

UVA-LED assisted persulfate/nZVI and hydrogen peroxide/nZVI for degrading 4-chlorophenol in aqueous solutions

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Abstract—Photocatalytic degradation of 4-chlorophenol (4-CP) using UVA-LED assisted persulfate and hydrogen peroxide activated by the nZVI (Nano Zero Valent Iron) in a batch photocatalytic reactor was investigated. The reaction involved a lab-scale photoreactor irradiated with UVA-LED light emitted at 390 nm. The efficiency of the reaction was evaluated in terms of 4-CP degradation and mineralization degree at different pH of solution, initial concentrations of nZVI, persulfate, hydrogen peroxide and 4-CP. In UVA-LED/H₂O₂/nZVI process, complete degradation of 4-CP (>99%) and 75% mineralization was achieved at pH of 3, hydrogen peroxide concentration of 0.75 mM, nZVI dosage of 1 mM and initial 4-CP concentration of 25 mg/L at the reaction time of 30 min. The optimum conditions obtained for the best 4-CP degradation rate were at an initial concentration of 25 mg/l, persulfate concentration of 1.5 mM, nZVI dosage of 1 mM, pH of 3 and reaction time of 120 min for UVA-LED/persulfate/nZVI process. It was also observed that the 4-CP degradation rate is dependent on initial 4-CP concentrations for both processes. The pseudo-first-order kinetic constant at 25 mg/L initial concentration of 4-CP was found to be 1.4×10^{-1} and 3.8×10^{-2} in UVA-LED/H₂O₂/nZVI and UVA-LED/persulfate/nZVI processes, respectively. Briefly, the UVA-LED/H₂O₂/nZVI process enhanced the degradation rate of 4-CP by 3.67-times in comparison to UVA-LED/persulfate/nZVI process at 30 min contact time, which serves as a new and feasible approach for the degradation of 4-CP as well as other organic contaminants containing wastewater.

Keywords: 4-Chlorophenol, UVA-LEDs, Nano Zero-valent Iron, Persulfate, Hydrogen Peroxide, Activation

INTRODUCTION

During the last decade, the release of recalcitrant organic contaminants into the environment has been a major source of surface and ground water contamination raising alarming concerns due to their adverse impacts on human health and ecosystems [1,2]. Unfortunately, since most of these organic compounds are nanobiodegradable, they cannot be effectively removed using conventional treatment methods. Among these organic contaminants, chlorophenols (CPs) can be considered as one of the most important hazardous environmental pollutants, which are extremely harmful to organisms at even very low concentrations [3,4]. From an environmental and health point of view, 4-chlorophenol (4-CP) as one of the most important members of CPs is non-biodegradable and has carcinogenic, mutagenic, acute and chronic toxic effects [3,5]. This pollutant is introduced into environment through various human activities, such as uncontrolled use of wood preservatives, pesticides, fungicides and herbicides, chlorination of drinking water and wastewater and effluent of wastewater generated by a large variety of industries including oil refineries, pharmaceutical factories, dyestuff, paper and leather producers [3,5]. Many wastewater treatment methods such as biological, physicochemical and

thermal treatment have been used to safely remove 4-CP. Its poor biodegradability leads to slow biological removal because the activities of microorganism are impaired by 4-CP. The concern regarding the production of chemical sludge, energy consumption and the transfer of pollutants from the liquid phase to the solid phase may restrict the practical use of physicochemical techniques. Furthermore, thermal treatment methods might emit other hazardous contaminants [6]. Advanced oxidation processes (AOPs) such as Fenton and photo-Fenton [7], ozone oxidation [8], sonolysis [9], and photo-catalytic oxidation [3] have been successful in treating a majority of refractory organic compounds in polluted water. In AOPs techniques, the radicals generated in the solution are responsible for oxidation and mineralization of organic compounds [7-9]. Among AOPs methods, photo-based AOP is an oxidation technology that introduces UV irradiation to enhance the formation of hydroxyl radical as a strong and non-selective oxidant [10]. The use of UV irradiation along with oxidants including hydrogen peroxide [3], ozone [11] and persulfate [12] is effective in the degradation of recalcitrant pollutants. Hydroxyl radical-based AOPs have been widely studied for the destruction of a wide range of recalcitrant organics due to the unpaired electrons produced by high reactive hydroxyl radicals [10,13]. However, the influence of wastewater quality on treatment efficiency is one of the main limitations in this process [13]. Another type of AOPs, which is based on persulfate producing sulfate radicals, has recently received much attention for its capability of destructing many organic contami-

