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Sonocatalytic Degradation of p-Chlorophenol by Nanoscale Zero-valent Copper Activated Persulfate under Ultrasonic Irradiation in Aqueous Solutions

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PAPER INFO

A B S T R A C T

In this study, nanoscale zero-valent copper (nZVC) as catalyst activated persulfate (PS) was used for the degradation of p-chlorophenol (p-CP) under ultrasonic (US) irradiation in aqueous solution. The effect of different operational parameters such as solution pH (3.5-10.5), PS concentration (1-7.5 mm/L), nZVC dosage (5-35 mg/L) and initial p-CP concentration (10-100 mg/L) were evaluated at different contact time. Results indicated that US/PS/nZVC system achieve higher efficiency in p-CP degradation than US/PS, US/nZVC and PS/nZVC systems. The optimal p-CP removal efficiency (98%) was achieved within 40 min with 5 mm/L PS and 30mg/L nanocatalyst at 25 mg/L initial p-CP concentration. It was also observed that the p-CP degradation rate depends on initial p-CP concentrations. To clarify the mineralization of p-CP, TOC and COD were analyzed at optimum conditions. COD and TOC removal rate obtained from the US/PS/nZVC system with contact time of 60 min were 61and 75%, respectively. Through the use of methanol (MA) and tert-butyl alcohol (TBA) as radical scavengers, $SO_4^{\circ-}$ was identified as the main radical species that are generated during processes. The removal process of p-CP could be described by the pseudo-first-order kinetics. The apparent degradation rate constant (k) was 0.076 min^{-1} in US/PS/nZVC system at optimal conditions.

1. INTRODUCTION

Nowadays, chlorinated phenolic compounds are used in many industries manufacturing processes producing different compounds in pharmaceutical, paper, paint, pulp and leather processing and wood preserving, which produce lots of wastewater in the world [1, 2]. These compounds can lead to soil, surface and ground water pollution problems due to their acute and chronic toxicity and low biodegradability [3]. In total, chlorophenols (CPs), known as one of the highly toxic and non-biodegradable environmental pollutants, normally exist in effluents from different sources. There are several such principal toxic phenolic compounds as the p-chlorophenol (p-CP), pentachlorophenol, 2-chlorophenol and 2,4 dichlorophenol regarded as the priority pollutants by the US Environmental Protection Agency [2-5]. p-CP

is extensively used in the production of pesticides, fungicides, herbicides, preservatives and often found in high diversity in wastewater outflow of many industries, i.e., oil refineries, pharmaceutical factories, dyestuff, paper and leather producers [3-6]. This compound is toxic and has carcinogenic and mutagenic effects on human and animals [1, 7]. Many wastewater treatment methods are available for the removal or/and degradation of CPs containing wastewater. p-CP can be decomposed by several biological treatment methods, however these treatments are suffering from the limitation of high p-CP concentration and long hydraulic retention time due to the toxic and the poor biodegradability nature of p-CP [2,8]. Although combined biological and chemical treatment might be enhanced the biodegradibilty of organic products at a contaminated waste [9]. Since physical methods such as membrane filtration and

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absorption only result in phase change (liquid to solid) of pollutants and not total degradation, it may wind up on secondary contamination [10]. Furthermore, the issue of chemical sludge and high energy consumption may limit the use of chemical methods in practice [11]. Similarly, hazardous contaminants emission following thermal treatment methods restricts practical use of this method. In order to solve these problems, the recently developed techniques such as advanced oxidation processes (AOPs) including Fenton and photo-Fenton [9], ozone oxidation [12], sonolysis [13], and photo-catalytic oxidation [14] and so on are considered to be the practical alternative treatment techniques for p-CP degradation in polluted water. In AOPs scheme, the oxidation and mineralization of organic compounds are mediated by radicals generated in the solution [7-9]. Among several AOPs methods, the ultrasonic (US) irradiation has gained interest in the degradation of organic pollutants via sonochemical oxidation in aqueous solutions [14]. Sonication of aqueous solutions leads to the formation, growth and collapse of cavitation bubbles which produced hot spots with high temperature and pressures [14-16]. These phenomena cause degradation of organic compounds by two mechanisms: oxidation by various active radicals and pyrolysis of water molecules in and surrounding of collapsing bubbles [15].

