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Pentachlorophenol degradation in the heterogeneous catalytic ozonation process using Al₂O₃ as a catalyst agent

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ABSTRACT

In this study, an investigation of the catalytic ozonation of pentachlorophenol (PCP) in the presence of aluminum oxide (Al₂O₃) and the formation of byproducts during the ozonation has been done. From the results, it is clear that catalytic ozonation in the presence of Al₂O₃ can substantially enhance the efficiency of the PCP degradation to a higher degree than when the ozonation process alone is used. Several environmental parameters, including the pH of the solution, initial PCP concentration, Al₂O₃ dosage and dissolved ozone concentration were also investigated in terms of their influence. The highest efficiency of PCP degradation (100% degradation) was achieved under the conditions mentioned, namely, pH 8, 1.87 g/L Al₂O₃, and 0.49 g/L dissolved ozone concentration. Further, the role played by the catalyst used was demonstrated. The catalytic action of the Al₂O₃ was linked to a highly hydroxylated surface. The surface hydroxyl groups on the Al₂O₃ were, in fact, the active sites during catalytic ozonation. According to the drastic changes in the solution color observed during ozonation in this study and from the results of some earlier researches, the formation of intermediate reaction products during ozonation was verified. The free chloride ions released, especially when the solution was slightly alkaline, was also studied in the catalytic ozonation process.

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1. INTRODUCTION

Pentachlorophenol (PCP), a highly toxic phenolic compound, is a white or brown organic solid, with needle-like crystals and a characteristic phenolic odor.[1] The most popular uses of PCP areas are as wood preservative and biocide. In fact, PCP ranks among the high priority pollutants featured on the list of the United States Environmental Protection Agency and is subject to a stringent maximum contaminant level (MCL) of 0.001 mg L⁻¹ set for drinking water. This pollutant is extremely toxic, refractory, and difficult to remove via conventional treatment processes [2][24]

Ozone is a powerful oxidant and an effective purifier, highly used in water and wastewater treatments. The ozonation treatment, particularly, is extensively employed to mineralize the organic pollutants in water. However, when ozone is used alone, mineralization is not completely effective and a few toxic and resistant byproducts (such as ketone, aldehyde, carboxylic acid, and bromate) are released.[3][4] To mitigate these problems, advanced oxidation processes (AOPs) have been developed to enable various classes of these organic compounds to be degraded. Pollutant removal by the AOP method is based on the production of free hydroxyl radicals having a high oxidation potential, facilitating the oxidation of most of the organic compounds. The Catalytic Ozonation Process (COP) is one among the AOP methods, and a new

one, at that. In this process, a catalyst is employed to increase the ozone decomposition, resulting in the formation of highly reactive hydroxyl radicals [7]. In COP, a variety of catalysts have been applied, including activated [5][6] magnesium oxide supported on alumina [7], natural sand, and zeolite [8]. Among these materials, aluminum oxide (Al₂O₃, alumina), activated alumina, and metal oxides supported on alumina have been used in ozonation, with success. A few catalysts like Al₂O₃, Fe₂O₃/Al₂O₃, CO₃O₄/Al₂O₃, and TiO₂/Al₂O₃ have been used to accelerate the decomposition process of the phenols, carboxylic acids, and phenolic [9][10][23]. The efficiency of a catalyst depends upon the method of its preparation [11]. Some studies propose that the ozonation of the PCP causes the production of some intermediate compounds, particularly, tetrachloro-p-hydroquinone (TCHQ), tetrachloro-p-benzoquinone (TCBQ), and tetrachlorocatechol (TCCA) [12]. As the reduction of the byproducts during any treatment process is an environmental necessity, the World Health Organization has established MCLs not only for parent compounds but also for their degradation byproducts, in different steps and types of water treatment [13]. Thorough knowledge regarding the formation of byproducts during ozonation will assist in optimizing any post-ozonation unit by providing information on the composition of the degradation products. In this work, PCP has been selected as a target compound. The main objectives of this paper are to investigate the catalytic activity of the Al₂O₃ and study the byproduct formation during PCP ozonation.