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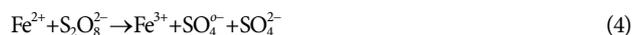
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nants due to the production of sulfate radicals [13-15]. Persulfate has received wide attention due to its higher oxidation-reduction potential ($E^\circ=2.01$ V) compared with hydrogen peroxide ($E^\circ=1.76$ V), high solubility in water, non-selectively reactivity, high stability in aqua solution and cost-effectiveness [13-16]. Both persulfate and hydrogen peroxide are generally stable under typical water treatment condition; however, they become very active with UV irradiation [10], microwave [4], ultrasound wave [17,18], heat [19] and metal [20] to form sulfate and hydroxyl radicals according to Eqs. (1)-(2) [15-19]:



Conventional UV lamps used in AOPs for the treatment of water and wastewater are low, medium, and high-pressure mercury lamps. High-power requirement along with low light efficiency makes the use of mercury lamp an energy-intensive process [14-16]. Recent advances in light emitting diodes (LEDs) technology have made it possible to use LEDs lamp in a wide range of wavelengths from 240 nm to 390 nm [21,22]. LED lamps offer several advantages over conventional UV lamps, such as short warm-up time, high efficiency, no mercury disposal problem, reduced replacement frequency, mechanical stability, easy handling, long life times, lower energy consumption and not getting overheated. It also converts all electrical energy into monochromatic light [21,23]. UV-LED lamps are currently being used either alone or in combination with photocatalyst and oxidants for the degradation of acetamiprid [24], antipyrine [25], anatoxin [20] and carmoisine [26]. Jamali et al. utilized the UV-LED in combination with hydrogen peroxide to study the photocatalytic degradation of phenol [22]. They revealed that phenol degradation significantly enhanced adding an optimum amount of oxidant; however, the maximum degradation rate of 42% was achieved after 4 hr. Another example was the study of photocatalytic oxidation of oxalic acid using wet peroxide with Fe^{2+} - Fe^{3+} activated carbon as a catalyst [27]. They observed an enhancement in TOC reduction after 180 min with the stoichiometric amount of hydrogen peroxide. Verma et al. evaluated the removal of anatoxin-a using UV-C LED with and without an oxidant. It was noticed that UV-C/ H_2O_2 process improved the oxidation rate of anatoxin-a by 4.5 times compared to direct photolysis by UV-C LED, which shows the significant increase in its degradation through hydrogen peroxide addition [21]. Furthermore, the degradation of antipyrine was studied using a UV-A LED photofenton reaction with the addition of persulfate anions [25]. Also, the application of the UV-LED in the treatment of formaldehyde as an indoor air pollutant was investigated in the presence of compound silver titanium dioxide Shie et al. [28] and Vilhuet et al. [29] evaluated the performance of UV-LED and hydrogen peroxide in the photodegradation of phenol in an aqueous solution.

Recently, Fe^{2+} , Fe^{3+} and Fe^0 have been widely studied as famous transition metal activators which activate persulfate and hydrogen peroxide to generate active radicals at ambient temperature according to Eqs. (3)-(6) [23,30]:



Fe^{2+} is often used as an activator due to its environmentally benign nature and cost effectiveness. However, undesired unproductive radical consumption occurs in the presence of excessive Fe^{2+} or rapid conversion of Fe^{2+} to Fe^{3+} , as shown in Eq. (7), in the activation of persulfate and sludge production in traditional Fenton process [30,31].



To resolve this problem, nZVI as an activator or chelating agent was proposed [32]. Many surveys have verified the effectiveness of nZVI activated persulfate and hydrogen peroxide with and without UV irradiation; however, to the best of our knowledge, there has not been any study on the degradation of 4-CP by nZVI activated persulfate and hydrogen peroxide in the presence of UV-A LED. Therefore, this study aimed at assessing the efficacy of 4-CP degradation using UV-A LED assisted persulfate/nZVI and H_2O_2 /nZVI processes via batch experiments. The effects of operational parameters such as the pH of solution, different dosages of persulfate, hydrogen peroxide and ZVI on the degradation of 4-CP were also evaluated.

MATERIALS AND METHODS

1. Materials

All chemical materials, including 4-CP ($\text{C}_6\text{H}_5\text{ClO}$), reagents (NH_4OH 0.5 N, KH_2PO_4 , K_2HPO_4 , 4-aminoantipyrine, potassium ferricyanide (with 99.9% purity)), oxidants (Hydrogen peroxide solution (30% W/W)) and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), were provided from Merck, Germany. The nZVI (>99% pure, particle size of 21 nm and surface area of $0.14 \text{ m}^2/\text{g}$) was purchased from Sigma-Aldrich (USA). H_2SO_4 and NaOH were used to adjust the initial pH of the 4-CP solution. All reagents employed in this study did not undergo any more treatment. All the solutions consumed were prepared by deionized water. The various concentrations of 4-CP solution examined were prepared by diluting the stock solution (1,000 mg/L).