A great deal of studies on functionality of sonolysis on a large array organic pollutants confirmed the potential of ultrasound (US) irradiation as a promising technique for hazardous wastewater treatment. Nonetheless, lack of expected efficiency especially in the case of refractory compounds is yet to be compensated. Hence, the simultaneous use of the US irradiation and oxidants such as persulfate (PS) [16], hydrogen peroxide [17] and ozone [18] is another possibility to maximize the efficiency of the degradation technique. The use of sulfate radical-based AOPs as the degradant agent for a wide range of organic compounds have been widely investigated due to the production of sulfate radicals [16-21]. Owing to its higher oxidation-reduction potential ($E°=2.01V$) in comparison to hydrogen peroxide ($E°=1.76V$), high water solubility, being non-selectively reactive and cost-effective, PS has received considerable scholarly attention and is extensively used as organic contaminants removal agent [16, 17]. PS is relatively stable under typical water treatment conditions; however, it can be activated to generate free sulfate radicals ($SO_4^{°-}$) by using different activators including UV irradiation [17], microwave [19], ultrasound irradiation [20, 22] and heat [23] according to Equation (1) [24]:

$$S_2O_8^{2-} + \text{activator} \rightarrow SO_4^{°-} \text{ and/or } OH^{°} \tag{1}$$
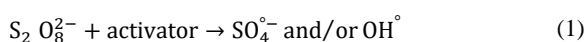
The system US/PS has already been applied for degrading propranolol [25], diclofenac [26], carmazepin [16] and dinitrotoluenes [26]. A considerable difference was observed in the organic pollutants elimination rate between US-PS system and each system alone in the case of diclofenac [22] and propranolol [25]. Recently, it has been discovered that PS can be activated by different transition metal ions such as Fe^{2+}, ZVI, ZVAl, nZVI, ZVNi, nZVNi, nZVAl through reactive radical generation for the degradation of organic pollutants [4, 17, 24-27]. Copper, known as another essential transition metal, has attracted much attention regarding its capacity for generation of various reactive oxygen species (ROS) including ($O_2^{-°}$), H_2O_2 and $OH°$ created through zero valent copper (ZVC)-induced change in reaction with molecular oxygen which degrades various organic pollutions [24, 26, 28]. Drijvers et al. [28] investigated the decomposition of phenol and trichloroethylene (TCE) by the ultrasound/H_2O_2 and ultrasound/H_2O_2/CuO processes. In the case of phenol, aqueous solutions of 1mM phenol with 100 mM H_2O_2 were sonicated at 520 kHz adding 1 mg/ml CuO as a catalyst. After 100 min, the degrading capacity of phenol enhanced by 20% and 70% in ultrasound and CuO/ H_2O_2 systems, respectively. Furthermore, the degradation level of phenol via ultrasound/ H_2O_2/CuO technique is higher than the sum of the decomposition achieved by using sonication and CuO/ H_2O_2 oxidation separately. Zhang et al. [29] studied the degradation of acetaminophen using Fe^{+2}/CuO activated PS. The results showed that the Fe^{+2}/CuO/PS system could reach the higher degradation level of acetaminophen (92% within 90 min) in comparison to Fe^{+2}/PS and CuO/PS system (79 and 10%, respectively). Additionally, many studies have verified the effectiveness of metal activated PS with and without US irradiation. Zhou et al. [1] , have determined the effectiveness and mechanism degradation of ZVC, nZVC and nZVI activated PS and peroxymonosulfate (PMS) for 2,4 DCP degradation. The result of this study indicated that the nZVC/PS system was the most effective method of decomposing organic matters as than that of ZVC/PS and nZVI/PS. Based on literature, increasing costs due to high concentrations of copper along with high reaction times are two of the major problems in conducting PS activation systems with copper nanoparticles. Therefore, a secondary factor may need to be considered.

To the best of our knowledge, there has not been any study on the degradation of p-CP by nZVC activated PS in presence of US irradiation. Therefore, the current study set to assess the efficacy of p-CP degradation using US/PS/ZVC processes via batch experiments. Furthermore, the effect of operational parameters such as the pH of the solution, different dosages of PS, and nZVC on the degradation of p-CP were also evaluated.

2. MATERIALS AND METHOD

2. 1. Materials   All chemical materials, including p-CP (C_6H_5ClO, ≥99.9%), reagents (K_2HPO_4, NH_4OH,

KH$_2$PO$_4$, 4-aminoantipyrine, potassium ferricyanide (≥99.9%)), potassium persulfate (K$_2$S$_2$O$_8$, ≥99%) were provided from Merck CO, Germany. The nZVC (≥99% purity, particle size of 40 nm and surface area of 20 m^2/g) was purchased from US research Nano material LTD, Co, USA. Other reagents were of analytical grade and used without further purification. All solutions were prepared in de-ionized water that was prepared with Milli-Q ultrapure water. Various concentrations of p-CP solution examined in this study were prepared by diluting the stock solution (500 mg/L).

2. 2. Batch Pilot Study   Figure 1 shows the schematic diagram of the pilot set-up adopted here. This study, carried out in a 5-L stainless steel tank, equipped with a digital US device (model LUC-405, Daihan Labtech Co., Ltd., Korea), at a constant power of 350 W operated under 40 kHz fixed frequency. The reaction was conducted in a double-walled open glass cylinder with an inside diameter of 10 cm and the height of 20 cm with temperature controlled at 20 ± 0.5 °C using a water circulator. To ensure homogeneous exposure, a magnetic stirrer was used under the reactor and the agitation speed was set constantly at 100 r/min.