2. MATERIALS AND METHODS

2.1 Chemicals

For the experiments, the PCP sodium salt (Na-PCP, >98% purity) and Al₂O₃ were obtained from Sigma Aldrich Chemical Company (USA). Prior to use, the alumina particles were washed thoroughly using boiling distilled water for 2 h and oven-dried at 110 °C for 48 h. The stock PCP solution was prepared by dissolving the PCP in NaOH solution to accelerate its dissolution. Also, Al₂O₃ had a particle size of 67 nm, and a specific surface area of 109 m² g⁻¹, based on the tests conducted using Brunauer-Emmett-Teller (BET) model.

2.2 Determination of PCP Concentration

The PCP concentration was analyzed by HPLC (Model Wellchrom, Knauer, Germany) using the Waters-C18 column with the UV detector (Model UV-K 2600, Knauer, Germany). The detection was performed at 254 nm, and the mobile phase was a mixture of 60:40 acetonitrile and 1% aqueous acetic acid, with a 0.5 mL min⁻¹ flow rate. An injection volume of 50 cc was used for all the samples. Besides, the COD concentrations during the reaction were determined using the standard potassium dichromate oxidation methodology, and the ozone concentration in the inlet gas stream was quantified via the iodometric titration method [14]. The chloride (Cl⁻) ions were estimated by potentiometry using a chloride selective electrode (Mettler Toledo).

2.3 Methods

In this study, the effectiveness of the Sole Ozonation Process (SOP) and COP using Al₂O₃ to remove the PCP from the aqueous solutions, as well as the intermediate compounds produced, were evaluated. We also investigated the influence of the various parameters of reaction time (3–60 min), pH (3, 8, and 10) and ozone solution dosage (change rate in the range of oxygen generators 1–5 mL oxygen min⁻¹) in both process and the catalyst dose (0.1–1.0 g) in the COP process. In order to test and determine the optimal conditions, a solution of the PCP of the specified concentration and pH within the reactor was ozonated, and sampling was done at 3 minute intervals to determine optimal time for ozonation. This experiment was also performed in a SOP reactor. Next, further tests were conducted to assess the other optimal parameters (reaction time, catalyst dosage, and ozone solution dosage), and the COD test was also performed to determine the rate of removal of the PCP. In this study, the ARDA generator (COG-1A, France) of 5 g h⁻¹ capacity was used for ozonation of the samples. All the experiments were conducted using several conical flasks of 1000 mL volume. The equation given below is used to calculate the removal efficiency of the PCP:

$$PCP\ Removal\ \% = \frac{initial\ PCP\ concentration - final\ PCP\ concentration}{initial\ PCP\ concentration} \dots\dots (1)$$

2.4 Determination of Point Of Zero Charge of Catalyst Used

The point of zero charge (pH_{pzc}) of the aluminum oxide was determined using the conventional method. Briefly, the initial pH values of 50 mL of 0.1 M NaCl were adjusted in the range of 2 to 12 using 1 M HCl or NaOH solutions with the assistance of the pH meter values. Next, 0.5 g of aluminum oxide was added to each solution and the suspensions thus obtained were shaken for 48 h. The aluminum oxide was

filtered and the final pH of the solution was estimated. The pHPzc value of the aluminum oxide was observed from the intersection of the curve of the final vs. the initial pH.

3. RESULTS AND DISCUSSION

3.1. The HPLC-UV analysis

The HPLC-UV chromatograph of the PCP prior to and post the ozonation process is shown in Figs. 1a and 1b. As depicted in Fig. 1b, after ozonation, besides the PCP peak, three other peaks could be detected before the main peak. These three peaks indicate intermediate production during ozonation. The PCP ozonation has been investigated by several researchers. Hong and Zeng (2002) reported that TCHQ and TCBQ were the most important byproducts. These byproducts were degraded even more by the ozone into ketones and organic acids. Other studies revealed that the TCHQ, TCBQ, and TCCA were identified as the three main intermediate compounds produced during PCP ozonation [15][16]. The molar ratio of ozone to PCP was identified as an effective parameter during degradation [16]. Therefore, based on the findings of the studies cited above, it can be concluded that the secondary peaks observed in this study are related to the intermediate byproducts (most likely to the production of TCHQ, TCBQ, and TCCA) [16, 20].

