# Comparison of the Performance of AOP Method Using $O_3/H_2O_2$ in the Presence of $TiO_2$ and $ZrO_2$ Nano Particles Stabilized on Pumice for the Removal of Pentachlorophenol from Aquatic Solution: Kinetic Studies

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## ABSTRACT

Pentachlorophenol is one of the resistant phenol compounds has classified in the group of the primary pollutants due to its high toxicity and carcinogenic potential. The aim of this study is determining the efficiency of advanced oxidation process method using $O_3/H_2O_2$ in the presence of $TiO_2$ and $ZrO_2$ nano-particles stabilized on pumice for the removal of PCP from aquatic solutions. This experimental study was performed in a batch reactor at laboratory scale. In this study, the effects of reaction time, initial concentration of PCP, pH, concentration of catalysts and $H_2O_2$ and also the amount of decline in chemical oxygen demand (COD) after the process were investigated. The concentration of PCP in the sample was determined using spectrophotometer at wavelength of 500 nm and, in the end, the results were analyzed using SPSS software and according to repeated measures analysis and statistical test of comparative ordered pairs with confidence interval of 95%. Scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR) and x-ray diffraction (XRD) images of modified pumice were taken and the kinetic degree of the processes was also determined. The results indicated that the PCP removal by the both processes increased with increasing reaction time, catalyst concentration, $H_2O_2$ concentration and pH and reduced with decreasing initial PCP concentration. The maximum removal efficiencies by the two processes: $O_3/nZrO_2/H_2O_2$ and $O_3/nTiO_2/H_2O_2$ were 100 and 95%, respectively, in the optimum conditions. The results illustrated that the two studied processes followed the pseudo-second -order kinetic model. Further, the findings revealed that the both processes mentioned in this study were of high capability in removing PCP and they could be used as an appropriate process in removing this organic material.

**Key words:** Pentachlorophenol, Advanced Oxidation, Zirconium Dioxide Nano Particles, Titanium Dioxide Nano Particles, Pumice

## INTRODUCTION

PCP being in the group of primary organic pollutants is one of the derivatives of the phenol family that has been under consideration more than other derivatives of phenol due to containing 5 atoms of chlorine on benzene ring and is considerably used in producing insecticides, wood preservatives, strengthening the wooden bridges and in producing antimicrobial substances [1-3].

Short-term exposure to phenol can lead to poisoning carrying bacteriostatic properties. Meantime, it can damage the liver, kidneys, blood, skin, digestive system, nervous system, stomach and intestines and finally resulting in death. The US Environmental Protection Agency (EPA) has considered o.oo1 mg/l of PCP in drinking water the maximum contaminant level (MCL) [4]. Therefore removal of this organic and hazardous pollutant from aquatic solution is necessary.

Conventional treatment and biological methods are unable to remove PCP. Different physical, chemical and biological methods such as surface adsorption, ultrafiltration, reverse osmosis, wet oxidation, and ion exchange have been used to treat this compound. These methods have disadvantages like high cost, the need for additional treatments, producing the secondary pollution and difficult and complex technologies [4].

Today, advanced oxidation processes (AOPs) are applied to remove many of the pollutants because of their high efficiency and also due to producing the least amount of secondary pollution. These processes are more efficient than the common oxidation ones to remove non-biodegradable organic pollutants.

In these processes, hydroxyl radicals, which are produced at the environment temperature, randomly attack all the organic materials and minerals. Due to the high prices of using AOP processes, in recent years, a modern approach called catalytic ozonation has been introduced, which is of high efficiency for the decomposition of organic materials [5].

To improve and accelerate this type of processes, different materials such as zirconium dioxide, titanium dioxide, zinc sulfide and tin dioxide have recently been used as catalyst in the catalytic oxidation of pollutants in water. Use of catalysts in the processes of advanced oxidation leads to achieving higher efficiency in shorter time periods. The nanoparticles of $TiO_2$ and $ZrO_2$ due to high specific surface and nano metric size are considered appropriate catalysts, but since using these elements and compounds homogeneously requires isolation strategies and some of these elements cause different environmental problems, the use of base material for stabilizing them prevents from their entry into the reaction solution and plays an important role in their efficiency. Also, studies have shown that the base material results in chemical, hydrolytic and thermal stability of catalysts and in this way results in an increase in useful life of the catalysts [6]. Given the point that there are plenty of pumice mines in the country and it has increasingly been used as the base for $TiO_2$ and $ZrO_2$ nanoparticles. Pumice is a very light and porous rock (with porosity volume of over 85%) and in terms of containing cavities at micro level, has high specific surface.