2. 3. Experimental Procedure   All the experiments were carried out in a batch mode sonoreactor indicated above. The aqueous solution containing p-CP, PS and nZVC as a catalyst was filled throughout the glass vessel installed in the center of the ultrasonic bath. All the experiments were carried out at room temperature and 0.1 M HCl and NaOH were used for pH adjustment an initial pH varying from 3.5 to 10.5. PS and nZVC were varied between 1-7.5 mm/L and 5-35 mg/L, respectively. Table 1 summarized the selected values for the experimental conditions. The effects of TBA and MA concentrations as radical scavenger were also investigated. At predetermined time intervals, an appropriate aliquot was sampled and filtered through 0.45 μm membranes
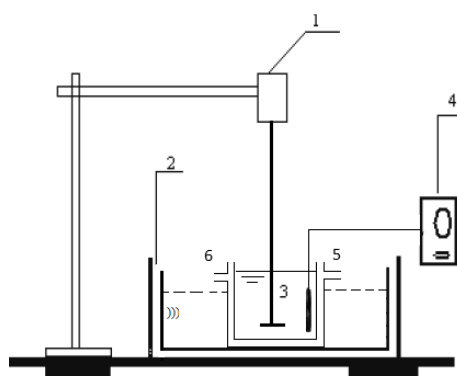

Figure 1. Schematic diagram of experimental apparatuses 1. Mixer, 2. Ultrasonic bath, 3. Reaction vessel, 4. pH-meter, 5. Water in, 6. Water out

TABLE 1. The ranges and levels of the experimental parameters

Run	PS concentration (mm/L)	pH	Initial p-CP concentration (mg/L)	nZVC dosage (mg/L)
1	5	3.5-10.5	50	25
2	5	3.5	50	5-30
3	1-7.5	3.5	50	30
4	5	3.5	10-100	30

(Millipore Co.), to remove all nZVC nanoparticles and then immediately analysis.

At present time intervals, appropriate aliquot samples were taken and analyzed immediately following the filtration (0.45 μm membranes, Millipore Co.) of the entire ZVC nanoparticles.

2. 4. Analytical Equipment   The p-CP was determined by UV-visible spectrophotometer (HACH DR- 5000, 500 nm) [7]. The removal efficiency of p-CP was calculated according to equation (2) stated as follows:

$$\%Removal = \frac{C_\circ - C}{C_\circ} t \qquad (2)$$

where C$_\circ$ denotes an initial concentration of p-CP (mg/L) and C$_t$ represents the concentration after sonodegradation at t minute[7]. Chemical oxygen demand (COD) was estimated based on standards for the examination of water and wastewater [30]. Total Organic Carbon (TOC) contents of the p-CP were analyzed by TOC analyzer (Elementar, Germany).

3. RESULTS AND DISCUSSION

3. 1. p-CP degradation in Different Systems Figure 2 compares p-CP degradation in different systems, including PS, nZVC, US, US/nZVC, US/PS, PS/nZVC and US/PS/nZVC processes. The experimental conditions were the following: ultrasonic intensity =40kHz, [p-CP]$^\circ$ =50 mg/L, [PS]$^\circ$=5mm/L, [nZVC]$^\circ$=25mg/l, temperature=20°C, pH=3, time=60min. As shown in Figure 2, the p-CP removal rate achieved by the two different systems including, nZVC and the US could be neglected, which represented that small amount of hydroxyl radicals formed by the ultrasonic fragmentation of water alone and limited adsorbing ability of nZVC. Also, the results indicated that 5 mm/L PS could obtaine18% p-CP removal rate, which attributed to the limited oxidizing ability of PS. As can be seen, the efficiency of p-CP removal by the US/nZVC and PS/nZVC systems are higher than single US, nZVC or PS systems.
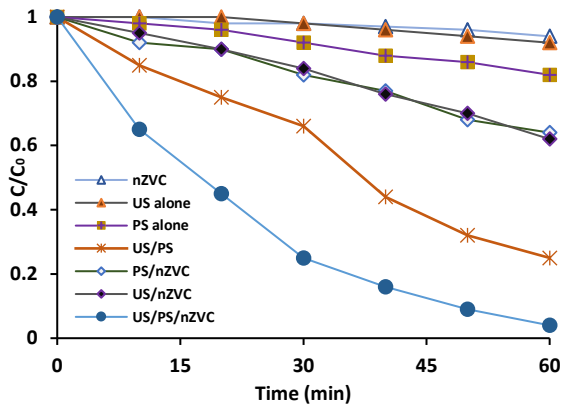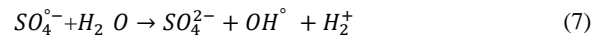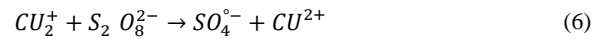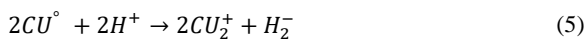
Figure 2. Degradation of p-CP under different systems. Experimental conditions: [p-CP]°=50mg/L, [PS]°=5mm/L, [nZVC]°=25mg/L, temperature=20°C, pH=3, time=60min