2. Batch Apparatus Photoreactor

LED lamps, manufactured by semiconductor technology, Seoul-Korea with a light peak emission wavelength of 390 nm were used as a UV-A source for the irradiation of solution. The UV-A LED module consisted of 18 small LEDs attached to a DC power supply. Fig. 1 shows the schematic diagram of the experimental setup. A quartz plate is placed between the reactor and the LEDs lamp emitting UV-A at 390 nm.

3. Experimental Procedure

All the experiments were carried out in a batch mode lab-scale photoreactor irradiated with a UV-A LED lamp indicated above. The aqueous solution containing 4-CP, persulfate or hydrogen peroxide, a catalyst and nZVI was filled throughout the glass vessel with a capacity of 500 ml volume installed in the center of a water-cooling jacket made from plexiglas to maintain the temperature of the suspension constant. A commercial UV-A LED lamp (18 lamps,

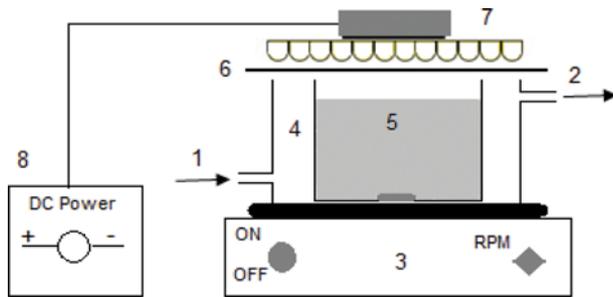


Fig. 1. Schematic diagram of experimental setup.

1. Water in
2. Water out
3. Magnetic stirrer
4. Water bath
5. Container
6. Quartz sheet
7. UV-LED lamps
8. Feed supply

diameter of 12 cm) was placed above the reactor vessel located at the center of the reactor. The distance between the lamp and the top surface of the reaction was 5 cm. The solution in the vessel was stirred continuously with a magnetic stirrer at 250 rpm during the experiments to maintain the catalyst suspended. A flat quartz sheet was placed between the LED lamp and at the top of the solution for confirmed transparency of UV radiation. All the experiments were at room temperature and an initial pH varying from 3 to 11 with an aqueous 4-CP solution of 25 mg/L. Hydrogen peroxide, persulfate and nZVI varied between 0.25-1.25 mM, 0.5-3 mM and 0.25-1.25 mM, respectively. Table 1 summarizes the selected values for the experimental conditions. The samples were taken at different periods and filtered through a 0.45 μm filter to remove all nZVI nanoparticles.

4. Analytical Equipment

A UV-visible spectrophotometer (HACH DR- 5000) was used to determine 4-CP at 500 nm wavelength [32]. The removal efficiency of 4-CP was defined using Eq. (8):

$$\text{Removal (\%)} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (8)$$

where C_0 is initial concentration of 4-CP (mg/L) and C_t is the concentration after photodegradation at t minute [7]. Chemical oxygen demand (COD) was determined according to standard methods for the examination of water and wastewater [33].

RESULTS AND DISCUSSION

1. The Effect of pH on 4-CP Degradation

Apparently, the pH of solution had a considerable influence on

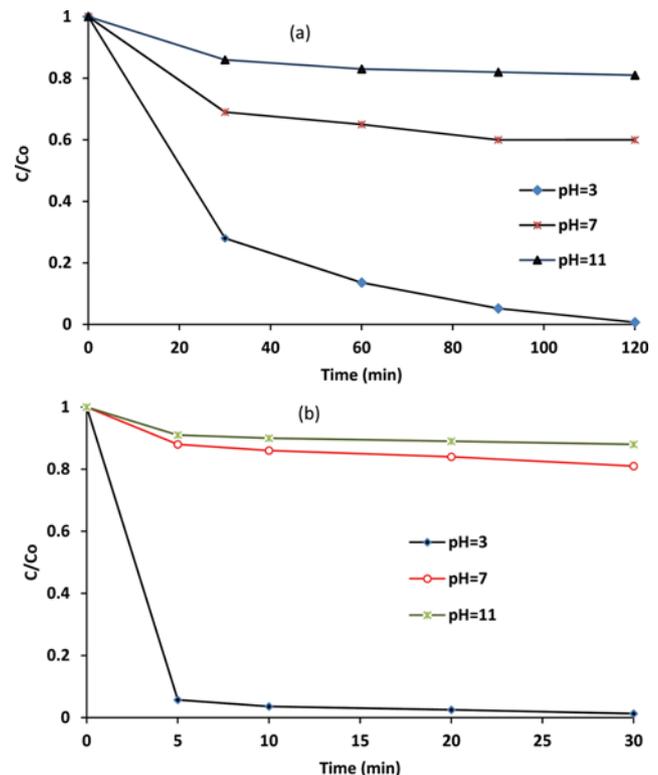


Fig. 2. The effect of initial pH in UV-A LED/persulfate/ZVI (a) and UV-A LED/H₂O₂/ZVI (b) processes on the degradation of 4-CP (4-CP=25 mg/L, ZVI=1 mM, persulfate=1.5 mM and H₂O₂=0.75 mM).

