the ratio of graphene, the efficiency of process was increased. In the present study, graphene and anatase titanium dioxide were used in the synthesis of nanocomposites. In another study, TiO₂-graphene nanotube composite was synthesized by hydrothermal method. The ratios synthesized in this study were 5, 10, 15 and 20% graphene to titanium dioxide nanotube (TNT); the results illustrated that the highest efficiency of process was 10% graphene and the composites with 5%, 15% and 20% of graphene were in next ranks, respectively. According to the results, increasing the amount of graphene up to a certain extent is led to enhance the process efficiency, but after that, a negative effect on the process efficiency is observed. This may be due to this fact that the graphene sheets don't allow the penetration of the light [43]. However, incorporation of graphene may delay the recombination of holes and electrons and also impede the absorption of photons and thereby reduce the degradation efficiency [44].

The effect of nanocomposite dose

The results of the changes in the dosage of graphene-dioxide titanium nanocomposite in the photocatalytic ozonation process are shown in Fig. 7(b). As shown in Fig. 7(b), the process efficiency for different dosages of graphene-dioxide titanium,

Fig. 6 TGA graphs of (a) TiO₂, b Graphen oxide, c G-TiO₂ nanocomposites with a ratio of G/T = 1/10 and d G-TiO₂ nanocomposites with a ratio of G/T = 1/20

i.e., 50, 100, 250, and 500 mg/L was 73.3, 88.11, 86.32 and 78.44% at 20 min, respectively. Results showed that by increasing the catalyst dosage up to 100 mg/L, PCP removal efficiency was increased, but then a decreasing trend was observed. Other studies also showed that increasing the catalyst dosage up to a certain extent led to increasing the efficiency but, after that, it had a deterrent effect that can also be due to the inhibition of light transmission. The effect of CFN catalyst dosage on dye removal was assessed, and it was found that increasing the catalyst dosage from 0.01 to 0.03 g/L increases the efficiency of the process, but increasing the dosage to values higher than 0.04 g/L had no positive effect on process efficiency [45]. In another study, the dye removal efficiency by MWCNT using photocatalytic ozonation method showed that increasing the catalyst dosage to 0.03 g/L increases the removal efficiency, but higher doses of the catalyst have an inhibitory effect on the dye removal [46]. Beltran et al. (2009) surveyed the Sulfamethoxazole removal using

photocatalytic ozonation and observed that increasing titanium dioxide dosage from 0.5 to 1.5 g/L has resulted in enhancing the Sulfamethoxazole removal efficiency but the removal efficiency remained constant for the dosages higher than 2.5 g/L [47]. Therefore, in all catalytic oxidation processes such as the present study, there is a specific dose of catalyst that provides the highest efficiency, but the dosages higher than this specific dosage causes problems including light penetration and thus reduces process efficiency. Because, by increasing the dosage, the catalyst surface for activation of ozone was and thus, more radicals were produced.

The effect of ozone concentration

In advanced oxidation processes, the type and concentration of the oxidizing agent are the effective factors in the removal of organic compounds [48]. The results of the study of the effect of ozone concentration on the efficiency of the

photocatalytic process for removal of PCP are shown in Fig. 7(c). As shown in Fig. 7(c), by increasing the flow rate of oxygen generator, the amount of soluble ozone was increased, which is consequently led to improve the PCP removal efficiency. So that the PCP removal efficiencies at concentrations of 0.25, 0.5, 1 and 1.25 mg/L ozone, at 20 min, were observed to be 67.33%, 81.55%, 88.11% and 86.25%, respectively. Therefore, the optimum ozone concentration was determined at 1 mg/L. In general, PCP removal was increased by an increase in ozone concentration (from 0.25 to 1 mg/L) while it was decreased from by increasing from 1 to 1.25 mg/L. Probably, this phenomenon is due to decrease in ozone activation and other active radical species, which are formed in high concentrations of ozone [23]. Rodríguez et al. showed that increasing ozone concentration enhances the pollutant removal efficiency. The reason is that as the amount of soluble ozone increases, the production of hydroxyl radicals increases and as a result, more molecules are exposed to contact with the hydroxyl radicals and are oxidized [49].