Therefore, this study was performed aiming at comparative study of catalytic ozonation by two methods of $O_3/nZrO_2/H_2O_2$ and $O_3/nTiO_2/H_2O_2$ using Titanium dioxide and zirconium dioxide nanoparticles stabilized on pumice in removing PCP from aquatic Solutions.

## MATERIALS AND METHODS

The present research is the result of a functional cross-sectional study conducted in an ozonation reactor with discontinuous current at laboratory scale of one liter. The schematic design of the reactor is shown in Fig.1. PCP was bought from American company of Sigma-Aldrich and the nanoparticles from the Spain Company of Tecnan-nano Mat. Sulphoric acid and sodium hydroxide were bought from Merck and Sigma -Aldrich. FTIR images were provided by Perkin Elmer Spectrum, XRD Images by X Pert Pro MPD, and SEM images by Stereo Scan 360. The reactor used consisted of oxygen generator model 7 F-3 and ozone generator with maximum production capacity of 5 mg of ozone gas per minute, CoG-1 A model, both sets were made by French company of ARDA. pH meter of Sension 1model by HACH Company, centrifuge with velocity of 4000rp, by German Sigma Company - model 19591, Oven mode FSL 908 by Iranian Rad lab Company, mixer by Italian VELP Company, Electric Furnace with $1200^{\circ C}$, model BATEC PC21 by Iranian Company of khodsaz and Spectrophotometer model DR6000 by HACH Company were also used in this study.

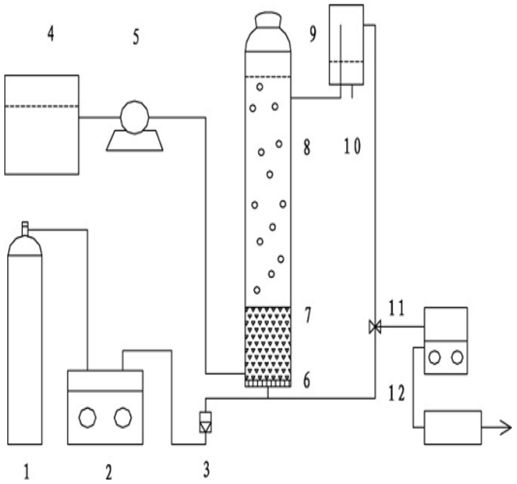

**Fig: 1 :**The schematic diagram of experiment. (1) Oxygen cylinder, (2) ozone generator, (3) gas flow meter, (4) solution tank, (5) diaphragm pump, (6) gas diffuser, (7 catalyst, (8) glass reactor, (9) gas and liquid separation device, (10) sample tap, (11)ozone gas monitor apparatus, and (12) vent ozone destructor

To stabilize each of the nanoparticles of $ZrO_2$ and $TiO_2$ on pumice, the desired amount of pumice stone with mesh 40 was poured into the laboratory beaker and solved the desired dose of each of the nanoparticles in distilled water and ethanol solution with a weight ratio of 8 to 1 and it was added to pumice. The resulted mixture after complete mixing for one hour using mixer was dried in Oven at $60^{\circ c}$ and in this way the desired nanoparticle was stabilize on pumice stone with weight percentage of 4.5% [7], in a way that each gram of catalyst contains 0.045 grams of nanoparticles deposited on it being placed in contact with pollutants. Then, the concentration of 1 gram per liter of PCP was prepared as the stock solution. The absorption calibration curve of PCP was drawn at wavelength of 500 using spectrophotometer with preparing synthetic solutions at concentrations of 10 to 100 mg/l in order to conduct tests for determining the optimum conditions for the removal of the PCP using processes under study.

In this study, we optimized all parameters by using the one factor at a time method. Firstly, the pH of the two processes: $O_3/nTiO_2/H_2O_2$ and $H_2O_2/nTiO_2/O_3$ was optimized and the values ranging from 3 to 11 were tested at the fixed conditions of PCP concentration=20mg/l, reaction time=30 min and catalyst dose=4g/l. Next, all other variables were optimized by fixing the optimized parameters as one factor was optimized by changing it at the fixed conditions of other parameters.

Then, the test solution was ozonated with flow rate of 5 gram per minute using ozonation set, the concentration Of PCP in the sample was read at wavelength of 500 nm according to phenol measurement using spectrophotometer and the efficiency of removal process was computed and the optimum pH was determined [8-9].

Other tests for determining the reaction time, catalyst concentration, PCP concentration and optimum concentration of $H_2O_2$ were also conducted using this method.

