



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

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A B S T R A C T

In this study, the catalytic ozonation of pentachlorophenol (PCP) in the presence of aluminum oxide (Al₂O₃) and the formation of byproducts during ozonation has been studied. Results showed that catalytic ozonation in the presence of Al₂O₃ can substantially enhance PCP degradation efficiency compared with the using only ozonation process. The influences of several environmental parameters including pH of the solution, initial PCP concentration, dosage of Al₂O₃ and dissolved ozone concentration were also investigated. The highest degradation efficiency of PCP was achieved at conditions: pH 8, 1.87 g/L Al₂O₃, and 0.49 g/L dissolved ozone concentration. The catalytic activity of Al₂O₃ was linked to highly hydroxylase surface. The surface hydroxyl groups on Al₂O₃ were the active places during catalytic ozonation. According to the drastic changes in the color of solution during ozonation this study and results of some previous researches, formation of the intermediate reaction products during ozonation was verified. Free chloride ion released, which was favored at slightly alkaline solution, was also followed in catalytic ozonation process.

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Introduction

Pentachlorophenol (PCP), a highly toxic phenolic compound, is a white or brown organic solid with needle-like crystals and a phenolic odor [1]. The greatest use of PCP is as a wood preservative and biocide. PCP is one of the pollutants that have been placed on the United States 'Environment Protection Agency's list of priority pollutants and subject to a stringent maximum contaminant level (MCL) of 0.001 mg L⁻¹ set for drinking water. However, it is highly toxic, refractory, and hard to remove by conventional treatment processes [2,3].

Ozone is a powerful oxidant and an effective purifier in water and wastewater treatment. Especially, ozonation treatment is widely applied to mineralize organic pollutants in water. However, when ozone is used alone, mineralization is not completely effective and also, some toxic and resistant byproducts (such as ketone, aldehyde, carboxylic acid, and bromate) are generated [4-6]. To reduce these problems, advanced oxidation processes (AOPs) have been developed for the degradation of various classes of these organic compounds. Removing pollutants by AOP method is based on the production of free hydroxyl radicals with high oxidation potential which oxidize most of the organic compounds. Catalytic ozonation process (COP) is one of and new AOP method. In this process, for increased ozone decomposition a catalyst is applied, consequently forming highly reactive hydroxyl radicals [7]. In COP,

variety of catalysts have been applied such as activated alumina [8, 9] magnesium oxides supported onto alumina [7], natural sand, and zeolite [10]. Among these materials, aluminum oxide (Al₂O₃, alumina), activated alumina, and metal oxides supported onto

alumina have been used successfully in ozonation. Some catalysts such as Al₂O₃, Fe₂O₃/Al₂O₃, CO₃O₄/Al₂O₃, and TiO₂/Al₂O₃ have been used to accelerate the decomposition process of phenols, carboxylic acids, and phenolic compounds [11-14]. Efficiency of a catalyst depends on the method of its preparation [13]. According to some researches, it should be mentioned that the ozonation of PCP causes the production of some intermediate compounds, especially tetrachloro-p-hydroquinone (TCHQ), tetrachloro-p-benzoquinone (TCBQ), and tetrachloro catechol (TCCA) [15, 16]. Since the reduction of byproducts during any treatment process is environmentally necessary, World Health Organization has established MCLs not only for parent compounds but also for their degradation byproducts in different steps and forms of water treatment [17]. Knowledge on the formation of byproducts during ozonation would help optimize any post-ozonation unit by providing information on the composition of degradation products. In this work, PCP has been selected as a target compound. The main aims of this paper are to investigate the catalytic activity of Al₂O₃ and study of the byproduct formation during PCP ozonation.

Materials and methods

Chemicals

PCP sodium salt (Na-PCP, >98% purity) and Al₂O₃ was obtained from Sigma Aldrich Chemical Company (USA). Also, Al₂O₃ had a particle size of 58 Å, The Brunauer, Emmett, and Teller (BET) surface area of 155 m² g⁻¹. Before use, alumina particles were thoroughly washed with boiling distilled water for 2 h and dried in an oven at 110 °C for 48h. The stock solution of PCP was

prepared by dissolving PCP in NaOH solution to accelerate its dissolution.