After 90 min, the elimination of p-CP was around 31 and 32% for the combined US/nZVC and PS/nZVC systems, respectively. The related results showed that the p-CP was refractory to the ZVC-induced oxygen activation, and the formation of sulfate radicals induced by the activation of PS by nZVC which was not enough to continue the degradation of p-CP[31, 32]. The removal of p-CP reached to 75% in the US/PS system owing to the sulfate radicals formed by Equations (3) and (4)[19, 29].

$$S_2 \, O_8^{2-}+))) \rightarrow 2SO_4^{°-} \tag{3}$$

$$SO_4^{°-} + OH^- \rightarrow SO_4^{2-} + OH^° \tag{4}$$
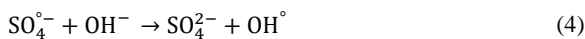
where the symbol ")))" denotes ultrasonic irradiation.

This result showed that US can be activated PS via Equation (3), but US/PS was not a comparatively efficient technique in consideration of energy consumption. According to results, PS is scarcely decomposed in the PS system, but it was quickly eliminated in the PS/nZVC system and may generate persulfate and hydroxyl radicals. According to the results of previous studies, PS/nZVC system can decompose 2,4 DCP at the concentration of 5mg/L as about 82.4% [24]. As presented in Figure 2, the p-CP degradation rate enhanced and reach up to 96% following addition of nZVC as a catalyst to the solution with PS in the presence of the US. This phenomenon indicated that a specific and synergistic effect exists between nZVC and PS in the presence of the US. The synergistic effect might be defined by ultrasound initiating which increased the mass transfer rate of the system and dispersed the aggregation of nZVC to accelerate the corrosion of ZVC to produce more Cu^{2+} made the decomposition of PS faster to produce more sulfate and hydroxyl radicals according to Equations (5)-(7) [1, 28, 29, 32].

$$2CU^° + 2H^+ \rightarrow 2CU_2^+ + H_2^- \tag{5}$$

$$CU_2^+ + S_2 \, O_8^{2-} \rightarrow SO_4^{°-} + CU^{2+} \tag{6}$$

$$SO_4^{°-}+H_2 \, O \rightarrow SO_4^{2-} + OH^° + H_2^+ \tag{7}$$
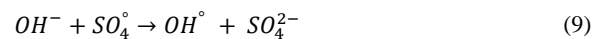
3. 2. The Effect of pH on p-CP Degradation

AOPs processes are affected by the acidity or alkalinity of reaction media for the degradation of organic contaminants [13, 16]. The effect of different initial pH ranging from 3.5 to 10.5 on the p-CP removal in US/PS/nZVC system was investigated by adding 5 mM/L PS, 25mg/L nZVC in a solution containing 50 mg/L p-CP. Figure 3(a) displays time-dependent changes in p-CP as the function of initial pH. As illustrated in Figure 3(a), the degradation efficiency of p-CP decreases with an increase in initial pH. For example, when the initial pH is increased from 3.5 to 7, the removal ratio of p-CP decreased from 96.3 to 83.5%. As the initial pH increased to 10.5, a 68.2% removal of p-CP was achieved within 60 min. Thus, it is clear that the rate of p-CP degradation efficiency increased with a decrease in initial pH, which was in accordance with previous studies [15, 33, 34]. As for free radicals, more sulfate radicals with the redox potential of 2.8-3.1 V are produced in acidic conditions, which may be partially responsible for the efficient p-CP decomposition under acid conditions [27, 33].

In this condition, the generation of sulfate radicals from PS anion could be catalyzed by decreasing the pH value, according to Equation (8) [4].

$$S_2 \, O_8^{2-} + SO_4^{°-} \rightarrow S_2 \, O_8^{2-} + SO_4^{2-} \tag{8}$$
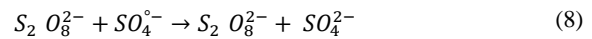
The effluent pH variations with the reaction evolution under different conditions were depicted in Figure 3(b). As shown in Figure 3(b), the pH of solution drops off as the reaction continues under acidic, neutral and alkaline conditions. This phenomenon is caused by the acidified from the transformation of sulfate radical to hydroxyl radicals, which consumes OH⁻ in the solution according to Equation (9). The result was in line with the research reported by Gu et al. [39].