At last, result analysis was conducted using SPSS software and statistical comparative test of ordered - pairs with confidence internal of 95%.

## RESULTS AND DISCUSSION

### *Unconfined compressive strength test results*

To determine the apparent specifications and the morphology of modified pumice, the SEM image (Fig.2), the related analysis of XRD spectrum (Fig.3) and FTIR spectrum (Fig.4) were conducted.

The image of SEM modified pumice with $TiO_2$ and $ZrO_2$ nanoparticles have been presented in Fig.2 the change from homogeneous porous structure state to heterogeneous State is as a result of the reduction in the diameter of the particles of pumice after its surface modification by $ZrO_2$ and $TiO_2$ nanoparticles. The improvement in the structure of pumice pores after being coated with different materials has been proved in different studies. In modified pumice, the specific surface and heterogeneous structure, particles and the number of canals increase compared to raw pumice [10]. The pattern of XRD from the pumice coated with $ZrO_2$ and $TiO_2$ nanoparticles (Fig.3) is indicative of the major elements in pumice, including pyroxene, feldspar, magnetite, and mica and $SiO_2$ groups. Fig.3 shows that the highest peak is related to quartz ($SiO_2$) and this mineral forms much of the pumice [11]. Fig.4 Shows the FTIR spectrum of the pumice coated with the two nanoparticles under study. The peak area of 2400 that is observed in both charts is connected to vibration tension of water molecules(humidity and the OH groups in pumice structure), the peak areas close to 1635 is also attributed to the vibration tension of OH group of the humidity absorbed from the outside. Peak areas of 1000 show Si-O and Al-O. The FTIR spectrum of natural pumice differs from that of its modified state using nanoparticles in terms of rather long peaks that are observed in the areas of 140 and 450. These peaks indicate changes in the functional groups of pumice surface at the presence of nanoparticles. The peak areas of 400-500 demonstrate the nanoparticles dioxide on pumice surface [11-12].

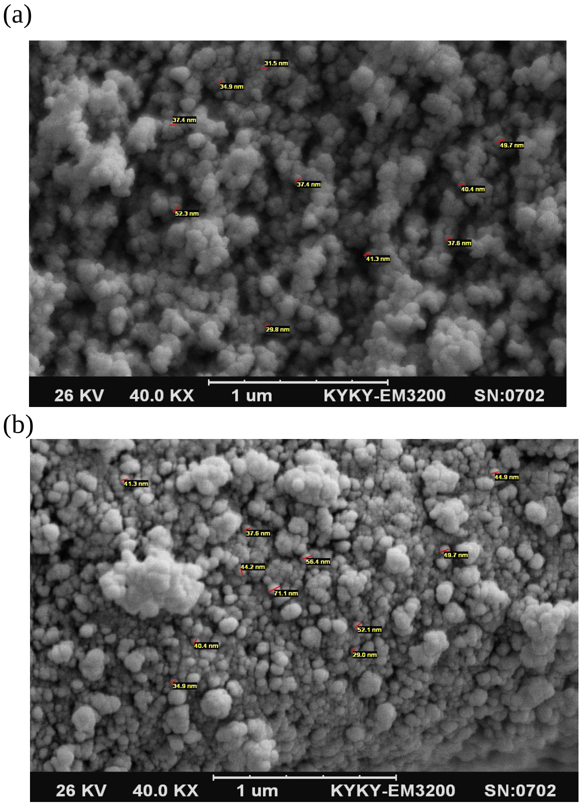

**Fig. 2:** a) The SEM Image of pumice modified with $ZrO_2$ nanoparticles b) The SEM Image of pumice modified with $TiO_2$ particles

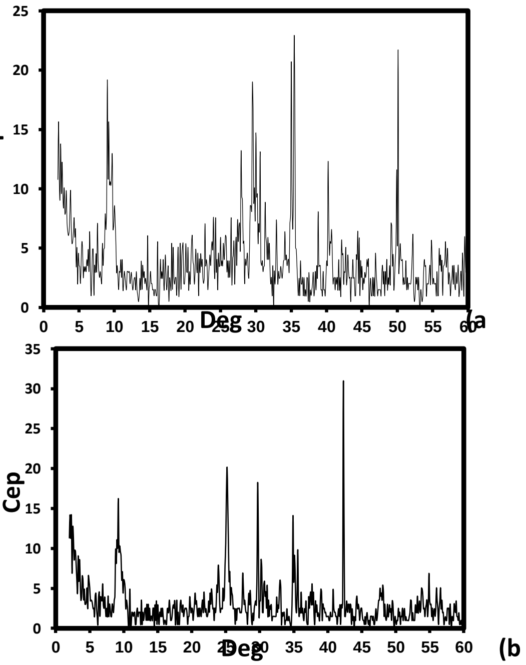

**Fig. 3:** a) XRD nanoparticles Spectrum of pumice modified with $ZrO_2$ ,b) XRD spectrum of pumice modified with $TiO_2$ nanoparticles