Determination of PCP concentration

Concentration of PCP was analyzed by HPLC (Model well chrome, Kenauer, Germany) using the Watters-C18 column with the UV detector (Model UV-K 2600, Kenauer, 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. The injection volume was 50 cc in all samples. In addition, the COD concentrations during the reaction were measured with a standard potassium dichromate oxidation methodology, and the ozone concentration in the inlet gas stream was quantified by iodometric titration [18]. Chloride (Cl⁻) ions were measured by potentiometer via a chloride selective electrode (Metler Toledo).

Methods

In this study, the effectiveness of sole ozonation process (SOP) and COP using Al₂O₃ for the removal of PCP from aqueous solutions and the intermediate compounds produced were evaluated. Also, the influence of various parameters such as reaction time (3–60 min), pH (3, 8, 10) and ozone solution dosage (change rate in the range of oxygen generators 1–5 mL oxygen min⁻¹) in both process and catalyst dose (0.1–1.0 g) in the COP process was studied. In order to perform tests and determine the optimal conditions, a solution of PCP with the defined concentration and pH inside the reactor was ozonized and sampling was performed at 3 min intervals to determine optimal time for ozonation. This experiment was also performed in a SOP reactor. Then, other tests were performed to determine other optimal parameters (reaction time, catalyst dosage,

and ozone solution dosage), and COD test was also done to determine the rate of PCP removal. In this study, ARDA generator (COG-1A, France) with a capacity of 5 g h⁻¹ was used for ozonation of samples. All experiments were carried out using several conical flasks with a volume of 1000 mL.

The following equation is used to calculate the PCP removal efficiency:

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

Determination of point of zero charge of used catalyst

Point of zero charge (pHpzc) of aluminum oxide was determined by conventional method. Briefly, initial pH values of 50 mL of 0.1 M NaCl were adjusted in a pH range of 2 to 12 using 1 M HCl or NaOH solutions with the helpful of pH meter readings. Afterward, a 0.5 g of aluminum oxide was added to each solution and the obtained suspensions were shaken for 48 h. Aluminum oxide was filtered and the final pH of the solution was measured. The value of pHpzc of aluminum oxide was found from the intersection of the curve of final vs. initial pH.

Results and discussion

The HPLC-UV analysis

The HPLC-UV chromatograph of PCP before and after ozonation process has been presented in Fig. 1a and 1b. As shown in Fig. 1b, after ozonation, in addition to PCP peak, other three peaks were detectable before the main peak. These three peaks indicate intermediate production during ozonation. Ozonation of PCP has been studied by numerous researchers. Hong and Zeng [19]

showed that the TCHQ and TCBQ were the most important byproducts. These byproducts were more degraded by ozone into ketones and organic acids. Other studies showed that TCHQ, TCBQ, and TCCA were found as three main intermediate compounds during PCP ozonation [16, 20]. The molar ratio of ozone to PCP was identified as an

effective parameter in the degradation process [20]. Therefore, according to the findings of aforementioned studies, it can be concluded that observed secondary peaks in this study are related to the intermediate byproducts (likely production of TCHQ, TCBQ, and TCCA) [16, 20].

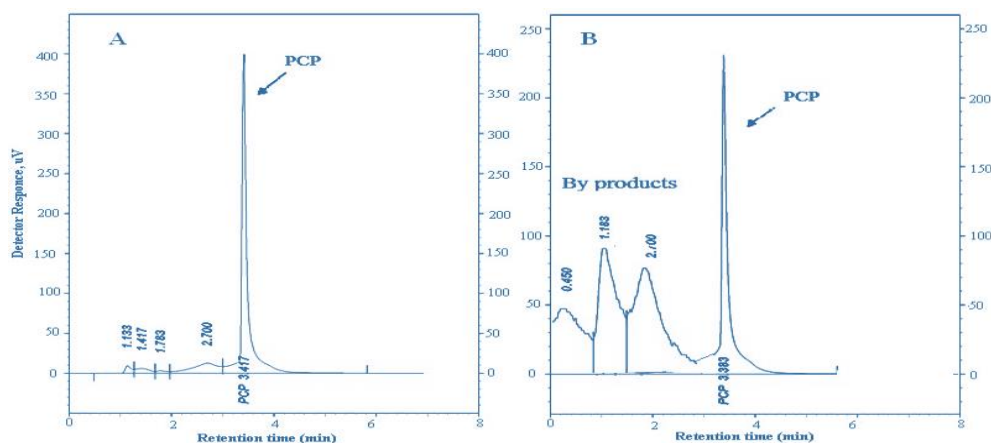


Fig. 1, (a) HPLC–UV chromatogram of PCP

Before ozonation and (b) HPLC–UV chromatogram of PCP and byproducts after ozonation [PCP concentration, 200 mg/L, reaction time 6 min]

