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Degradation of Pentachlorophenol in Aqueous Solution by the UV/ZrO_2/H_2O_2 Photocatalytic Process

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Abstract

Pentachlorophenol (PCP), which is one of the resistant phenolic compounds, has been classified in the category of EPA's priority pollutants due to its high toxicity and carcinogenic potential. Therefore, its removal from water and wastewater is very important. Various methods have been studied for removing the compound, among which advanced oxidation processes (AOPs) have attracted much attention because of ease of application and high efficiency. Thus the aim of this study was to investigate the efficiency of the UV/ZrO_2/H_2O_2 process, as an AOP, for PCP removal from aquatic environments. The effects of several parameters such as ultraviolet (UV) exposure time, initial PCP concentration, pH, concentration of zirconium dioxide (ZrO_2) nanoparticles, and H_2O_2 concentration were studied. Kinetics of the reaction was also detected. The concentration of the stated materials in the samples was determined using a spectrophotometer at 500 nm. The results showed that the highest efficiency (approximately 100%) was reached at optimized conditions of pH 6, contact time of 30 minutes, initial PCP concentration of 20 mg/L, the nanoparticles concentration of 0.1 g/L and H_2O_2 concentration of 14.7 mM/L. Also, the process followed the first order kinetics reaction. The obtained results illustrated that the UV/ZrO_2/H_2O_2 process has a high ability in removing PCP.

Keywords: Zirconium Dioxide, Hydrogen Peroxide, Ultraviolet Radiation, Pentachlorophenol Removal

1. Introduction

Persistent organic pollutants (POPs) generated by various industries can highly contaminate the environment. Pollution of groundwater and surface water with aromatic compounds such as phenolic compounds is one of the most serious environmental problems that humanity faces today (1). Pentachlorophenol (PCP) is a derivative of phenol family that due to 5 chlorine atoms on the benzene ring is used more than other phenolic derivatives (2). Pure PCP exists in colorless crystals with a strong smell as well as white, brown or dark gray. Figure 1 shows the chemical structure of this compound (3).

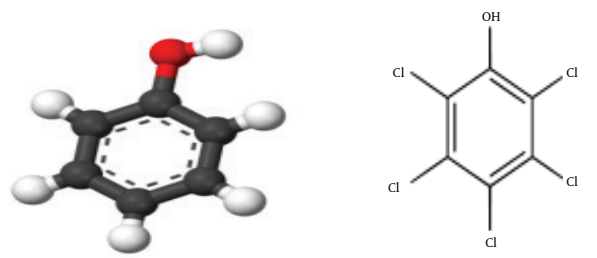

Figure 1. The Chemical Structure of PCP

Pentachlorophenol is applied in the manufactures of biocides, wood preservatives, making herbicide compounds, and strengthening wooden bridges and fences in large quantities. It can be harmful to kidney, liver, blood, lungs, central nervous system, immune system, digestive system, skin, and eyes. Among the properties of this material is absorption through the gastrointestinal tract (4). Due to the health effects of PCP, various methods have been examined to investigate its removal; among different methods of phenol removal, one can refer to the process of adsorption and advanced oxidation processes (AOPs) such as H_2O_2/microwave, H_2O_2/UV radiation, ozone/H_2O_2, ozone/UV, H_2O_2/UV, ozone process/titanium dioxide/UV and so forth (5). The main mechanism in the AOPs method is based on the production of hydroxyl radical ($OH^{\bullet}$) with high oxidation power. As a strong oxidant, it is capable of destroying resistant compounds that