$$OH^- + SO_4^° \rightarrow OH^° + SO_4^{2-} \tag{9}$$

3. 3. Effect of PS Concentration on p-CP Degradation

Figure 4 shows the effect of initial concentration of PS ranging from 1 to 7.5 mm/L on the degradation of p-CP based on different contact time. The effects of various concentrations of PS activated with 25 mg/L nZVC in the presence of US were also examined. As depicted in Figure 4, when PS concentration increased from 1 to 5 mm/L, the p-CP degradation efficiency gradually enhanced. The degradation efficiency of p-CP in 60 min was only 75.2% with 1 mm/L PS, whereas p-CP was almost entirely eliminated using 5mM PS in 60
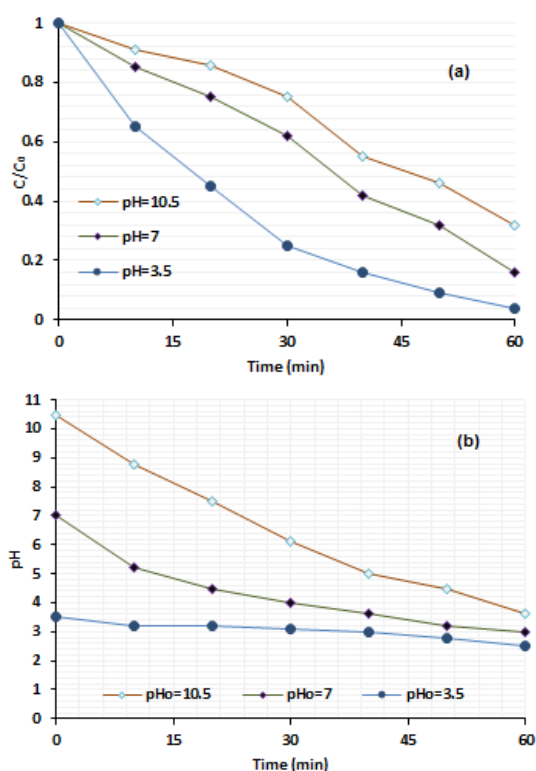
Figure 3. Effect of the initial pH on the p-CP degradation rate (a), and pH variation during the reaction (b). Conditions: [p-CP]=50 mg/L, [PS]=5 mm/L, [nZVC]=25 mg/L, temperature=20°C
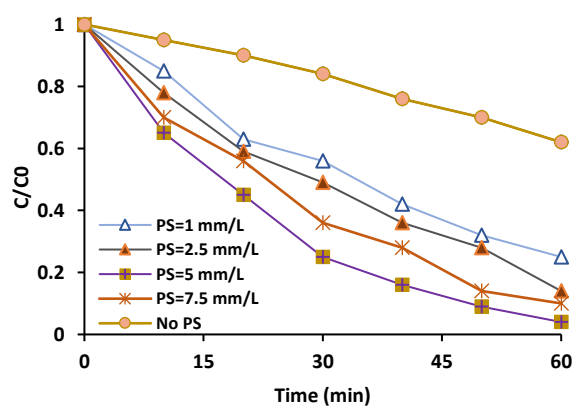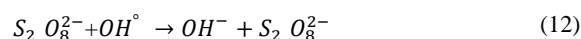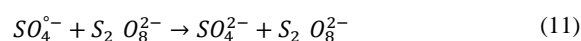

Figure 4. Effect of initial PS concentration on the p-CP degradation. Conditions: [p-CP]=50 mg/L, [pH]=3, [nZVC]=25 mg/L, temperature=20°C

min. These results indicates that persulfate has a key role in p-CP degradation; however, the highest removal rate was gained in 60 min. The improvement of p-CP degradation achieved through adding PS is due to increase in the sulfate radicals as an oxidizing agent in the US/PS/nZVC system according to Equations (3)-(6). However, further increasing the initial PS concentration

above 5 mm/L, decreased p-CP degradation. In agreement with Monteagudo et al. [22], Zhang et al. [29] and Hussein et al. [39], this is due to (a) recombination of sulfate radicals and decreasing the concentrations of oxidant agent to degrade p-CP, b) consumption of sulfate radicals by reaction with excess PS and c) unproductive decomposition of PS by hydroxyl radicals that decrease the availability of hydroxyl radicals according to Equations (10)-(12) [39-41].