the degradation of organic contaminants using AOPs [22,25]. The effects of initial pH on 4-CP degradation using UV-A LED/persulfate/nZVI and UV-A LED/H₂O₂/nZVI processes were examined under different initial pHs (3-11). Fig. 2(a) shows time-dependent changes in 4-CP as the function of initial pH in UV-A LED/Per-sulfate/nZVI process. The results from Fig. 2(a) indicated that 4-CP degradation rate decreased when initial pH increased from 3 to 11. In Fig. 2(a), after 120 min of irradiation, the 4-CP removal efficiency at pH of 3, 7 and 11 was 18.9%, 41% and 99.8%, respectively. As shown, acidic solution improved the degradation of 4-CP, which was in accordance with previous studies [25,27]. Hus-sain et al. demonstrated that sulfate radical has a higher redox potential in acidic conditions [34]. In addition, the hydrolysis of persulfate in an acidic solution could generate hydrogen peroxide, which gives rise to a Fenton reaction in the presence of nZVI. Furthermore, sulfate radicals could even oxidize H₂O to produce

Table 1. The ranges and levels of the experimental parameters

Run	H ₂ O ₂ concentration (mM)	pH	Persulfate (mM)	Initial 4-CP concentration (mg/L)	nZVI dosage (mM)
1	-----	3-11	1.5	25	1
2	0.75	3-11	-----	25	1
3	-----	3	0.5-3	25	1
4	0.25-1.25	3	-----	25	1
5	-----	3	1.5	25	0.25-2
6	1	3	-----	25	0.1-2

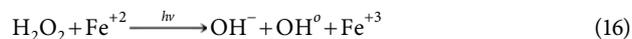
hydroxyl radicals (OH°). The reactions mentioned above could be described as follows in Eqs. (9)-(13) [31,34].



The decreased rate of 4-CP degradation in basic condition can be explained by the fact that the precipitation of Fe^{3+} ions occurs whenever the pH of solution is higher than 7. In this condition, oxyhydroxides of Fe^{3+} such as FeOH^{2+} , $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}_2(\text{OH})_2^{4+}$ are produced which have low efficiency for the generation of sulfate radicals [20,31,34]. Additionally, the production rate of sulfate radicals converted from persulfate anions could be accelerated by raising the acidity of solution according to Eqs. (14)-(15) [15,34].



Fig. 2(b) illustrates the effect of different amount of pH ranging from 3 to 11 in UV-A LED/ H_2O_2 /nZVI process. As can be seen from Fig. 2(b), the lower pH of solution was favored for the degradation of 4-CP. It is clear that 4-CP degradation rate was much faster at pH=3, in which more than 94% and 99% of 4-CP were removed within 10 and 30 min. However, the 4-CP removal efficiency was significantly reduced to 18% and 11% at pH 7 and 11, respectively. As known, the oxidative species generated by the Fenton reaction are the hydroxyl radicals, as one of the most powerful oxidants ($E^\circ=2.73$ V), are non-selective and fast-reacting with organic compounds. In this condition, Fe^{2+} reacts with hydrogen peroxide to produce Fe^{3+} and OH° according to Eq. (16) [27].



Since the OH° yield in the Fenton process depends on the pH value, the Fenton reaction is conducted under acidic conditions [24,26]. Also, above pH 3, first, the ferrous ions get converted to ferric ions which then are combined with hydroxyl radicals to produce ferric hydroxide precipitated and settled down, which reduces the ferrous availability in the solution. Secondly, more hydrogen peroxide is decomposed without improving oxidation [21].

2. The Effect of Oxidant Concentration on 4-CP Degradation

Fig. 3(a) shows the effect of different amounts of initial persulfate concentration on the degradation of 4-CP according to different contact time. The effects of various concentrations of persulfate ranging from 0.5 to 3 mM that were activated with 1 mM nZVI in the presence of UV-A LED were examined. Fig. 3(a) clearly indicates that the removal rates of 4-CP first increased with increasing the persulfate concentration from 0.5 mM to 1.5 mM. These results show that adding persulfate plays an essential role during 4-CP degradation; however, the highest removal rate was at the contact time of 120 min. The enhancement of 4-CP degradation from adding persulfate is due to the increase in the sulfate radicals ($E^\circ=2.6$ V) as an oxidizing agent according to Eqs. (9)-(10) [30,33].