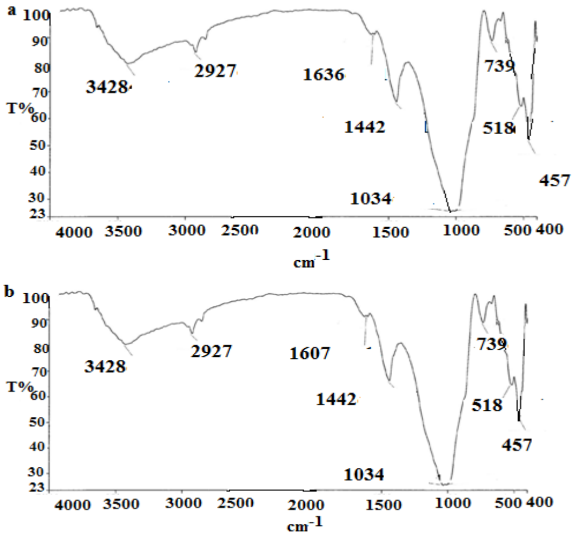

**Fig. 4:** FTIR spectrum a) pumice modified with $TiO_2$ nanoparticles b) pumice modified with ZrO nanoparticles

### *Effect of pH on removal of PCP*

The effect of pH on the efficiency of the process in stable conditions of catalyst concentration 4g/l, initial concentration of PCP: 20mg/l, reaction time: 15 min and pH range of 3-11 was studied (Fig.5). The results of this study showed that changes in the initial pH of the solution affected the efficiency of removal related to both processes and by increasing pH from 3 to 9, the removal efficiency increased and reached its maximum at pH 9. But increasing pH from 9 to 11 had adverse effect on the reaction and reduced removal efficiency. Since there was little difference in removal efficiency at pH 7 and 9, and increasing pH to 9, requires time and cost, pH 7 was considered the operational pH for conducting the rest of experiments. During conducting chemical processes especially advanced oxidation processes, the pH environment plays a very important role and affects the processes in two ways, that is, transferring ozone from gas phase to liquid phase(direct effect) and through decomposing ozone into hydroxyl radicals(indirect effect) [13].The results from determining the effect of pH have been presented in Fig.5. This chart indicates increase in the efficiency of removal with increasing pH. Destruction of pollutants using ozonation process is conducted during two tracks of direct and indirect oxidation that is, using ozone molecules and hydroxyl, radicals produced under the effect of ozone. Destruction of pollutants is done by indirect oxidation method in alkaline conditions and by direct oxidation method in acidic conditions. Indirect oxidation system has higher efficiency compared to direct oxidation system due to the presence of hydroxyl radicals and their higher oxidation power in comparison with ozone. For this reason, with increasing pH, the efficiency of catalytic ozonation Process in removing PCP rises. In addition, in heterogeneous catalytic ozonation process, the surface and density properties of hydroxyl groups on catalyst surface play an important part. The surface of metal oxides is capable of absorbing water molecules due to the existence of unsaturated electrons, and this leads to the formation of hydroxyl group on the surface. Then, the surface channels of hydroxyl groups will achieve proton balance according to relationship 1.

$$MeOH_2 + \rightarrow MeOH + H \rightarrow Meo - + H^+ \qquad (1)$$

According to above relationship, the surface hydroxyl groups represent various patterns of electrical change in different pHs. For this reason, pH is one of the most important effective surface factors in metal oxides [14]. Gang Li *et al.* studied the direct relationship between pH and Removal efficiency of bis-phenol using catalytic ozonation process with grapheme oxide and found that with the increase in pH from 3 to 9, the removal efficiency rises from 13% to 67% [14]. Moreover, in a study by Tingyi Liu *et al.*, in which heavy metals were treated by means of a new and beneficial composite named: Pumice-supported nanoscale zero-valent iron, it was shown that the variable is an important factor in the process because the removal efficiency increased with raising the value from 3 to 8 [7].

### *Effect of reaction time on removal of PCP*

In this stage, in the time range of zero until the approval of the process efficiency, sampling and reading the remained concentration of PCP (Fig.6).