$$SO_4^{°-} + SO_4^{°-} \rightarrow S_2\,O_8^{2-} \tag{10}$$

$$SO_4^{°-} + S_2\,O_8^{2-} \rightarrow SO_4^{2-} + S_2\,O_8^{2-} \tag{11}$$

$$S_2\,O_8^{2-} + OH^{°} \rightarrow OH^{-} + S_2\,O_8^{2-} \tag{12}$$

3. 4. Effect of nZVC Dosage on p-CP Degradation

The effect of initial nZVC dosage ranging from 5 to 35mg/L in US/PS/nZVC system on the removal efficiency of p-CP is depicted in Figure 5. As illustrated, addition of nZVC in the US/PS system can enhance the degradation rate of p-CP. Hence, the results revealed that a certain synergistic effect exists between nZVC and PS. After 60 min, the degradation efficiencies of p-CP were 84, 88 and 96% with nZVC concentrations of 5, 15 and 25 mg/L, respectively. It is suggested that, with the increase of nZVC dosage from 25 to 30 mg/L, the p-CP degradation efficiency increased from 76.5 to 97% after 40 min reactions. Results indicated that the optimum initial concentration of nZVC required to achieve the highest p-CP removal efficiency is 30 mg/L (97% of p-CP removal). This is owing to the fact that, higher initial nZVC dosage provides more active sites and releases Cu^+ in a more considerable amount. As a result, the degradation of PS was accelerated with the generation of more sulfate radicals, which improved the p-CP removal rate. Nonetheless, the excessive amount of nZVC, higher than the optimum amount, may lead to a decline in the p-CP removal efficiency.
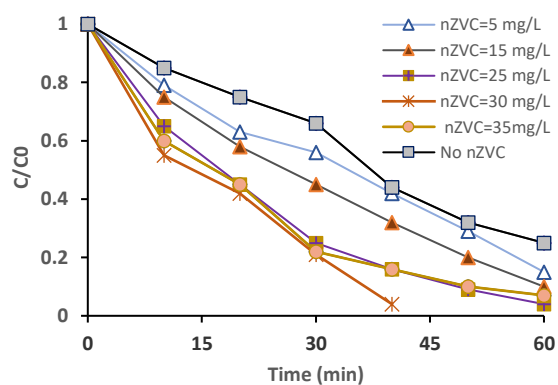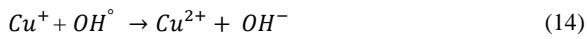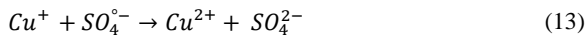

Figure 5. Effect of the initial nZVC concentration on the p-CP degradation. Conditions: [p-CP] = 50 mg/L, [pH] = 3, [PS] = 5mm/L, temperature=20°C

It is going to the fact that the system released more Cu^+, much of it could be consumed by produced sulfate radicals leading to a decrease in p-CP removal rate according to Equations (13) and (14) [24, 42]. Therefore, a catalyst dosage of 30 mg/L could be suitable to optimize the catalytic activity for further experiments in this study.

$$Cu^+ + SO_4^{°-} \rightarrow Cu^{2+} + SO_4^{2-} \tag{13}$$

$$Cu^+ + OH^° \rightarrow Cu^{2+} + OH^- \tag{14}$$

3. 5. The Effect of Initial p-CP Concentration

The ability of the US/PS/nZVC system for the degradation of p-CP for different initial p-CP concentration in the range of 10 to 100 mg/L was also investigated. The results are shown in Figure 6. At a concentration of 10 and 25 mg/L p-CP, complete degradation was achieved in 30 min. When the initial p-CP concentration were 25 and 50 mg/L, p-CP removal degradation reached to 99% at 40 min reaction time. The decomposition efficiency significantly decreased as the initial p-CP concentration reached to about 100 mg/L, where 70% of p-CP degraded within 60 min. This is due to insufficient oxidative radicals would be used up when the initial p-CP was increased, resulted in lower p-CP degradation. However, when the initial p-CP concentration was lower, radicals generation amount would be higher than the consumption rate by p-CP degradation, considering higher p-CP removal rate. The pseudo-first order kinetic model for p-CP degradation was also achieved to experimental data obtained from different the initial p-CP concentration. As shown in Figure 6. The apparent k values were obtained as 0.095, 0.076, 0.066, 0.033 and 0.028 min^{-1} for p-CP at 10, 25, 50, 75 and 100mg/L, respectively. According to the results, the appearance rate of the 10 mg/L p-CP was the highest that was inversely proportional to the p-CP concentration. The minimum p-CP removal rate recorded at the highest p-CP l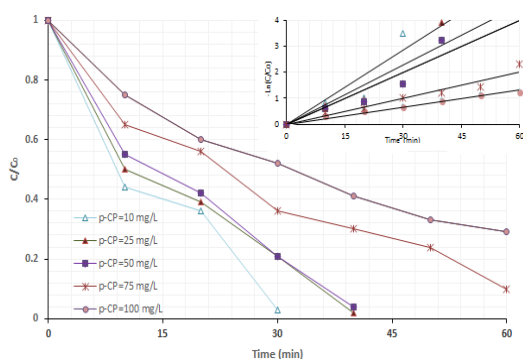evel that might be the result of limited amount of available active radicals in the reaction zone or the insufficient number of reaction sites. These results are consistent with those reported by Wang et al. [43] and Davididou et al. [44] in their studies on the photocatalysis of various organic pollutants. Specifically, these results confirmed that the organic degradation rate is dependent on the pollutant initial concentrations in which degradation rates gradually decreased with increasing initial organic concentrations.