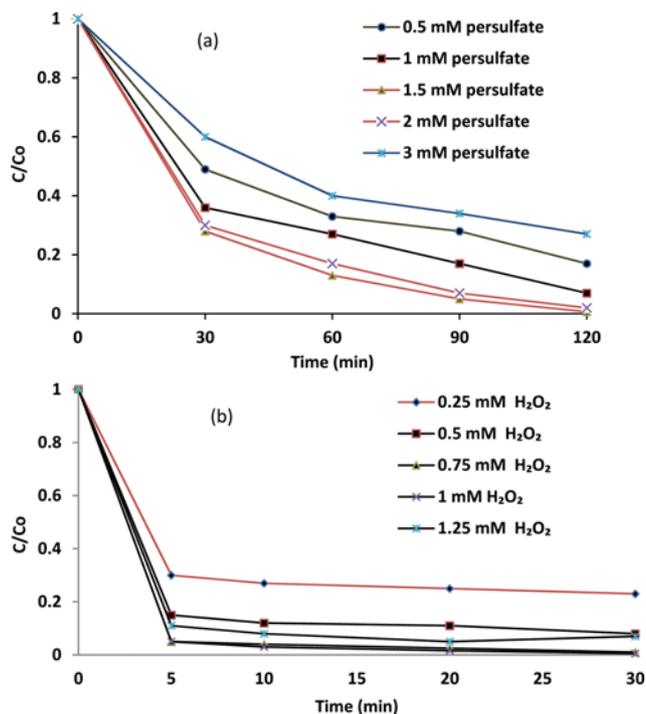
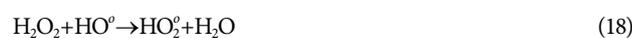


Fig. 3. The effect of initial oxidant dosage in UV-A LED/persulfate/ZVI (a) and UV-A LED/ H_2O_2 /ZVI (b) processes on the degradation of 4-CP (4-CP=25 mg/L, ZVI=1 mM and optimum pH).

However, an increase in the concentration of persulfate up to 1.5 mM, resulted in a significant adverse effect on 4-CP degradation. On the other hand, when initial persulfate concentration increased, the scavenging effect to capture sulfate radicals also increased according to Eq. (17) [15].



In addition, the effect of different initial hydrogen peroxide concentration ranging from 0.25-1.25 mM on 4-CP degradation using UV-A LED/ H_2O_2 /nZVI process is shown in Fig. 3(b). As shown, the optimal initial concentration of hydrogen peroxide over the range studied was 1 mM. After 60 min contact time, the degradation efficiencies of 4-CP were about 75%, 92%, 98% and 99% when the initial concentrations of hydrogen peroxide were 0.25, 0.5, 0.75 and 1 mM, respectively. It is well known that at higher concentrations, hydrogen peroxide can contact more efficiently with nZVI, and consequently produce a higher amount of hydroxyl radicals [25,30-32]. Nevertheless, an excessive amount of hydrogen peroxide can induce more hydroxyl radicals available to degradation of 4-CP to be consumed, which produces the well-known scavenger effect as shown in Eq. (18) [7,30].



The produced radicals (HO_2^\cdot) have much smaller oxidation potential than those of hydroxyl radicals. Moreover, the decomposition of hydrogen peroxide to form water and oxygen happens when an excessive amount of hydrogen peroxide is used according to Eq. (19) [10,14].

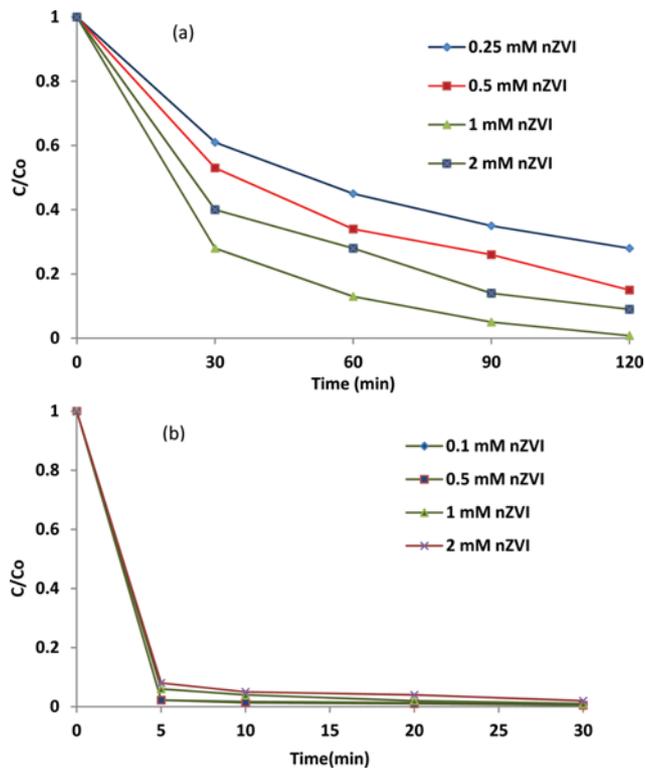


Fig. 4. The effect of initial nZVI dosage in UV-A LED/persulfate/nZVI (a) and UV-A LED/H₂O₂/nZVI (b) processes on the degradation of 4-CP (4-CP=25 mg/L at optimum oxidant dosage and pH).