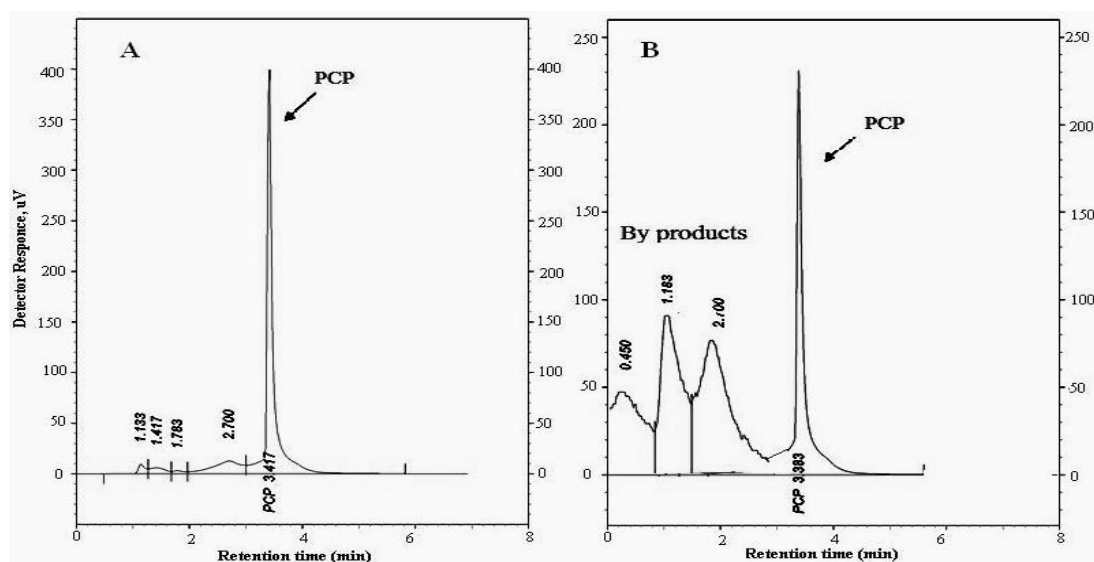


Fig. 1-(a) HPLC–UV chromatogram of PCP before ozonation and (b) HPLC–UV chromatogram of PCP and byproducts after ozonation [PCP concentration, 200 mg/L, and reaction time 6 min].

3.2. Effect of Solution Ph

In this study, the pHPzc value determined of the Al_2O_3 used was 8.6. The effect of the pH of the initial solution (3, 8, and 10) on the degradation of PCP in SOP and COP was investigated. Indeed, Fig. 2 represents the effects of the pH on PCP degradation in COP and SOP. As evident, after 15 min and at pH 10, it is clear that 83 and 100% of the PCP were removed in SOP and COP, respectively. These findings indicate that the oxidation of the PCP in both processes, under the experimental conditions applied, was raised by increasing both the pH and reaction time. Also, at different pH readings, the PCP removal in COP was higher than in SOP, overall. Furthermore, the results confirmed the influence of the pH on drastic changes in color of the PCP solution during ozonation. Therefore, at pH 3 the solution color changed from yellow to orange, at pH 8 it became brownish orange, and at pH 10 it was dark brown.