Effect of solution pH

In this study, the determined pH_{pzc} value of used Al_2O_3 was 8.6. The effect of initial solution pH (3, 8, and 10) was investigated on the degradation of PCP in SOP and COP. Fig. 2 represents the effects of pH on PCP degradation in COP and SOP. As can be seen, after 15 min and in pH 10, 83 and 100% of PCP was removed in SOP and COP, respectively. These findings indicate that oxidation of PCP in both processes under the applied experimental conditions was increased by increasing pH and reaction time. Also, at different pH points, the PCP removal in COP was overall higher than SOP. Furthermore, the results confirmed the

influence of pH on drastic changes in color of the PCP solution during ozonation. So, the solution color changed from yellow to orange at pH 3, to brownish orange at pH of 8, and to dark brown at pH of 10.

In heterogeneous catalytic ozonation, surface properties including pH_{pzc} and the density of the hydroxyl groups on catalyst's surface have an important function in the ozonation process. Surface of metal oxides would absorb water molecules due to their unsaturated electrons which cause the formation of hydroxyl groups on the surface. Solution pH is one of the most important factors affecting the surface properties of metal oxides including Al_2O_3 . The surface hydroxyl groups showed different charge properties at different solution pH [21, 22]. Therefore, pH of solution is one of main effective factors in metal oxides such as Al_2O_3 and ozone decomposition. Fei et al.

[23] studied the influence of Al₂O₃ surface properties on catalyzed ozonation of 2,4,6-trichloroanisole (TCA). They found that the solution pH was more effective on the rate of catalytic ozonation of TCA in the presence of Al₂O₃. As when solution pH is closed to pH_{zpc} of the Al₂O₃, the oxides revealed the maximum effect on ozone. Therefore, zero charge surface of Al₂O₃ was more active than electropositive or electronegative surface in catalytic ozonation of TCA. Hence, based on the results of our study, according to the pH_{zpc} of alumina (8.6) and due to the economic problems caused by the increasing pH, the more experiments were carried out at pH of 8. Also, the effects of different pH (3, 8, and 10) resulted in drastic changes in the color of PCP solution during ozonation that is consistent with the result of Hong et al. [19]. In their study and within the first 7 min of ozonation, color of PCP solution was shifted from yellow to red due to the production of

ketones and kinneorganic compounds, and then within 45 min, the color intensity of the solution was gradually reduced. They also assessed the change in color of the solution by changes in the optical absorption spectrum and indicated that optical spectra and changes in its absorption is quite different at various pH points during ozonation caused by generation of byproducts and balance of organic acids at different pHs.

Chloride anion was another experimental reaction product. The release of Cl⁻ was dissimilar in different pHs (3, 8, and 10). The maximum of Cl⁻ concentration was obtained at pH 10, which amounted to 66 mg/L after complete degradation of PCP (initial concentration = 200 mg/L) at 15 minutes of ozonation process. The results of this experiment are depicted in Fig. 3.

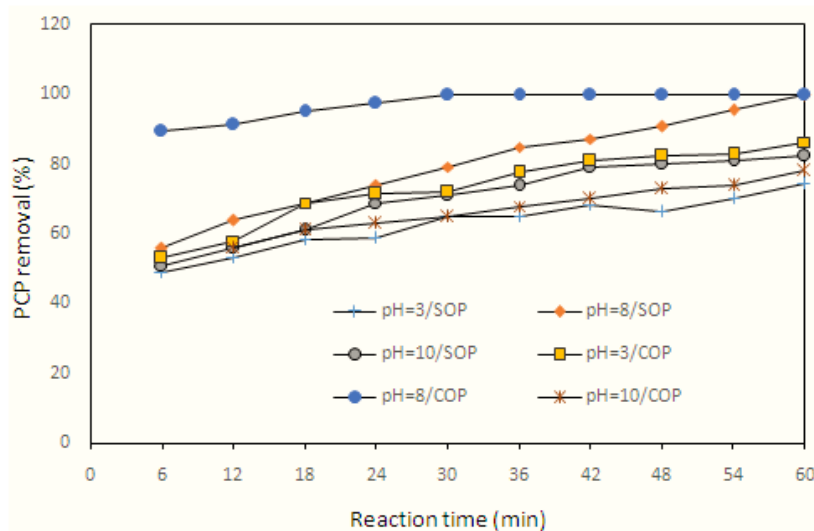


Fig. 2 Effect of initial pH on PCP removal from aqueous solutions using SOP and COP treatment methods [PCP Concentration 200 mg/L, solution volume 400 mL, catalyst Dosage 0.75 g, dissolved ozone emission rate 0.49 mg/min]