Were conducted and ultimately, when the efficiency of the process was proved, sampling ended. Thirty minutes after the process, maximum removal efficiency was 92% for $O_3/nZrO_2/H_2O_2$ process and 74% for $O_3/nZrO_2/H_2O_2$ (Fig. 6). In advanced oxidation system, by increasing the contact time, larger amounts of pollutants are decomposed due to the increase in the production of hydroxyl radicals.

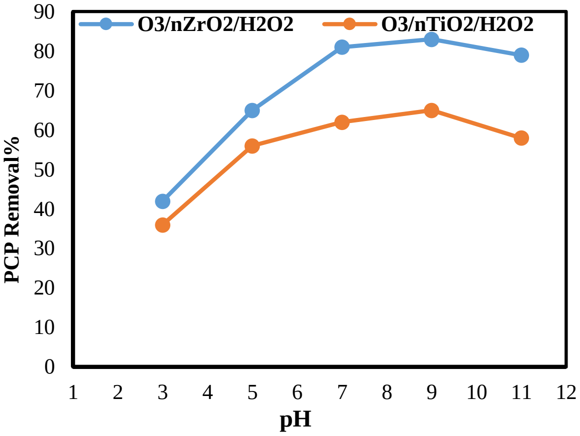

**Fig. 5:** Dependency of PCP removal to the pH and reaction time (PCP= 20mg/l, catalyst dose= 4g/l)

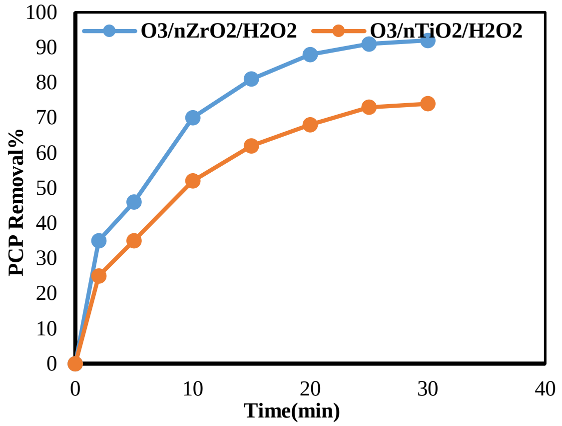

**Fig. 6:** Dependency of PCP removal to the reaction time (PCP= 20 mg/l, catalyst dose=4g/l)

### *Effect of catalyst dose on removal of PCP*

The results indicate that in both processes of $O_3/nZrO_2/H_2O_2$ and $O_3/nTiO_2/H_2O_2$, there was direct relationship between the catalyst dose and removal efficiency and the process efficiency increases with increasing catalyst beyond optimal level, removal efficiency gradually reduces. In $O_3/nZrO_2/H_2O_2$ process with dose of 4 g/l, the maximum efficiency is 92% and in $O_3/nTiO_2/H_2O_2$ with 8g/l, the maximum efficiency is 74% (Fig.7).

Thus, requiring lower amounts of catalyst in the process of $O_3/nZrO_2/H_2O_2$ could be considered as one of the advantages of $nZrO_2$ nanoparticle compared with $nTiO_2$ nanoparticle. Given the data from experiments, increasing the amount of hydroxyl production (the most powerful oxidizing radicals in the environment) leads to increase in the production of this radical and as a result in increase in the decomposition of PCP. Increasing catalyst leads to increase in the surface area and the active site that result in the increase in the absorption of Ozone on the surface and consequently raises the absorption of surface reactions and production of hydroxyl radicals. Nanoparticles function as the initiator for the production of hydroxyl radicals and absorption of Ozone from their surface leads to the destruction of ozone molecules and production of active radicals [15]. In catalytic ozonation process, three major mechanisms occur due to the presence of catalyst: At first, the ozone dissolved on the surface of the catalyst is absorbed and is rapidly decomposed in the presence of hydroxyl groups. Then, following ozone decomposition, active atomic oxygen is produced and enters into the reaction with hydroxyl groups on the catalyst surface. Therefore, increasing the concentration of catalyst in the solution causes an increase in the density of surface hydroxyl groups and
Effect of H2O2 concentration on Removal of PCP

The effect of H2O2 on the efficiency rate of processes studied was determined under optimal conditions in the experiments conducted in previous stage and in concentrations of 1, 2,5,10, and 20mmol/l of H2O2. As the chart shows in O3/nZrO2/H2O2 process up to the concentration of 5mmol/l and in O3/nTiO2/H2O2 process up to 10mmol/l of H2O2, with increase in H2O2 concentration, the efficiency of the process goes up, too, but with raising the H2O2 concentration above this amount, the process efficiency declines. The chart in a Fig.9 shows that with increasing the H2O2 concentration, at first, the efficiency of the process rises with rather sharp slope due to more production of hydroxyl radicals, but if concentration exceeds the optimal level, OH2 radical is produced instead of OH2 and in consequence, the process of PCP is disturbed.