In heterogeneous catalytic ozonation, the surface properties including the pHPzc and density of the hydroxyl groups on the catalyst surface play an important part in the ozonation process. The metal oxide surfaces would absorb the water molecules via their unsaturated electrons, resulting in the formation of the hydroxyl groups on the surface. The pH of the solution is one of the most crucial factors which affects the surface properties of the metal oxides, including Al_2O_3 . The surface hydroxyl groups displayed different charge properties at different solution pH readings [17][18]. Therefore, the pH of the solution is one among the principal effective factors in metal oxides such as Al_2O_3 and ozone decomposition. In their study, [19] explored the influence of the surface properties of Al_2O_3 on the catalyzed ozonation of 2,4,6-trichloroanisole (TCA). They identified that the pH of the solution more effectively influenced the rate of the catalytic

ozonation of TCA, in the presence of Al_2O_3 . Therefore, when the solution pH was close to the pH_{pzc} of the Al_2O_3 , the oxides revealed the maximum effect on the ozone. Therefore, the zero charge surfaces of the Al_2O_3 were more active than the electropositive or electronegative surfaces during the catalytic ozonation of TCA. Hence, based on the findings of the current study, and on the pH_{pzc} of the alumina (8.6), as well as due to the economic issues caused by the rising pH, more experiments were performed at pH 8. Also, the effects of different values of the pH (3, 8, and 10) were observed to produce drastic changes in the color of the PCP solution during ozonation, consistent with the results reported by [12]. In their study and within the first 7 minutes of ozonation, the PCP solution changed color from yellow to red, due to the production of ketones and kinone-organic compounds, and then within 45 minutes, the intensity of the solution color gradually decreased. They also assessed the color change in the solution by alterations in the optical absorption spectrum. They found that the optical spectra and changes in the absorption were quite different at various pH readings during ozonation, which was due to the generation of byproducts and balance of the organic acids.

The chloride anion was another experimental reaction product. The Cl^- release was also different at different pH levels (3, 8, and 10). The maximum of Cl^- concentration was obtained at pH 10, which was 66 mg/L after the PCP was completely degraded (initial concentration = 200 mg/L) at 15 minutes of the ozonation process. The results of this experiment are revealed in Fig. 3.

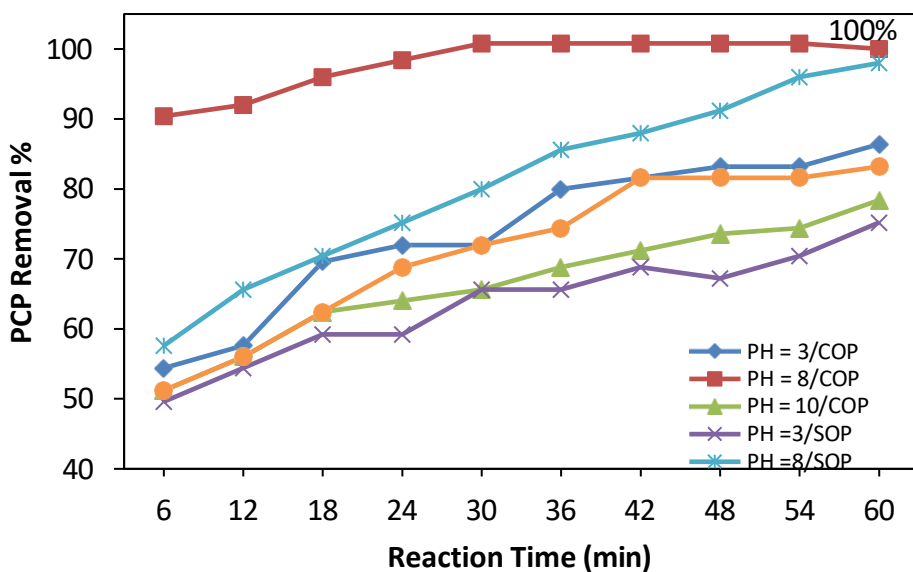


Fig. 2- Effect of the initial pH on PCP removal from aqueous solutions using the SOP and COP treatment methods [PCP concentration 200 mg/L, solution volume 400 mL, catalyst dosage 0.75 g, and dissolved ozone emission rate 0.49 mg/min].