3. 6. Mineralization Rate of p-CP

Along with the degradation of organic pollutant, an acceptable amount of mineralization should be done on pollutants in order to convert to carbon dioxide, water and other mineral ions. This process is considered as a practicable alternative to treatment of wastewater contaminated with organic pollutants [4, 17]. Monitoring of TOC and COD contents of the solutions during the experiments gave a direct suggestion of the level of mineralization achieve. Figure 7, shows TOC and COD removal efficiency of p-CP at an initial concentration of 50 mg/L in the optimal conditions. As shown in Figure 7, the mineralization level is lower than the amount of degraded organic pollutant which has been similar to those reported by Zhou et al. [1]. As shown, the rates of mineralization in terms of TOC and COD removal efficiency were 58 and 72% after 30 min, whereas the p-CP removal rate rose to 96% under the same operational condition due to this fact that p-CP was transformed into intermediate metabolites. When the irradiation time was extended to 60 min, TOC and COD removal efficiency gradually increased and reached to 72 and 82%, respectively. As a result, the irradiation times which affects the photocatalytic mineralization efficency is one of the main paramerters for the oxidation process.

3. 7. The Effect of Radical Scavengers

The mechanism of AOPs is complex because many radicals are produced, while some radicals disappeared in series and/or in parallel [45]. Radical scavenger experiments

Figure 6. Effect of the initial p-CP concentration on the p-CP degradation. Conditions: [nZVC]=30 mg/L, [pH]=3, [PS]=5mm/L, temperature=20°C
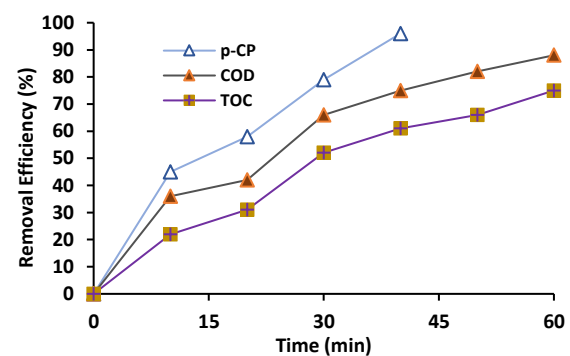
Figure 7. TOC, COD and p-CP removal efficiency at optimal conditions. Conditions: [p-CP]=50 mg/L, [pH]=3, [PS]=5mm/L and [nZVC]=30 mg/L, temperature=20°C

were achieved with selective compound probes to detect the most significant radicals. These chemical probes have different kinetics to distinguish the contributions of OH° and $SO_4^{\circ-}$ radicals in the PS avdance oxidation system. Based on literature [46], Tert –butanol (TBA) and methanol (MA) are the two most widely used scavengers in AOPs. Owing to the high rate constant with $SO_4^{\circ-}$ and OH°, MA was selected as a practical scavenger for both hydroxyl and sulfate radicals [45, 46]. Owing to the high rate constant with hydroxyl radical, TBA was selected as an effective scavenger for OH° [42]. The radical scavenger analyses were carried out through repeating the reaction of p-CP with the addition of different radical scavengers i.e., TBA and MA at optimum experimental conditions. The data shown in Figure 8. As can be seen in Figure 8, 96% of p-CP can be removed in 40 min without scavenger (Control). The addition of MA (100mm/L) and TBA (100mm/L) decreased p-CP degradation by 18% and 42% compared with free radical scavenger system within 40 min contact time. Baced on the results, MA illustrated a comparatively stronger suppression effect than TBA. This results indicated that both sulfate and hydroxyl radicals are important radicals in US/PS/nZVC system degrading p-CP. The contribution of $SO_4^{\circ-}$ was calculated using Equation (15) [47].

$$\%Contribution \ of \ SO_4^{\circ-} = \frac{\%Removal \ with \ OH^{\circ} \ scavenger}{\%Removal \ without \ scavenger} \times 100 \qquad (15)$$

The contribution of sulfate and hydroxyl radicals were 81.25 and 18.75% according to Equation (15). Therefore, the results in Figure 8 indicated that sulfate radicals are predominate reactive which generated during the oxidation process, even with nearly 18% contributions to the oxidation process of hydroxyl radicals. Zhang et al. [45] showed that sulfate radicals are the main radical species for degradation of acetaminophen in $Fe_2O_3@Cu_2O$ activated PS system which is similar to the
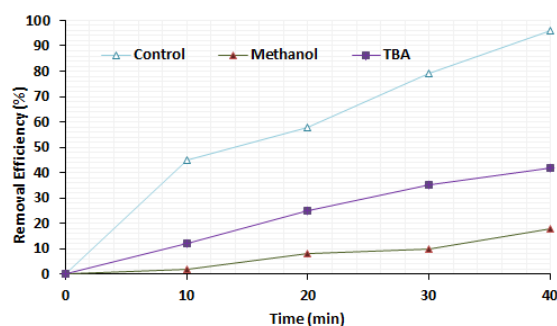