cannot simply be oxidized by conventional oxide donors such as, ozone and chlorine dioxide. Compared to conventional oxidation methods, advanced AOPs have significant advantages, because they produce fewer residues and by-products (6). Photo catalytic processes which are based on absorption of light energy are carried out by a solid material (7). In these processes, as catalytic nanoparticles, absorb high-energy photons of UV spectrum and subsequently active chemicals such as $OH^{\bullet}$s are formed (8). When photo catalysts are set under ultraviolet (UV) radiation, they stimulate and stir up valence band electrons and cause the electron to move from the valence band to the conduction band. In so doing, some holes are made in the valence band that are very active and they can react either directly with organic contaminants at the catalyst levels or indirectly through the formation of $OH^{\bullet}$s. Moreover, active electrons which has excited into the conduction band, such as superoxide and $OH^{\bullet}$ formation react with organic material (9). In recent years, photocatalytic oxidation processes have received considerable attention by metal oxides in the removal of organic contaminants and microbial agents (10). Among these metal oxides is the nano zirconium dioxide (ZrO_2), which has a catalytic property for many applications (11). Heidari Farsani et al. (12) studied the efficiency of UV/ZrO_2/H_2O_2 on the removal of nickel and found that this process is able to remove 60% of nickel from a real wastewater. This nanoparticle, 20 nm size and a surface area greater than 25 m^2/g is regarded as an appropriate catalyst (11).

To our best knowledge, no studies have been conducted on PCP destruction by means of the UV/ZrO_2/H_2O_2 process. Thus, since the performance of each treatment system may change with different pollutants. Moreover, in order to study the effects of operating parameters and their impact on the removal efficiency, comprehensive investigations are needed. In this study, the performance of the UV/ZrO_2/H_2O_2 process was studied and the variables of concentration of nanoparticles of ZrO_2, initial pH, initial PCP concentration, H_2O_2 concentration and dioxide were optimized.

2. Materials and Methods

The present study was conducted on laboratory scale discontinuously using a photo reactor (Figure 2) on synthetic solution containing PCP in different concentrations of 10, 20, 30, 40 and 50 mg/L. In this study, a 150 watt low pressure mercury lamp with a quartz envelope within a steel chamber of high reflection was used. The reaction on the samples of contaminated water was done in the space between the UV-C lamp and the steel cover. To perform this experiment, first by dissolving 1 g of PCP in 1000 mL of distilled water of the stock solution of 1000 mg/L was prepared then by making solutions with a concentration of 10 to 100 mg/L and reading the absorbance by a spectrophotometer 500 nm, PCP calibration curve was drawn (13). Next, the impact of the variables pH, reaction time, H_2O_2 concentration, concentration of PCP and nano- ZrO_2 concentration on removal efficiency was examined. All parameters were optimized as one at a time (14). First, pH values of 2, 4, 6, 8 and 10 were adjusted; at this stage, based on the literature review PCP content was set at the real degree (20 mg/L). The pH level was adjusted using NaOH and H_2SO_4 (0.1 N). The pH value was optimized in the presence of 0.5 g of nanoparticles of ZrO_2 and 14.7 mM/L of H_2O_2, and pH = 6 was selected as the optimum amount. Contents of 0.1, 0.25, 0.5, 0.75 and 1 g of nanoparticles of ZrO_2 were used to optimize, which was 0.1 g/L at pH = 6 and H_2O_2 = 14.7 mM/L. Next, in order to optimize the PCP concentration, of which 10, 20, 30, 40 and 50 mg/L were made. So as to investigate all variables and the procedure of pollutant removal, samples were taken from the solution at contact times of 10, 20, 30, 40, 50 and 60 minutes and then were filtered using a 0.2 M syringe filter and finally the concentration of PCP in the samples was measured. The percentage of the removal of PCP was obtained using Equation 1 (14).

$$\text{Removal efficiency}(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where C_0 represents the initial concentration of PCP (as mg/L) and C represents the remaining concentration (as mg/L) in the solution after performing all functions. In order to measure PCP concentration and pH value, a spectrophotometer (UV/Vis spectrometer-DR 5000) and portal pH meter (Sensl Hack, Germany), respectively, were used.