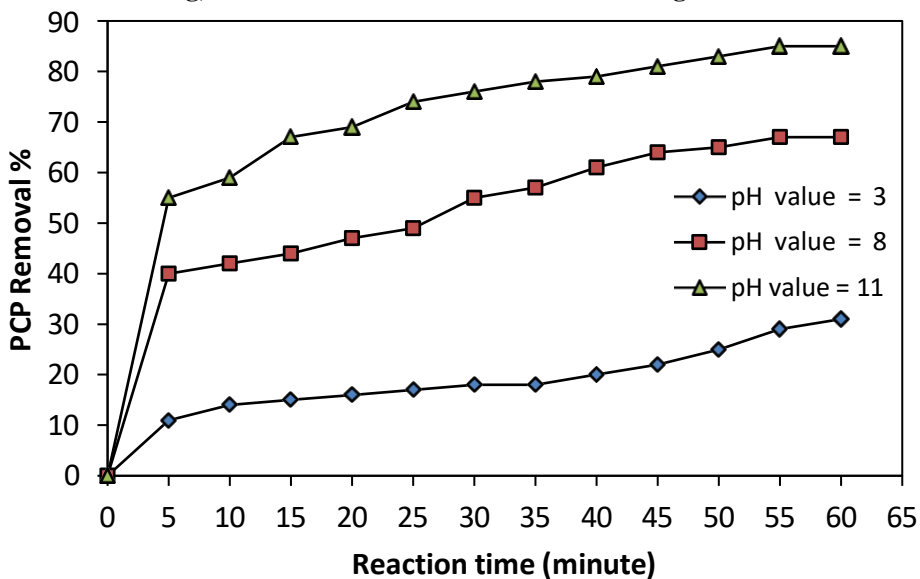


Fig. 3-The chloride concentrations determined throughout the ozonation of PCP at different pH values [PCP concentration 200 mg/L, catalyst dosage 1.87 g/L, and dissolved ozone emission rate 0.49 mg/min].

In the SOP, the rate of degradation of the PCP was found to rise with the increase in the pH values from 3 to 8. This can be explained by the fact that the decomposition of the ozone molecules rises as the pH increases. However, the PCP removal was much faster in the COP than in the SOP, confirming the positive effect of the combination of ozonation and Al₂O₃ in the degradation of toxic compounds, such as PCP.

An experiment was also performed to bring more clarity to the role played by the Al₂O₃ in the COP. In this experiment, Al₂O₃ saturated with PCP was used as a replacement for a fresh one. The PCP removal percentages did not differ much from those obtained with the use of fresh Al₂O₃, under the same experimental conditions. These findings suggest its catalytic role in the degradation process, which is the dominant reaction in the COP, rather than an adsorption-oxidation [20]. It also demonstrates the effect of the Al₂O₃ with ozonation in the removal of PCP. In Fig. 4 the removal of PCP in the COP, SOP, and single Al₂O₃ (adsorption) systems using the same PCP concentration are evaluated, at pH 8, and an Al₂O₃ dosage of 1.87 g L⁻¹.

Besides, all three processes were compared in terms of their removal efficiencies for PCP, namely the COP, SOP, and adsorption processes. It is evident that the COP has highest removal efficiency. This finding reveals the benefit of using both the ozonation process and Al₂O₃ as a catalytic agent for PCP degradation. Also, it is clear that 100% degradation can be achieved at 60 minutes of reaction time. Thus, the effect of the catalyst dose should be further studied.