But, like the previous works, we found that the increase of H2O2 content can enhance the removal efficiency by the optimum amount and after that, it started to decline because a reaction between radicals, which have been generated, and excess H2O2. H2O2 can be regarded as an inhibitor because of its reaction with these radicals capable of decomposing the contaminant [1, 21.[

Study by Zihang Chang and co-workers on phenol removal using Aw/ZVAL/H2O process revealed that increase in H2O2 from 1 to 2mmol/l leads to increase in efficiency but increasing concentration from 2 to 8mmol/l has little impact on removal efficiency and removal efficiency remains almost constant [22].as a result, it leads to as much decomposition of gas ozone molecules on the surface of the catalyst as possible. With increasing the decomposition of the ozone, the production of active hydroxyl radicals and consequently the oxidation of organic molecules increase, too. Lower effect of catalyst at concentrations higher than the optimal level could be explained in this way that the optimal concentration of the catalyst is strongly dependent on the type of the catalyst, reaction conditions, target compound and its surface area [16]. Yang yixin *et al.* in their study in 2014 studied the amount of atrazine removal using catalytic ozonation process with $TiO_2$ nanoparticles and reported the existence of direct relationship between removal efficiency and the catalyst dose [17]. It should also be noted that Moussavi *et al.*, reported the same findings; in the case of catalyst dosage increase, catalyst surface area and active sites available for ozonation increase, which, in turn, enhance the creation of t reactive radicals, mainly •OH, and the removal efficiency [18].

### *Effect of initial concentration of PCP*

The $O_3/nZrO_2/H_2O_2$ and $O_3/nTiO_2/H_2O_2$ processes efficiency in removing different concentrations of PCP has been shown in Fig.8. With increasing the Concentration, the efficiency rate of above processes reduced in a way that with increasing concentration from 20 to 100mg/l, the efficiency of $O_3/nZrO_2/H_2O_2$

and $O_3/nTiO_2/H_2O_2$ reduced from 92% to 70% and 80% to 52%, respectively. It should be noted that the two processes: $O_3/nZrO_2/H_2O_2$ and $O_3/nZrO_2/H_2O_2$ at high concentrations also have a good ability to remove PCP.

Another effective factor on the efficiency of removal process is the initial concentration of the pollutant. Increasing the concentration of the pollutant leads to more consumption of oxidants such as ozone and hydroxyl radical.

The reduction in removal efficiency could be interpreted in the way that in the conditions that all factors such as input ozone, catalyst concentration, pH and reaction time are constant and the same amount of oxidant is produced, the pollutant concentration rises. As a result, the decomposition process is not done completely and leads to reduction in the process efficiency and production of intermediate products. Furthermore, an increase in PCP content may result in more generation of byproducts caused by decomposition of these compounds using more OH•. Thus, a lower removal efficiency is expected [19].The results of this study are completely in conformity with the study by Shookohi *et al*., on the biological removal of PCP [20]. The results of this study are in close agreement with a study by Samarghandi *et al*. [19].