3. Results and Discussion

pH is one of the most important factors affecting the decomposition of organic compounds. Solution pH plays an important role in photocatalytic reactions and UV/ZrO_2/H_2O_2 has a better function in acidic conditions (15). The effect of pH on the removal efficiency has been shown in Figure 3. In order to evaluate the effect of pH on the process, the pH values of 2, 4, 6, 8 and 10 at the fixed nanoparticle concentration of ZrO_2 (0.5 g/L), the concentrations of H_2O_2 14.7 mM/L and PCP 20 mg/L were adjusted. The results showed that in acidic conditions, with increasing pH, the removal efficiency enhanced gradually to a maximum 99% until the contact time 30 minutes and pH = 6. However, by increasing pH from acidic to alkaline conditions (from pH of 6 to 10), the removal efficiency was declined from 99% to 75%.

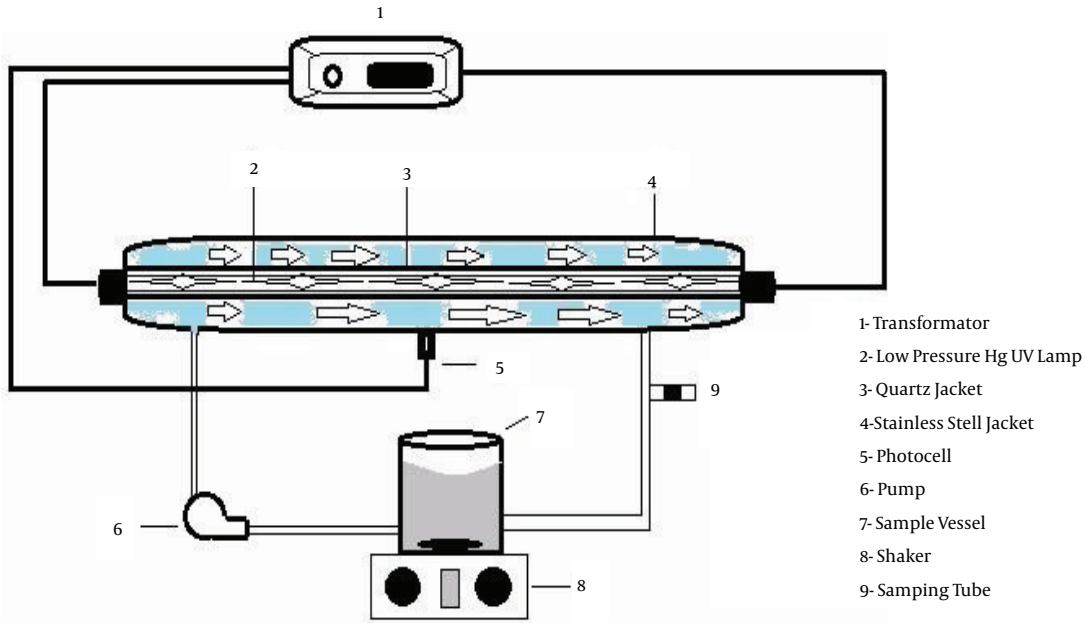

Figure 2. A Schematic Diagram of the Photo-Reactor Containing Low-Pressure Mercury Lamp

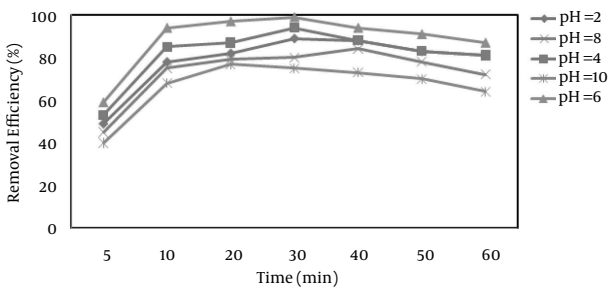

Figure 3. Effect of pH Variations on PCP Removal Using the UV/ZrO_2/H_2O_2 Process (ZrO_2 = 0.5 g/L, PCP = 20 mg/L, H_2O_2 = 14.7 mM/L)