3. The Effect of nZVI Dosage on 4-CP Degradation

The effect of the initial nZVI dosage ranging from both 0.25 to 2 in UV-A LED/S₂O₈²⁻/nZVI process and 0.1 to 2 mM in UV-A LED/H₂O₂/nZVI process on removal efficiency of 4-CP is illustrated in Fig. 4(a), (b). As indicated in Fig. 4(a), the 4-CP removal efficiency increased with increasing the amount of nZVI in UV-A LED/S₂O₈²⁻/nZVI process. The degradation efficiencies of 4-CP were 72%, 84.7% and 99% with nZVI of 0.25, 0.5 and 1 mM, respectively, after 120 min. This is because with increased nZVI dosage, the production rate of sulfate free radicals enhanced, which improved the 4-CP removal rate. However, an excessive dosage of nZVI, higher than the optimum amount, could decrease the 4-CP removal efficiency because the generated Fe²⁺ itself scavenges the produced sulfate radicals, leading to a decrease in 4-CP removal rate according to Eqs. (9)-(20) [30,32,35]. Therefore, the nZVI dosage of 1 mM was chosen for further experiments.



Iron dosage as one of the Fenton reagents is a major chemical parameter determining the operation costs as well as efficacy in the Fenton process; therefore, determining the optimum amount of iron is highly critical [34]. Fig. 4(b) shows that the degradation rate of 4-CP in UV-A LED/H₂O₂/nZVI process was dependent on nZVI dosage. It is clear that the removal efficiency of 4-CP obvi-

ously increased with the increase of initial nZVI dosage from 0.1 to 1 mM, while the removal efficiency decreased after the initial nZVI dosage was more than 1 mM. As shown in Fig. 4(b), the optimum initial concentration of nZVI required to achieve the highest 4-CP removal efficiency was 1 mM, which removed 99% of 4-CP after 30 min. The previous studies clearly indicated that the activation of hydrogen peroxide by nZVI is due to the Fe²⁺ release from nZVI in the presence of hydrogen peroxide. During this process, Fe²⁺ is continuously being supplied to the systems, which can convert hydrogen peroxide to hydroxyl free radicals according to Eqs. (9)-(12) [35]. Note that the higher 4-CP removal efficiency achieved at high Fe²⁺ concentration is due to the fact that increasing nZVI concentration consequently produced more hydroxyl radicals. Moreover, excessive nZVI concentration, over optimum dosage, can participate in the reaction as a reductant, which consumes hydroxyl radicals used for 4-CP degradation [30].

4. Comparing the Effect of Different Oxidation Processes on 4-CP Degradation

To quantify the synergistic reaction of the parameters including UV-A LED, oxidants and catalyst occurring during the simultaneous process, some individual experiments were carried out separately by persulfate alone, hydrogen peroxide alone, nZVI alone, nZVI with persulfate, nZVI with hydrogen peroxide, UV-A LED with hydrogen peroxide, and UV-A LED with persulfate (Fig. 5(a) and (b)). As shown in Fig. 5, no significant degradation of 4-CP occurred with the direct photolysis using UV-A LED (<10%). As known, photoreactivity of organic pollutants achieved under UV light irradiation depends on the type of UVs (including UVA, UVB, or UVC) and its intensity [11,13,21]. Therefore, the lowest 4-CP

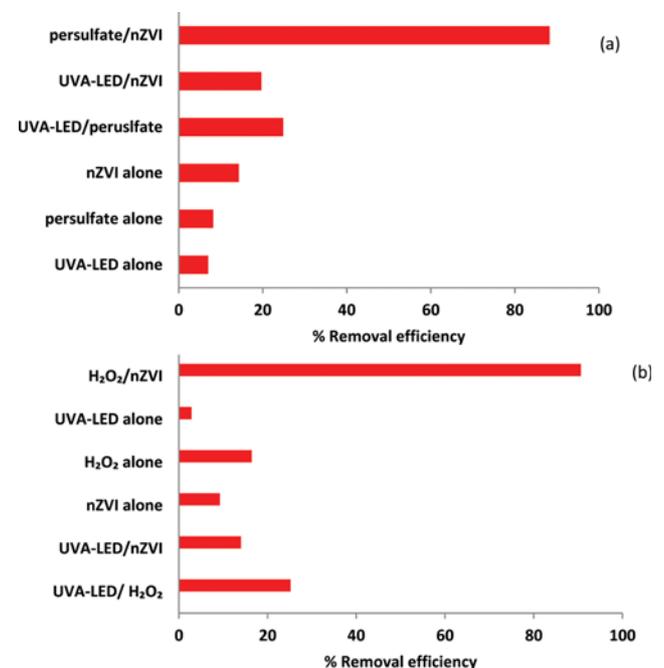


Fig. 5. 4-CP degradation efficiency using UV-A LED, nZVI, persulfate, UV-A LED/nZVI, UV-A LED/persulfate, persulfate/nZVI at 120 min (a), and UV-A LED, nZVI, hydrogen peroxide, UV-A LED/nZVI, UV-A LED/hydrogen peroxide, hydrogen peroxide/nZVI at 30 min (b).