The effect of initial concentration of PCP

The effect of the initial PCP concentration on the efficiency of the photocatalytic process for PCP removal are shown in Fig. 7(d). As shown in Fig. 7 (d), the removal efficiency was decreased by increasing PCP concentration. With an increase in PCP concentration from 10 to 100 mg/L, the removal efficiency was also decreased from 95.61 to 69.49% at 20 min. The results also showed that the removal efficiency of PCP was higher than 98% for all concentrations at a contact time of 60 min. In fact, the rate of degradation of PCP can be controlled by the limitation in number of adsorption sites of the photocatalyst. The reduction in PCP removal efficiency by increasing its concentration can also be due to two following reasons: 1) Due to the same conditions for all samples, the amount of hydroxyl radicals produced at each initial concentration of PCP was also equal and thus the percentage of PCP degradation will be more for the samples with lower concentration; 2) The production of intermediates at higher concentrations of PCP may also lead to competition between PCP molecules and intermediates for the reaction with hydroxyl radicals and thereby reduce removal efficiency [50].

Comparison of the efficiency of different processes in PCP removal

The results of the comparison of the efficiency of different processes for PCP removal are shown in Fig. 8 (a). As shown in Fig. 8 (a), the removal rate of PCP at contact time of 60 min for UV + TiO₂ (photocatalytic process using titanium dioxide nanoparticles), GT (graphene-titanium dioxide nanocomposite alone), UV (UV lamp alone), O₃ (ozonation alone), O₃ + UV (ozone and UV), UV + GT (photocatalytic process using

graphene-titanium dioxide nanocomposite) and O₃ + UV + GT (photocatalytic ozonation process using graphene-titanium dioxide nanocomposite) at optimum condition was 58.24, 39, 46.39, 61.3, 76.69, 83.4 and 98.82%, respectively. Therefore, according to the results, the highest PCP removal efficiency was related to UV/G-TiO₂/O₃ process. Graphene sheets have a very specific surface area and also tend to have aromatic compound molecules through π - π interactions. Thus, 39% of removal efficiency is obtained by graphene-dioxide titanium nanocomposites alone. However, production of nanocomposite has increased the adsorption ability of graphene sheets, because titanium dioxide nanoparticles prevent the interconnection and bulking of graphene sheets due to strong π - π bonding between them [35].

Recent studies also show that in addition to direct ozonation, ozone in the presence of titanium dioxide under UV irradiation can produce hydroxyl radicals (HO $\cdot$) through the formation of O₃ $^{\cdot-}$ in the absorption layers. The radical produced from O₃ $^{\cdot-}$, rapidly reacts with H $^+$ in the solution, and produces the radical HO₃ $^{\cdot}$, which eventually results in O₂ and HO $\cdot$. In the absence of ozone, dissolved oxygen alone can receive the conduction electron band and produce O₂ $^{\cdot-}$. Compared to HO₃ $^{\cdot}$, O₂ $^{\cdot-}$ species cannot generate hydroxyl radicals in one step. This mechanism requires a total of three steps to generate HO $\cdot$. Since through the O₃ $^{\cdot-}$ reaction pathway, an electron is required, so this is a more favorable position [51]. Dong (2010) investigated the removal of phenol using photocatalytic ozonation process with activated carbon and titanium dioxide, and declared that the combined process investigated was much more efficient than individual processes [52]. Moreover, Li et al. studied the efficiency of the photocatalytic ozonation process using carbon/carbon dioxide/aluminum nanocomposites in the removal of catechol, the results showed that the process investigated was more efficient than ozone alone and photocatalyst alone [53], which was in agreement with the results of the present study.

Comparison of different processes in mineralization of pentachlorophenol

The mineralization of pentachlorophenol in different processes was investigated using TOC and COD analysis (Fig. 8b, c). The results showed that the removal rates of TOC at contact time of 60 min for UV + TiO₂ (photocatalytic process with titanium dioxide nanoparticles), GT (graphene-titanium dioxide nanocomposite alone), UV (UV lamp alone), O₃ (ozone), O₃ + UV (ozone and UV), UV + GT (photocatalytic process with graphene-dioxide nanocomposite), and O₃ + UV + GT (photocatalytic ozonation process with graphene-titanium dioxide) at the optimum condition were 34.38%, 12.2%, 25.13%, 41.19%, 48.88%, 55.19% and 81.5%, respectively. Therefore, the results show that the UV/G-TiO₂/O₃ process had the highest efficiency in TOC removal (Fig. 8b). The

Fig. 7 **a** The effect of G/T ratio ($C_0 = 50$ mg/L, nano = 100 mg/L, pH = 7, $O_3 = 1$ mg/L), **b** The effect of nanocomposite dosage ($C_0 = 50$ mg/L, GT = 1:20, pH = 7, $O_3 = 1$ mg/L), **c** The effect of ozone concentration

(nano = 100 mg/L, GT = 1:20, pH = 7) and **d** The effect of initial concentration of pentachlorophenol (nano = 100 mg/L, GT = 1:20, pH = 7, $O_3 = 1$ mg/L) on photocatalytic ozonation process efficiency

results also showed that the COD removal rate at contact time of 60 min for the processes under optimum conditions was 58.24, 0.39, 46.39, 61.3, 79.69, 83.49 and 98.82%, respectively (Fig. 8c), Nishimoto et al. evaluated the efficiency of photocatalytic ozonation using WO_3 powder in removal of phenol and reported that studied process was more efficient than ozonation alone in mineralization of phenol [54], which was consistent with the present study.