The reason of increasing the removal efficiency in acidic pH is that the surface of nano-ZrO_2 is positively charged and attracts more PCP. As a result of more adsorption of PCP, generation of $OH^{\bullet}$s as well as the decomposition rate in acidic environment are increased resulting in the removal efficiency heightening. The efficiency decline in the alkaline condition is because of the fact that the nano-particle surface gets a negative charge, which reduces the adsorption of PCP reducing the production of $OH^{\bullet}$s and that also leads to the reduction of the rate of decomposition in the alkaline environment; thus, it decreases removal efficiency (16). Another reason for the decline of the removal efficiency of UV/ZrO_2/H_2O_2 in alkaline conditions is that H_2O_2 is converted to water and oxygen (7). On the other hand, in acidic environments it acts as the dominant oxidant and will have more oxidation power (17). The results of this study are perfectly constant with the obtained results of a study done by Quan et al. (18) In order to remove PCP, they used titanium dioxide nanotubes and found that the removal efficiency decreased with increasing pH value. Also, in a study conducted by Asadi et al. (19) titled using the photocatalytic process UV/NiO in eliminating direct poliazo dyes, the pH optimum of 4 was achieved. Dependence of PCP elimination on the concentration of nanoparticle at concentrations of 0.1 to 1 g/L of nanoparticles was studied. The results presented in Figure 4 indicates that the process, which is examined in this study, with an increase in the concentration of nanoparticles, PCP removal rate decreased and the highest removal efficiency for this compound related to the concentration was 0.1 g/L nanoparticle. With concentrations above this, the removal efficiency reduced. The reason behind this efficiency decline lies in the fact that increasing the initial amount of nanoparticles, due to their accumulation, causes turbidity and thereby reduces the intensity light of UV as well as decreasing the production of $OH^{\bullet}$s (20). This result is

consistent with the results of Samarghandi et al. (7) in the field of the efficiency of the photocatalytic process of titanium dioxide in removing reactive black 5 and cyanide from aqueous solutions.

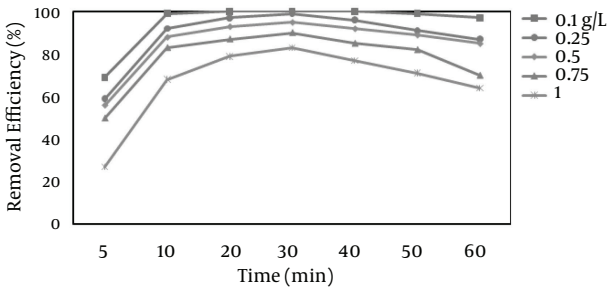

Figure 4. Effect of ZrO_2 Variations on Pentachlorophenol Removal Using the $UV/ZrO_2/H_2O_2$ Process (pH = 6, PCP = 20 mg/L, H_2O_2 = 14.7 mM/L)

In AOPs, the type and concentration of an oxidizing agent is one of the effective factors in the removal of organic compounds. To determine the effect of the concentration changes of hydrogen peroxide on the process of $UV/ZrO_2/H_2O_2$, the experiments were performed at the concentration of pollutants in fixed conditions: 20 mg/L of PCP, pH 6 and the concentration nanoparticles of 0.1 g/L. The results of hydrogen peroxide concentration changes (Figure 5) showed that different concentrations of 2.9, 7.3, 14.7, 22.0 and 29.4 mM/L of hydrogen peroxide for 30 minutes could remove 78%, 95%, 100%, 80% and 77% of organic matter. These results indicated that the removal efficiency of organic matter is under the influence of the ionic conditions and polarity of the system. Also, as expected, with the increase of the concentration of hydrogen peroxide removal efficiency of organic matter, the removal efficiency rose and then decreased gradually. It has been determined that in the existence of a high dose of hydrogen peroxide, $OH^{\bullet}$ reacts with hydrogen peroxide and this leads to the production of peroxide radical ($HO2^{\bullet}$) which is weaker than peroxide radical (21, 22). Also, in excessive amounts of hydrogen peroxide, hydroperoxyl radicals, which are less active, are produced (reaction 1) and exceeded amounts of hydroxyl are converted to hydrogen peroxide through dimerization (reaction 2). According to reactions 2 to 4, hydroperoxil radicals do not participate in oxidation reactions and contribute to the chain reactions and hydrogen peroxide is decomposed to O_2 and HO_2 anions (21).