Figure 8. Degradation of p-CP with and without scavengers. Conditions: [p-CP]=50 mg/L; [pH]=3; [PS =5mm/L, [nZVC]=30 mg/L, [TBA]=100mm/L and [MA]=100mm/L, temperature=20°C

result of present study. Similarly, Wu et al. [46] showed that hydroxyl radicals was more important than sulfate radicals in Fe-citric acid (CA) activated PS system.

4. CONCLUSIONS

In the present study, different oxidation processes, i.e., US, PS, nZVC, US/PS, PS/nZVC, US/nZVC and US/PS/nZVC have been applied to compare the degradation of p-CP in aqueous solutions. The US/PS/nZVC system was the most effective, exhibiting a maximum 98% degradation of p-CP at 25 mg/L when using 5 mM/L PS and 30mg/L nZVC within 40 min contact time. The degradation efficiency of p-CP depends on solution pH and decreased with increasing pH from 3.5 to 10.5. After 60 min treatments, the p-CP removal rate were 96, 83.5 and 68% at pH 3.5, 7 and 10.5, respectively. The p-CP degradation rate is depended on persulfate concentrations and the removal rate decreased with increasing over than investigated range.

The rsults indicated that p-CP remaval rate increased from 75 to 96% when nZVC disage increased from 5 to 30 mg/L. The p-CP degradation rate is depended on oxidant and catalyst dosages and the removal rate decreased with increasing over than investigated range. In the case of mineralization, COD and TOC removal rates were 75 and 61% achieved in optimum conditions after 60 min using US/PS/nZVC processes, respectively. The removal process of p-CP could be described by the pseudo-first-order kinetics. The apparent first-order rate constants (k) were 0.095, 0.076, 0.066, 0.033 and 0.028 min^{-1} at an initial p-CP concentration of 10, 25, 50, 75 and 100 mg/L, respectively. Both sulfate ($SO_4^{\circ-}$) and hydroxyl (OH°) free radicals are possibly responsible for the degrading p-CP in the US/PS/nZVC combined system. However $SO_4^{\circ-}$ radicals are predominate reactively that was generated during the oxidation process. Finally, the combined US/PS/nZVC process appears to have a positive synergistic effect on the degrading of p-CP which performance with adding a minimal amount of oxidant and catalyst.

5. ACKNOWLEDGMENT

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Persian Abstract

چکیده

در این مطالعه تجزیه ٤-کلروفنل با استفاده از پرسولفات فعال شده با کاتالیست نانو ذرات مس در حضور امواج فراصوت در محلول های آبی مورد بررسی قرار گرفت. اثرات پارامترهای مختلف بهره برداری نظیر pH محلول (٣/٥-١٠/٥)، غلظت پرسولفات (١- ٧/٥ میلی مول)، غلظت نانو ذره مس (٥-٣٥میلی گرم بر لیتر) و غلظت اولیه ٤-کلروفنل (١٠٠-١٠ میلی گرم بر لیتر) در زمان های مختلف بهره برداری مورد بررسی قرار گرفت. نتایج بیانگر آن بود که فرایند التراسوند/پرسولفات/نانو ذره مس در مقایسه با فرایندهای التراسوند/پرسولفات، التراسوند/نانو ذره و پرسولفات/نانو ذره کارائی بیشتری در حذف ماده آلی داشته است. بیشترین کارائی حذف ٤-کلروفنل (٩٨٪) در غلظت اولیه ٢٥ میلی گرم بر لیتر در زمان ٤٠ دقیقه با افزودن ٥ میلی مول پرسولفات و ٣٠میلی گرم در لیتر نانو ذره مس مشاهده شد. همچنین نتایج نشان داد که میزان حذف ٤-کلروفنل به غلظت اولیه آن بستگی داشته است. به منظور تعیین میزان معدنی سازی ٤-کلروفنل مقادیر TOC و COD اندازه گیری شد. با استفاده از فرایند التراسوند/پرسولفات/نانو ذره مس به ترتیب ٦١ و ٧٥ درصد COD و TOC در شرایط بهینه حذف شد. طی استفاده از متانل و تترابوتیل اتر به عنوان ربیاینده رادیکال، رادیکال سولفات به عنوان نوع غالب معرفی شد. حذف ٤-کلروفنل با استفاده از این فرایند از معادلات درجه اول تبعیت نموده است. میزان سرعت واکنش در شرایط بهینه ٠/٠٧٦ بر دقیقه گزارش شد.