The effect of scavengers

The results of the effects of scavengers, e.g., sodium azide (NaN_3), tert-butanol and potassium iodide are presented in Fig. 9. To determine the effects of scavengers, the photocatalytic ozonation processes with graphene-titanium dioxide nanocomposite and the photocatalytic process with graphene-titanium dioxide nanocomposites was studied in the absence of scavengers (control) and in the presence of scavengers including t-butanol (t-BuOH), potassium iodide (KI) and sodium azide (NaN_3). Experiments were performed

at optimum conditions including ozone concentration of 1 mg/L, nanocomposite ratio of 1:20 and nanocomposite dosage of 100 mg/L and pentachlorophenol concentration of 100 mg/L and contact time of 30 min. Results showed that potassium iodide decreased the efficiency of photocatalytic ozonation and photocatalyst processes (27.18% and 14.65%, respectively). In fact, adding potassium iodide to the process eliminates the OH and h^+ bonds from the surface [55]. Therefore, it can be concluded that 27.28% and 14.65% of the removal using the photocatalytic ozonation process and photocatalyst process were corresponded by OH and h^+ bonds in the surface of substance and, in fact, was related to surface reactions.

As classic scavenger, t-BuOH is a well-known agent which is applied to scavenge hydroxyl radicals [56]. By adding, the efficiency of photocatalytic ozonation and photocatalyst processes is reduced by 37% and 22%, respectively. Therefore, it was found that about 37% of the photocatalytic ozonation process was due to the hydroxyl radical. But in the same process without the presence of ozone, about 22% of the efficiency is due to the hydroxyl radical.

Fig. 8 Comparison of the efficiency of different processes in removal (a) Pentachlorophenol ($O_3 = 1$ mg/L, $C_0 = 100$ mg/L, pH = 7, nano = 100 mg/L, GT = 1:20) and (b) TOC ($O_3 = 1$ mg/L, $C_0 = 100$ mg/L, pH = 7, nano = 100 mg/L, GT = 1:20)

Fig. 9 The effect of scavengers factors on the efficiency of photocatalytic and photocatalytic-ozonation processes

The presence of sodium azide in the process also inhibits the activity of singlet oxygen ($^1\text{O}_2$) [57]. Since 29 and 17.2% of the efficiency of the photocatalytic ozonation and photocatalyst processes has been reduced in the presence of sodium azide, so it seems that 29% of the efficiency of the photocatalytic ozonation process is related to singlet oxygen contribution, but in the photocatalyst, which applied in absence of ozone, only 17% of efficiency is due to singlet oxygen. Therefore, the most important and dominant factor in the photocatalytic ozonation process is the hydroxyl radical. After that, oxygen singlet and active bands at the surface have been identified to be effective, which the effect of these two factors was almost identical. Furthermore, in the ozone-free processes, i.e., the photocatalytic process studied, the order of mechanism of effect was the same. But the comparison of the efficacy of these two processes shows that the hydroxyl radical in the absence of ozone has about half of the effect on the process compared to the presence of ozone. Also, the effect of the mechanisms in the photocatalytic process is not very different and all the mechanisms studied are equally effective in the photocatalytic process, but in the photocatalytic ozonation process, the hydroxyl radical is the most important factor.

Conclusions

In this study, the capability of photocatalytic ozonation using graphene-titanium dioxide nanocomposite in removing PCP from aqueous solutions was investigated and the effect of some operational parameters on the efficiency of the process was assessed to determine the optimum conditions. The results showed that by increasing the catalyst dosage, contact time and concentration of soluble ozone and decreasing PCP concentration, the PCP removal efficiency was increased. The optimum catalyst ratio was determined to be 1:20. The most important and dominant factor in the photocatalytic ozonation process was hydroxyl radical. After this agent, the singlet and active bands were effective, which the effect of these two factors was approximately similar. In addition, the results also showed that UV/G-TiO₂/O₃ process is a very efficient process and the graphene-dioxide titanium nanocomposite can be used in photocatalytic process and particularly in the photocatalytic ozonation process for removal of resistant organic compounds such as PCP.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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