degradation occurred in UV-A LED irradiation at 390 nm because no available radicals were generated, which eventually decreased the removal rate [22,23]. As shown, the degradation efficiencies of 4-CP were 8% and 14% with persulfate and nZVI alone, which increased to 88% in nZVI/persulfate at optimum pH value at 120 min. This confirmed that a direct reaction did not occur between persulfate or nZVI and 4-CP in the solution. Also, the combination of UV-A LED with nZVI can remove about 20% of 4-CP (Fig. 5(a)). Fig. 5(a) represents that the 4-CP removal efficiency during UV-A LED/persulfate process was 24% at 120 min. As shown in Fig. 5(b), the 4-CP degradation efficiency of combined hydrogen peroxide/nZVI process (>90%) was much higher than that of UV-A LED/nZVI (14%) and UV-A LED/H₂O₂ (25%) after 30 min. Surprisingly, the 4-CP degradation efficiencies achieved by direct UV-A LED photolysis, hydrogen peroxide alone and nZVI alone at 30 min contact time were only about 3%, 16% and 9%, respectively. In the literature it is clear that organic compounds are resistant in nZVI alone because oxidation was simultaneously happening between nZVI and dissolved oxygen in the process [31,34]. As a result, no possible oxidative free radical species was generated. However, in the nZVI/hydrogen peroxide system, Fenton reaction was initiated to produce the hydroxyl radicals and improve the degradation rate of 4-CP. Also, the production amount of hydroxyl and sulfate radicals using UV-A LED, persulfate, H₂O₂ and UV-A LED/nZVI was very low, which cannot be suggested for the degradation of this concentration of the pollutant. The lowest 4-CP removal efficiency achieved using UV-A LED/hydrogen peroxide and UV-A LED/persulfate is because hydrogen peroxide and persulfate can only absorb the UV light below wavelength of 280 nm, which could not be activated with UV-A LED at 390 nm [26].

5. Mineralization and the Rate of Degradation

Apart from the degradation of organic pollutant, an acceptable amount of mineralization should be done on pollutants to convert them to carbon dioxide, water and other mineral ions to use the process as an applicable alternative for treating wastewater already contaminated with organic pollutants [36,37]. It has been observed that the extent of mineralization is lower than the amount of organic pollutant [15,37]. To investigate the mineralization of 4-CP, COD analysis was carried out during the photochemical degradation of 4-CP at initial 4-CP concentration of 25 mg/L. Experimental conditions were set based on the obtained optimum parameters, including the initial pH of 3, nZVI dosage of 1 mM, persulfate concentration of 1.5 mM, contact time of 120 min for UV-A LED/persulfate/nZVI and initial pH of 3, nZVI dosage of 1 mM, hydrogen peroxide concentration of 0.75 mM, contact time of 30 min for UV-A LED/H₂O₂/nZVI system. Data shown in Fig. 6 reveal that the rates of 4-CP mineralization in terms of COD removal were 77% and 75% after 120 and 30 min in UV-A LED/persulfate/nZVI and UV-A LED/H₂O₂/nZVI processes, respectively. However, the results in Fig. 6 indicate that the 4-CP removal rates were 99.2% and 99% for UV-A LED/persulfate/nZVI and UV-A LED/H₂O₂/nZVI processes, which is significantly higher than the COD removal rates under the same operational condition, because 4-CP was transformed into intermediate metabolites.