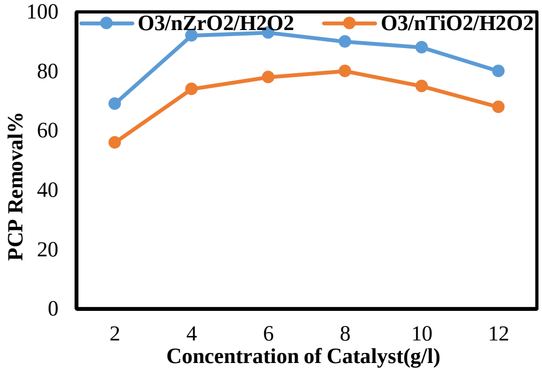

**Fig.7:** Dependency of PCP removal to the PCP Concentration (reaction time= 30 min, pH=7)

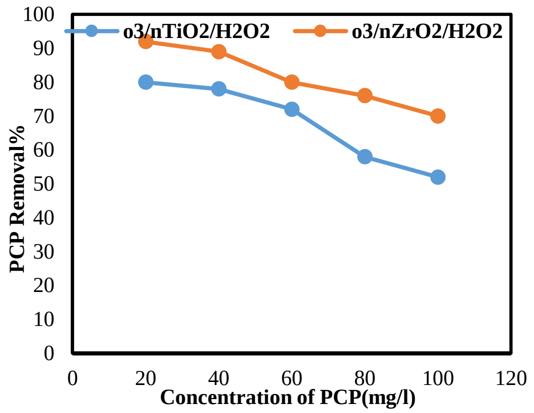

**Fig.8:** Dependency of PCP removal to the catalyst Concentration (reaction time= 30 min, pH=7)

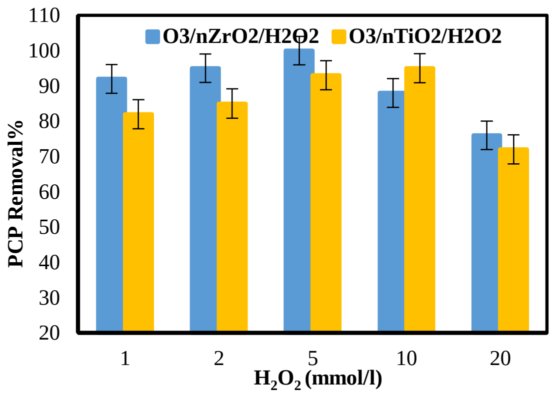

**Fig. 9:** Dependency of PCP removal to the $H_2O$ concentration (PCP= 20 mg/l, catalyst dose= 4g/l, reaction time= 30 min, pH= 7)

## *Determining Kinetic Model of Reaction*

Result from determination of the kinetic model of PCP removal reaction using two catalytic ozonation methods studied have been presented in Fig.10 and Table 1.Given the graphs, the removal reaction of this organic material by above processes follows the pseudo-second -order kinetic model. Zhou and his colleagues also studied the removal of PCP using multi-walled carbon nano-tubes Coated with $SiO_2/Fe_3O_4$ in 2014 and achieved similar results [23].

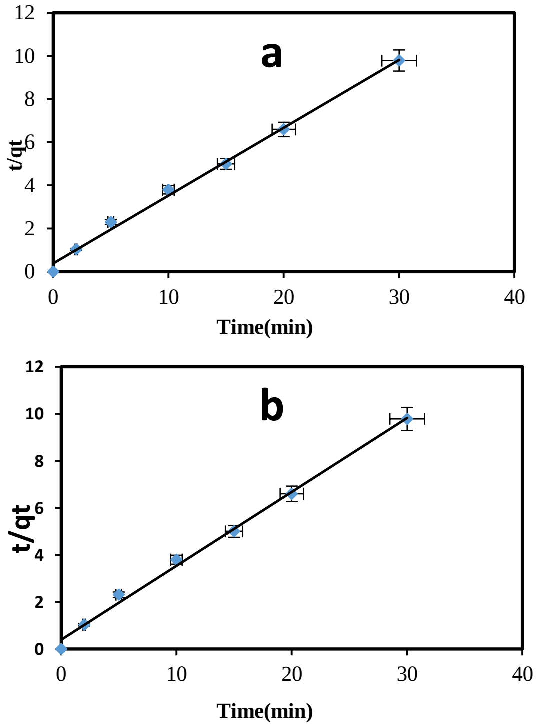

**Fig.10:** Determination of kinetic model of reaction a) pseudo-second -order reaction of $O_3/nZrO_2/H_2O_2$ process b) pseudo-second -order reaction of $O_3/nTiO_2/H_2O_2$ process (PCP= 20 mg/l, catalyst dose= 4g/l, concentration of $H_2O_2$= 5mmol/l, Reaction time= 30 min, pH=7)

**Table.1:** coefficient of Pseudo- second order equation

| Pseudo- second order equation | | |
|---|---|---|
| **Processes** | **K ( l/mg min )** | **$R^2$** |
| $O_3/nZrO_2/H_2O_2$ | 0.39 | 0.9948 |
| $O_3/nTiO_2/H_2O_2$ | 0.26 | 0.9983 |

### *Removal rate of COD in optimal conditions*

Efficiency determining experiments for processes studied in removal of COD in optimal conditions (catalyst dose of $O_3/nZrO_2/H_2O_2$ process: 4 mg/l and $O_3/nTiO_2/H_2O$: 8g/l, initial concentration of PCP 20 mg/l, H2O2 concentration in two processes of $O_3/nZrO_2/H_2O_2$ and $O_3/nTiO_2/H_2O$, 5 and 10mmol /l ,reaction time: 30 min, pH=7) revealed that in $O_3/nZrO_2/H_2O_2$ and $O_3/nTiO_2/H_2O$ 70% and 52% of the initial COD were respectively removed during 30 minutes of reaction time and for higher removal longer time is required Fig.11 indicates the two processes in the removal of COD. In the discussion on using the process at environment scale, in addition to the removal of the given pollutant, the efficiency of the process in reducing the rate of pollution is also raised. Given the results of the studies, each mg of PCP produces 0.81 mg of COD and the removal efficiency of both processes is lower than that of PCP.This indicates that removal of COD is more difficult than the removal of PCP and this is due to the complex nature of the substances that require mineralization. In general, it could be said that the above-mentioned processes are of appropriate potential in the mineralization of organic pollutants but longer time is required for complete mineralization [24]