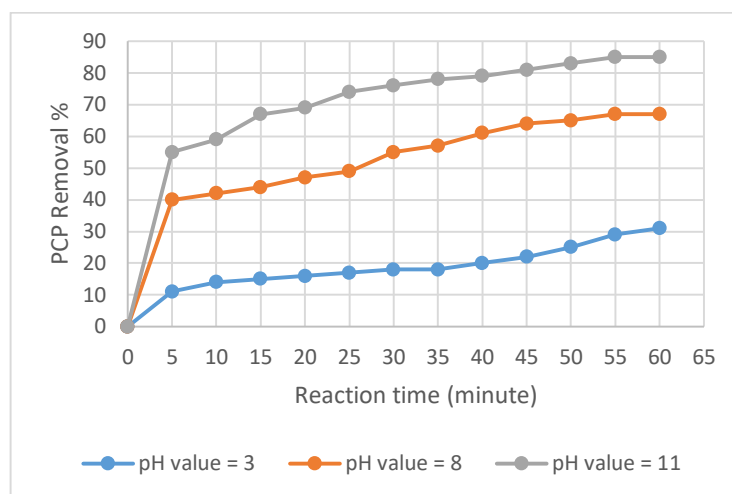


Fig. 3 Concentrations of chloride that measured throughout ozonation of PCP at different pH values [PCP concentration 200 mg/L, catalyst dosage 1.87 g/L, dissolved ozone emission rate 0.49 mg/min]

In the SOP, the degradation rate of PCP was increased with increasing pH values from 3 to 8. It can be explained by the information that the decomposition of ozone molecules increases with increasing pH. However, the PCP removal was extremely faster in the COP than the SOP, confirming the positive effect of combination ozonation and Al₂O₃ to degrade toxic compounds such as PCP.

Also, it was carried out an experiment to clarify more the role of Al₂O₃ in the COP. In this experiment a Al₂O₃ saturated with PCP was used as a replacement for a fresh one. The PCP removal percentages did not digress much from those obtained with the fresh Al₂O₃ at the same experimental conditions. These findings suggest that the

catalytic role in the degradation process which is the dominant reaction in the COP rather than adsorption-oxidation one [24] and shows a synergistic effect of Al₂O₃ with ozonation in the removal of PCP.

Fig. 4 evaluates the removal of PCP in COP, SOP, and single Al₂O₃ (adsorption) systems in the same PCP concentration, at pH 8, and with 1.87 g L⁻¹ Al₂O₃ dosage.

A synergistic effect is detected in combining ozonation and Al₂O₃. For instance, removal efficiency in COP process at 6 and 15 min was 24 and 29% more than sum removal efficiencies in Al₂O₃ adsorption system and SOP, respectively.

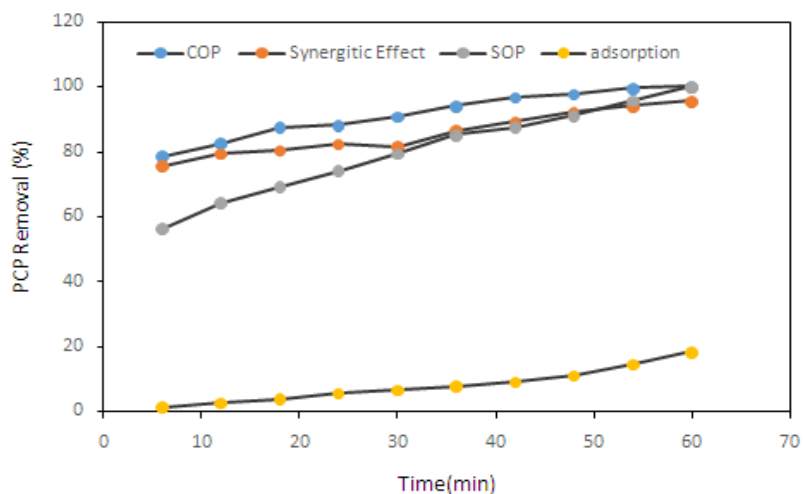


Fig. 4. The effect of Synergitic rate of Al₂O₃ on ozonation process [PCP concentration 200 mg/L, catalyst dosage 1.87 g/L, pH 8, dissolved ozone emission rate 0.49 mg/min]