(1) $H_2O_2 + OH^- \rightarrow HO^{\bullet}_2 + H_2O$

(2) $OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$

(3) $HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2$

(4) $OH^{\bullet} + H_2O_2 \rightarrow O_2 + H^+ + H_2O$

(5) $HO^{\bullet}_2 + H_2O_2 \rightarrow O^{\bullet}_2 + OH^{\bullet} + H_2O$

The results of Jamshidi et al. (23) study, in which the removal of phenol from aqueous solutions using advanced photochemical oxidation technologies was investigated, verifies the results of the present study.

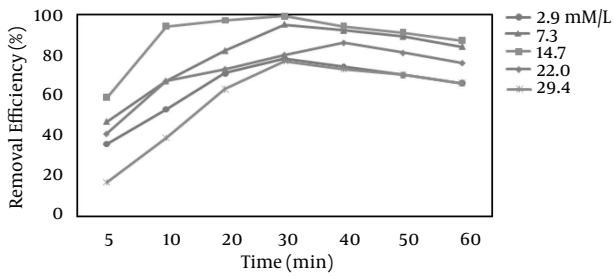

Figure 5. Effect of H_2O_2 Concentration Changes on Pentachlorophenol Removal Using $UV/ZrO_2/H_2O_2$ (ZrO_2 = 0.1 g/L, PCP = 20 mg/L, pH = 6)

The effect of the concentration of PCP figure (Figure 6) showed that the efficiency of the $UV/ZrO_2/H_2O_2$ process had an inverse relation with PCP concentrations and with increasing concentrations of PCP, its removal rate gradually reduced. It should be noted that the process under the investigation at high concentrations also enjoys a good ability to remove PCP. As can be seen in the results, PCP at the concentration of 30 mg/L $UV/ZrO_2/H_2O_2$ had a removal efficiency of 92%. The reason is that by increasing the initial concentration, more PCP molecules are adsorbed on the surface of the nanoparticle; thus, it prevents the reaction of PCP molecules with the photonic cavities and $OH^{\bullet}$s produced, due to the lack of a direct contact between them (7). In addition to this, the high concentration of organic matter in the environment leads to greater consumption of antioxidants and increase the duration of complete decontamination. So, by increasing the concentration of organic matter, process efficiency reduces. On the other hand, the low concentration of organic matter in the environment also reduces the efficiency of the process (24). In this case, the existence of much more oxidizing agents in the environment has a negative impact on the process efficiency. That is, when the concentration of hydrogen peroxide ions in the environment increases in the ratio of PCP concentrations, with it forms a stable complex with the hydroxyl radicals; therefore, reducing the amount of free radicals in the environment resulting in reduced efficiency of the process or in other words, increasing the concentration of pollutants in intact stationary conditions of operation, because of two main reasons, it reduces efficiency; in constant quantities of $OH^{\bullet}$, with increase in the concentration of pollutants, the extent of contact and encountering increases (25-27). Also, increasing the concentration of the pollutant can cause producing more byproducts aris-

ing from the oxidation of these compounds. These compounds will consume more $OH^{\bullet}$. The results of this study indicated that increasing the concentration of PCP causes reducing the rate of reaction thereby lessening the efficiency. The results of other studies also have put an emphasis on this fact and they have recognized the solutions in increasing the reaction time (28). It is worth mentioning that the process under this study in high concentrations is of a good ability in removing PCP. As can be seen in the results, in PCP at a concentration of 30 mg/L, the process of $UV/ZrO_2/H_2O_2$ had a removal efficiency of 92%.The results obtained from Malakootian et al. (24) study on removal of phenol from aqueous solutions using advanced oxidation technologies also verify the present results. Also, because of the impact of advanced oxidation reaction, kinetics curves were determined (Figure 7). It showed that this process follows the optimized kinetic model, which indicates that the rate of decrease in the concentration of PCP is a function of reaction time.