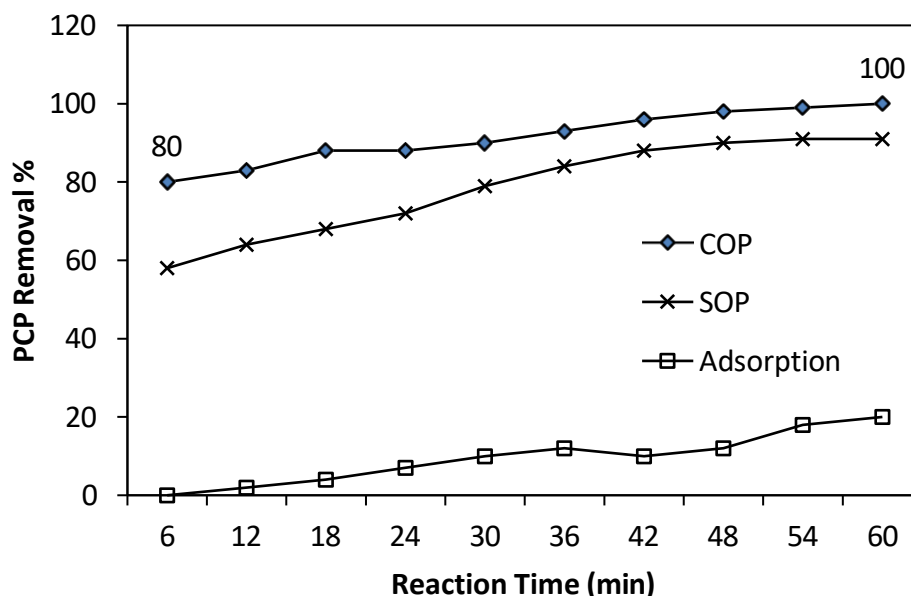


Fig. 4 - A comparison among the use of COP, SOP, and adsorption employing only Al₂O₃ for the PCP removal [PCP concentration 200 mg/L, catalyst dosage 1.87 g/L, pH 8, and ozone emission rate 0.49 mg/min].

3.3. Effect of Al₂O₃ Dosage

The removal of PCP was investigated for the ozonation process in the presence of different doses of Al₂O₃, in the range of 0.05 to 1g in 400 mL of the PCP solution. In Fig. 5 the removal of PCP induced by the Al₂O₃ dosage, is shown, indicating a considerable enhancing effect of the Al₂O₃ on the ozonation process. As evident from Fig. 5, at the reaction time of 30 min, the PCP removal increased from 57% in the presence of 0.05 g of Al₂O₃ to 97% in the presence of 1g (2.5 g/L) of Al₂O₃. The escalation in the PCP degradation during the catalytic ozonation process was induced by an increase in the ozone decomposition which had occurred on the Al₂O₃ surface, resulting in the increased density of the free hydroxyl radicals on the alumina surface. These findings are commensurate with Qi et al., (2009) who revealed that during the catalytic ozonation process by solid metal oxides, the surface hydroxyl groups are the active sites for the catalytic reactions. The surface charge position of the surface hydroxyl groups determines the catalytic activity during catalytic ozonation. Therefore, by increasing the dosage of the solid metal oxide, the density of the surface free hydroxyl radicals will also increase. Thus, in the COP, the increase in the dosage of the solid metal oxide together with the increase in the density of the surface free hydroxyl radicals caused the high degradation of the PCP.