Effect of Al₂O₃ dosage

The removal of PCP was studied for ozonation process in the presence of different dosages of Al₂O₃ ranging from 0.05 to 1 gram in 400 mL of PCP solution. Fig. 5 shows the removal of PCP as a role of Al₂O₃ dosage, showing a considerable enhancing effect of Al₂O₃ on the ozonation process. As seen in Fig. 5, at 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 increase of PCP degradation in the catalytic ozonation process was caused by an increase in ozone decomposition which occurred in the surface

of Al₂O₃ leading to increased density of free hydroxyl radicals on the surface of alumina. These findings are commensurate with Qi et al. [23] who showed that in catalytic ozonation process by solid metal oxides, surface hydroxyl groups are the active sites for the catalytic reactions. The surface charge position of surface hydroxyl groups determines the catalytic activity in the catalytic ozonation. Therefore, by increasing solid metal oxide dosage, the density of surface free hydroxyl radical will be increased. Thus, in COP, the increase of solid metal oxide dosage equal with increase of density of surface free hydroxyl radical causes high degradation of PCP.

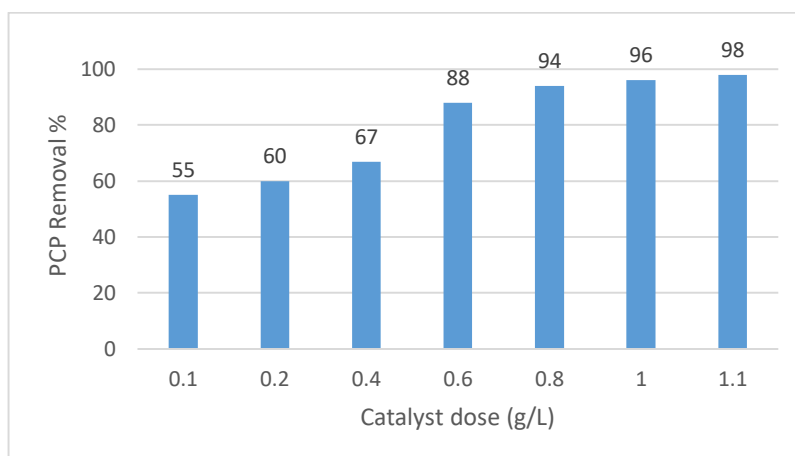


Fig. 5 Effect of alumina dosage on PCP s from aqueous solutions in the COP [PCP Concentration 200 mg/L, solution volume 400 mL, pH 8, dissolved ozone dosage 0.49 mg/min, reaction time 30 min]

COD and PCP removal using COP process with the pH

The removal of COD in COP from a wastewater was evaluated at optimum pH and Al₂O₃ conditions to determine the effectiveness of the process for degradation of the organic intermediates of the reaction. According to Fig. 7, the removal efficiency of COD in COP was 55% within the first 15 min which increased to 81% after 30 min. The COD removal was slightly slower than PCP removal in COP, and the final pH of the solution at different times in ozonation process was significantly reduced. This fact can be explained because former to complete oxidation, and particularly in first minutes of

the reaction, the compound is converted to some organic intermediates, including benzoquinone and acetic acid [25]. The PCP is thus considered removed, but the intermediates still add to the COD. The higher the degree of oxidation, the simpler are the acidic intermediates formed and thus the more pH decreases, and/or the more simple intermediates are mineralized, thereby reducing COD [26]. The fast drop of solution pH versus the reaction time (Fig. 6) verifies the formation of acidic intermediates in the oxidation of PCP. Hong and Zeng[19] also reported production of intermediate compounds such as organic acids within PCP ozonation and decrease of final pH of solution.