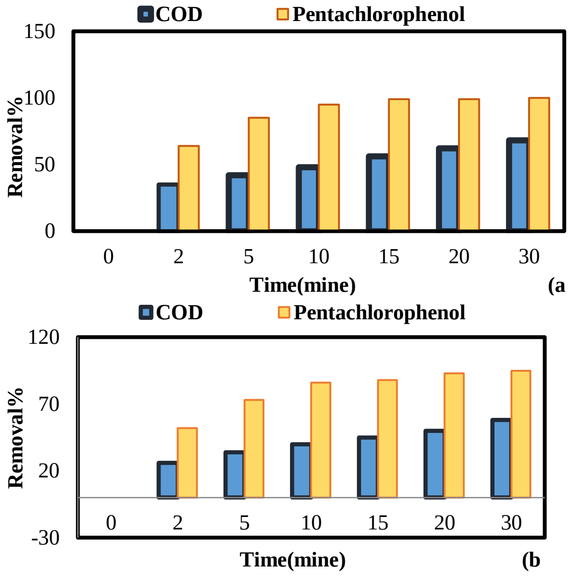

**Fig.11:** Comparison of COD and PCP removal efficiency in optimal conditions a) $O_3/nZrO_2/H_2O_2$processes b) $O_3/nTiO_2/H_2O_2$processes (PCP=20 mg/l, catalyst dose =4g/l, concentration of$H_2O_2$=5mmol/l, Reaction time=30 min, pH=7)

### *General comparison of efficiency of $O_3/nZrO_2/H_2O_2$ and $O_3/nTiO_2/H_2O_2$ in the removal of PCP*

Given the results of statistical analysis of the data using SPSS software and according to the analysis of repeated measures and comparison of processes of $O_3/nZrO_2/H_2O_2$ and $O_3/nTiO_2/H_2O_2$ have good capability for removing the organic substance of PCP, but based on the analysis of repeated measures, the mean of removal efficiency is different in two groups and at different times (p-value < 0.001 and p-value L< 0.001 respectively. Also, the change procedure over time in two groups was significant statistically (p–value < 0.001) and $O_3/nZrO_2/H_2O_2$ was of better efficiency in the removable of this organic materials, and it reaches the maximum efficiency in a smaller amount of catalyst (pumice modified with $nZrO_2$), it has good potential in removing high concentrations of PCP and removes 70% of the PCP in the sample with 100 mg/l concentrations, Whereas the $O_3/nTiO_2/H_2O_2$ process in constant conditions, is capable of removing 52% of PCP. This applies to the discussion of organic materials mineralization and removal of COD and the results prove higher capability of $O_3/nZrO_2/H_2O_2$ process in removing COD.

Also, results indicate the important role played by catalyst in the procedure of conducting the processes and its considerable effect in increasing the efficiency of PCP removals in a way that in optimal conditions, the maximum efficiency of removal for $O_3/nZrO_2/H_2O_2$ is 100%, and for $O_3/nTiO_2/H_2O_2$ process, 95%, While simple ozonation process is just capable of removing 38% of the PCP in constant and optimal conditions.

## CONCLUSION

This study investigated the clean-up efficiency of S/S In this study, the effect of two catalytic ozonation methods of $O_3/nZrO_2/H_2O_2$ and $O_3/nTiO_2/H_2O_2$ were studied using nanoparticles deposited on pumice in removing PCP from aquatic solutions. The results revealed that the efficiency of both processes in alkaline and neutral solutions was higher than that of acidic solutions, and it has inverse relationship with concentration of PCP and direct relationship with reaction time, catalyst concentration and the concentration of hydrogen peroxide and it could generally be concluded that both processes studied are capable of removing PCP.

## ETHICAL ISSUES

There are no ethical issues in this study.

## CONFLICT OF INTEREST

There is no conflict of interest to be reported by the authors

## AUTHORS’ CONTRIBUTION

All authors participated in the prepared manuscript including accomplishment of all experiments, analysis of the results and writing the manuscript.

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