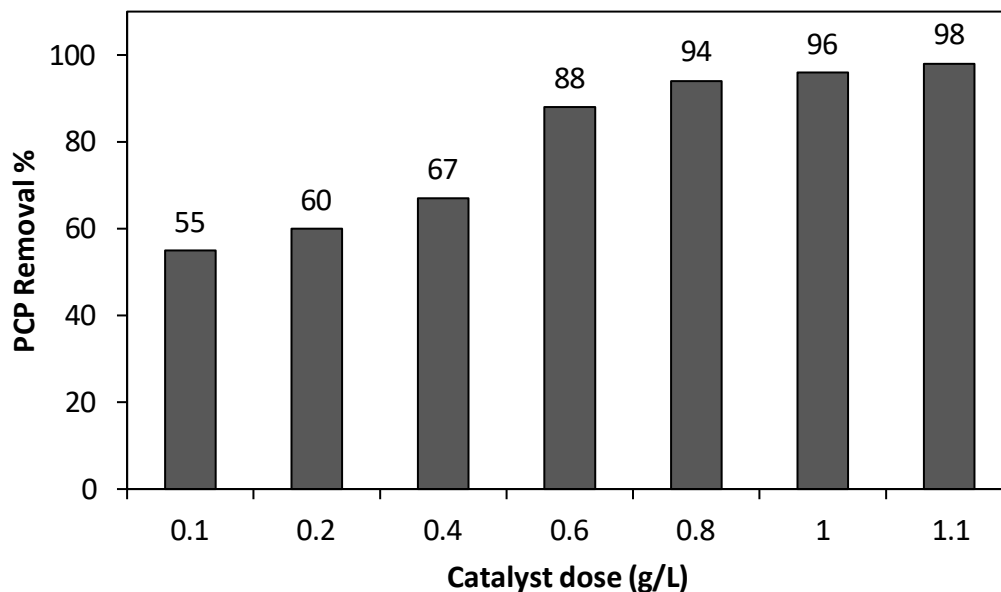


Fig. 5 - Effect of the alumina dosage on PCPs from aqueous solutions in the COP [PCP concentration 200 mg/L, solution volume 400 mL, pH 8, dissolved ozone dosage 0.49 mg/min, and reaction time 30 min].

3.4 COD and PCP Removal Using COP Process With The Ph

The removal of COD in COP from wastewater was assessed at the optimum conditions of pH and Al₂O₃ to determine the effectiveness of the process for the degradation of the organic intermediates of the reaction. According to Fig. 7, the removal efficiency of the COD in COP was 55% within the first 15 min, which increased to 81% after 30 min. The COD removal was slightly slower than the PCP removal in COP, and the final pH of the solution at different times during the ozonation process was significantly reduced. This fact can be explained because for the former to complete oxidation, and particularly during the first few minutes of the reaction, the compound is converted to some organic intermediates, including benzoquinone and acetic acid [21]. While the PCP is thus considered as having been removed, the intermediates continue to add to the COD. The higher the oxidation, the simpler are the acidic intermediates formed, and hence, the more the pH decreases, and/or the more simple are the intermediates mineralized, thereby reducing the COD [22]. The fast decline in the pH of the solution versus the reaction time (Fig. 6) confirms the formation of the acidic intermediates during the oxidation of PCP [12] also reported the production of intermediate compounds, such as organic acids during the PCP ozonation and a lowering of the final pH of the solution.

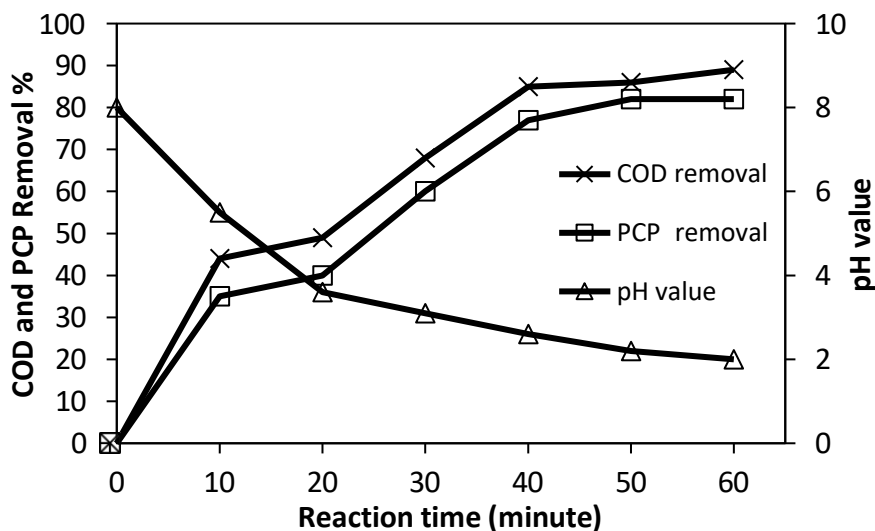


Fig. 6 COD and PCP removal using COP with simultaneous readings of the solution pH values [catalyst dosage 1.87 g/L, pH 8, dissolved ozone emission rate of 0.49 mg/min, and PCP concentration 200 mg/L].