It was demonstrated that photocatalytic decomposition of organic

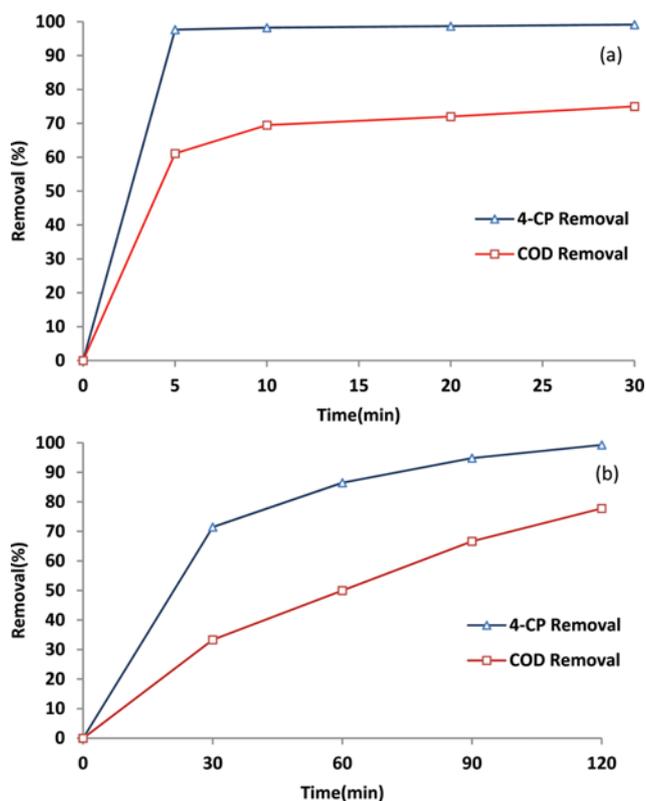


Fig. 6. COD removal efficiency (%), along with 4-CP removal efficiency (%) for UV-A LED/persulfate/nZVI (a) and UV-A LED/nZVI/hydrogen peroxide (b).

pollutants follows the pseudo-first-order kinetic model with respect to the initial pollutant concentration [13,24,31]. The reaction rate of 4-CP degradation at each AOP processes can be described by the following pseudo-first-order kinetic model Eq. (21) [3].

$$\ln\left(\frac{C_t}{C_0}\right) = -Kt \quad (21)$$

C_t is the 4-CP concentration (mg/L), and C_0 is the initial 4-CP concentration (mg/L), t is the reaction time (min), and k is the observed pseudo-first-order rate constant (min^{-1}), which is obtained from the slope of $-\ln(C_t/C_0)$ versus t . As demonstrated in Table 2, the degradation of 4-CP by different AOP processes could be well fitted to the pseudo-first-order kinetic model, as indicated by high correlation coefficient ($R^2 > 0.9$). As shown in Table 2, the degradation rate constants for the UVA-LED/H₂O₂/nZVI process were calculated to be 0.14, 0.087 and 0.054 (min^{-1}) at an initial 4-CP concentration of 25, 50 and 100 mg/L, respectively, which are higher than the corresponding constants obtained in the UVA-LED/persulfate/nZVI process (0.038, 0.012 and 0.004 (min^{-1})) at the initial concentrations of 25, 50 and 100 mg/L. UVA-LED/H₂O₂/nZVI process significantly affects the 4-CP degradation rate, approximately producing 3.7-fold (initial 4-CP, 25 mg/L), 7-fold (initial 4-CP, 50 mg/L) and 13.5-fold (initial 4-CP, 100 mg/L) compared with UVA-LED/persulfate/nZVI process at same initial concentrations. Similar trends were observed by Verma et al. [21] and Davididou et al. [25] in their studies on the photocatalysis of various

Table 2. Pseudo first order rate constants for the different 4-CP degradation processes at different initial 4-CP concentration

Type of process		4-CP concentration (mg/L)		
		25	50	100
UVA-LED/H ₂ O ₂ /ZVI	Rate constant (min ⁻¹)	0.038	0.012	0.004
	Correlation coefficient, R ²	0.969	0.937	0.954
UVA-LED/persulfate/ZVI	Rate constant (min ⁻¹)	0.14	0.087	0.054
	Correlation coefficient, R ²	0.927	0.927	0.951

organic pollutants. Specifically, these results verified that the rate of 4-CP degradation was dependent on the 4-CP initial concentration in which degradation rates gradually decreased with increasing initial 4-CP concentrations. These results are in good agreement with other findings in the literature [3,35].

CONCLUSION

The photodegradation of 4-CP was investigated by two different UV-A LED-mediated advanced oxidation processes under various conditions. The degradation efficiency of 4-CP decreased with increasing pH from 3 to 11, and faster degradation of 4-CP was achieved in acidic condition (pH=3) in both processes. During both processes, 4-CP removal efficiency significantly depends on the oxidants and catalyst concentration. The presence of hydrogen peroxide, persulfate and nZVI over the investigated range had a significant scavenging effect on OH[•] and SO₄^{•-}, and thus 4-CP removal efficiency decreased. The 4-CP removal efficiency was significantly improved by the AOPs, which was as follows: persulfate/ZVI (88%)>UV-A LED/persulfate (24%)>UV-A LED/nZVI (20%) at the optimum condition after 120 min contact time in UV-A LED/persulfate/nZVI process, and hydrogen peroxide/nZVI (90%)>UV-A LED/hydrogen peroxide (25%)>UV-A LED/nZVI (14%) at the optimum condition after 30 min contact time in UV-A LED/H₂O₂/nZVI process. In the case of mineralization, COD removal of 77% and 75% was achieved in optimum conditions after 120 and 30 min using UV-A LED/persulfate/nZVI and UV-A LED/H₂O₂/nZVI processes, respectively. According to our findings UV-A LED/H₂O₂/nZVI processes can be considered as efficient photocatalyst for the treatment of wastewater containing 4-CP. However, other investigations are needed to evaluate the applicability of this process in various aspects.

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