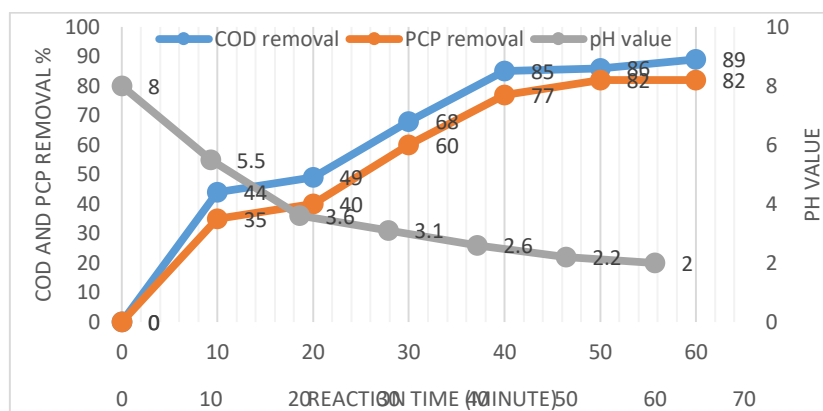


Fig. 6 COD and PCP removal using COP with simultaneous reading of solution pH values [catalyst dosage 1.87 g/ L, pH 8, dissolved ozone emission rate 0.49 mg/min, PCP concentration, 200 mg/L.

Effect of ozone emission rate

The effect of dissolved ozone dosage on PCP removal in the catalytic ozonation (with 0.75 g catalyst in 400 mL of solution) was investigated by regulating the dial-up setting of the oxygen generator. The concentration of ozone in solution then was determined by iodometric method. As shown in Fig. 7, PCP degradation increases with the increase in

ozone concentration in solution. For instance, the removal of PCP increased from 33 to 88% in 0.17 and 0.49 g/min of ozone concentration at 30 min reaction time. The increase in PCP degradation with increasing ozone dosage is related to the increase in the production of highly reactive free hydroxyl radical, thereby PCP degradation is increased. It can be seen that the COP process is efficient than SOP process in PCP removal.

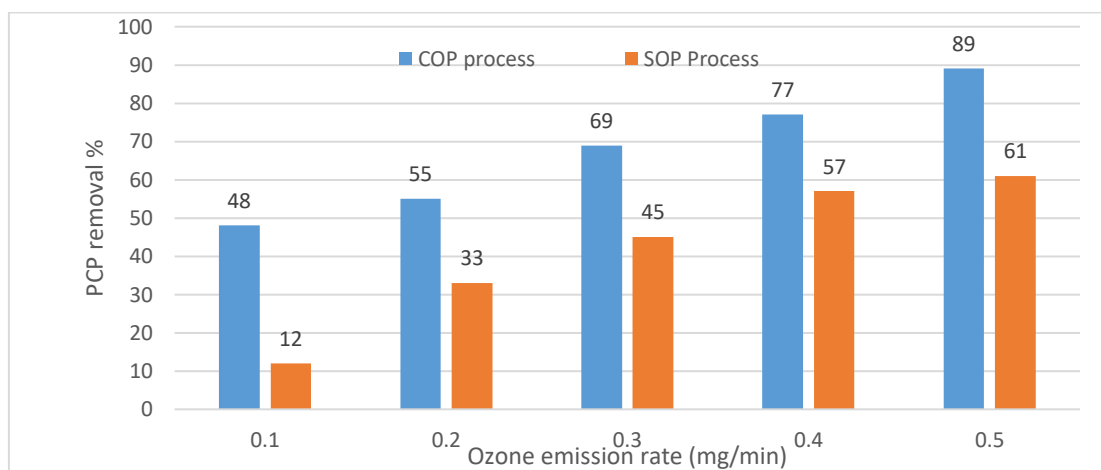


Fig. 7 Effect of soluble ozone dosage on PCP removal from aqueous solutions using SOP and COP processes [PCP Concentration 200 mg/L, pH 8, catalyst dosage 0.75 g/L, contact time, 30 min]

Conclusions

In this study, the capacity of the catalytic ozonation process (COP) with activated alumina for PCP removal from aqueous solutions was studied. Activated alumina is shown to improve the removal efficiency of PCP by ozonation. Zero charge surfaces of Al₂O₃ were more active in catalytic ozonation of PCP. The densities of surface hydroxyl groups also play an important role in the catalytic ozonation. The results demonstrated that the COP could reduce the concentrations of PCP and COD from about 200 and 400 mg/L, respectively, to 35 and 180 mg/L after 15 min of reaction time. In addition, COP has more efficiency than sole ozonation process for removing PCP.

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