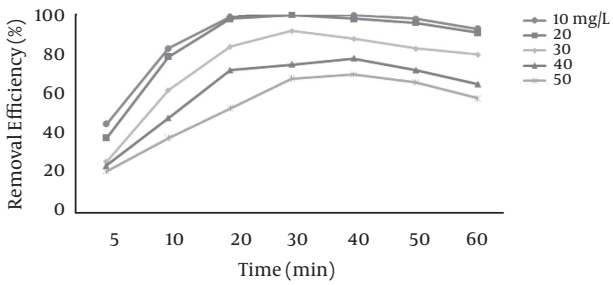

Figure 6. Effect of Initial Concentration of Pentachlorophenol on the Removal Efficiency Using $UV/ZrO_2/H_2O_2$ (ZrO_2 = 0.1 g/L, H_2O_2 = 14.7 mM/L, pH = 6)

The findings showed that each process of AOPs could not remove PCP well separately. For example, the processes of H_2O_2 and UV irradiation are applied separately because of high resistance of PCP against destruction. However, when they are combined together the efficiency increased dramatically because of the rapid generation of $OH^{\bullet}$s and an increase in a reaction rate. It should be noted that the $UV/ZrO_2/H_2O_2$ photocatalytic process can enhance the efficiency and meet economical aspects.

4. Conclusions

The use of nanotechnology in the removal of environmental pollutants is among the methods, which has attracted much attention in recent years. In this study, the PCP removal through using the process of $UV/ZrO_2/H_2O_2$ was examined and it was found that the highest removal efficiency (100%) was attained at pH = 6, contact time of

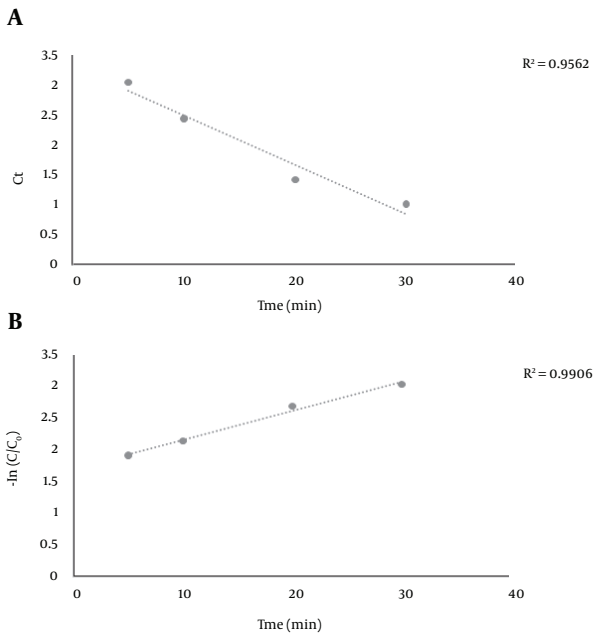

Figure 7. A, The Zero-Order Kinetic Model; B, First-Order Kinetic Model

30 minutes, nanoparticle concentration of 0.1 g/L and the H_2O_2 concentration of 14.7 mM/L. Furthermore, pertaining to the correlation coefficients obtained for the data in the kinetic models, it is inferred that this process follows the first-order kinetic model. Generally, it can be concluded that the $UV/ZrO_2/H_2O_2$ process with a high efficiency is capable of removing PCP from aquatic environments.

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Footnote

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