3.5. Effect of Ozone Emission Rate

The effect of the ozone dosage on PCP removal that was present or discharged during catalytic ozonation (with 0.75 g catalyst in 400 mL of the solution) was investigated by regulating the dial-up setting of the oxygen generator. The concentration of ozone in the solution then was determined via the iodometric method. As shown in Fig. 7, the PCP degradation rises with the increase in the ozone concentration in the solution. For instance, the PCP removal escalated from 33 to 88% in 0.17 and 0.49 g/min of ozone concentration, at 30 min reaction time. The escalation in the PCP degradation in response to the increasing ozone dosage is related to the rise in the production of highly reactive free hydroxyl radicals, thereby boosting the PCP degradation. It is evident that the COP process is clearly more efficient than the SOP process in terms of PCP removal.

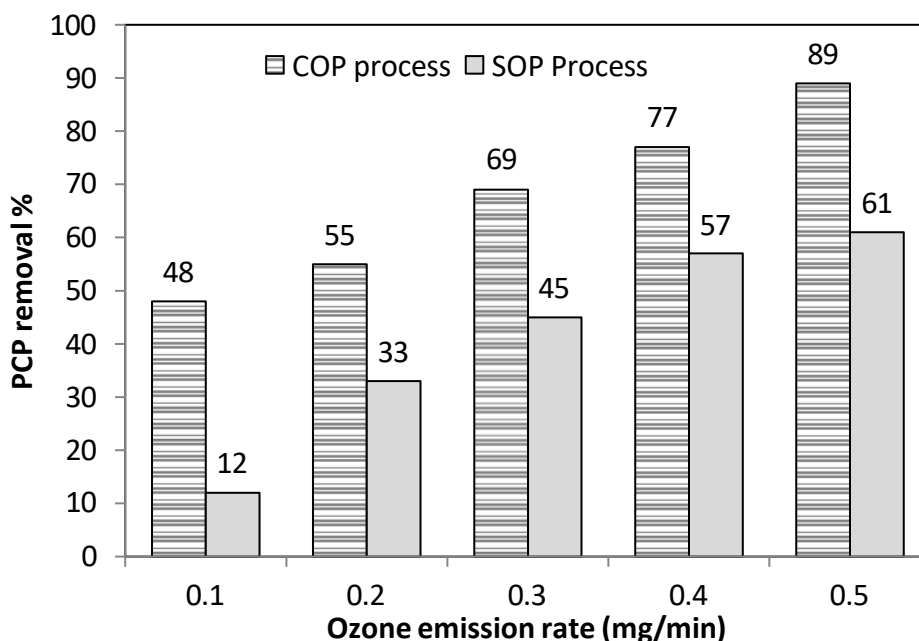


Fig. 7 Effect of the soluble ozone dosage on PCP removal from aqueous solutions using the SOP and COP processes [PCP concentration 200 mg/L, pH 8, catalyst dosage 0.75 g/L, and contact time 30 min].

4. CONCLUSIONS

In this study, the capacity of the catalytic ozonation process (COP) using activated alumina for the PCP removal from aqueous solutions was investigated. Activated alumina is demonstrated to improve the removal efficiency of the PCP via ozonation. The zero charge surfaces of the Al₂O₃ were more active during the catalytic ozonation of PCP. The densities of the surface hydroxyl groups also vitally affected the catalytic ozonation process. The results demonstrated that the COP could reduce the PCP and COD concentrations from about 200 and 400 mg/L to 35 and 180 mg/L, respectively, after 15 min of reaction time. Besides, COP showed greater efficiency than the sole ozonation process for PCP removal. The complete degradation of the PCP pollutant was achieved under optimized conditions. For further work in the future, a kinetic study should be implemented.

5. ACKNOWLEDGMENTS

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