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Photocatalytic synergistic degradation of 2,4-dichlorophenol using ultraviolet LED light/ZnO hybrid oxidation process

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ABSTRACT

2,4-Dichlorophenol (2,4-DCP) one of the most common and abundant pollutants, is widely found in various industrial effluents such as resin and plastic products in the petrochemical industry. The apparent effect of this recalcitrance compound on the health and environment is enhancing its efficient degradation before wastewater discharged into the receiving water. Hence, the removal of 2,4-DCP from aqueous solutions using the photocatalytic UV-LED/ZnO process was investigated. In this experimental study, the removal of 2,4-DCP using UV-LED in the presence of ZnO in the bench scale reactor was examined. The effects of operational parameters such as the pH of the solution (3–11), initial concentration of 2,4-DCP (50–200 mg/L), the amount of ZnO dose (0.003–0.025 mol/L) and different ionic strengths were evaluated. The experimental results indicated that different operational parameters influenced the removal of 2,4-DCP. The highest 2,4-DCP removal rate was obtained at pH = 11 by adding 0.006 mol/L ZnO into the solution with an initial concentration of 50 mg/L 2,4-DCP, removing more than 98.2% of 2,4-DCP. When UV-LED and ZnO were used alone, the removal efficiencies were 32.11% and 30.93%, respectively. Also, the maximum chemical oxygen demand removal rate was 64.45% in optimum conditions and ionic strength was reported to be ineffective. The results indicated that combined ZnO and UV-LED processes in optimal conditions could be used as an alternative technology for the treatment of various industrial wastewater containing 2,4-DCP.

Keywords: 2,4-Dichlorophenol; Photocatalytic; ZnO; UV-LED; Aqueous solution

1. Introduction

One of the most important environmental challenges of the present century is the existence of non-biodegradable organic compounds in various chemical industries. The presence of such compounds in the environment and their entry into aquatic resources significantly alter the chemical and physical quality of these important aquatic resources and in some cases make it impossible to use them [1]. Phenol and its derivatives such as chlorophenols are applied in the formation of various compounds 2,4-dichlorophenol is a chlorinated aromatic compound, among a wide range of chlorophenol group compounds and is widely used to produce pesticides, herbicides, resin, and in plastics manufacturing industries, paints, medicines, oil refineries, petrochemicals, coal mines, steel, aluminum and lead, synthetic

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textiles and tannery [2]. Chlorophenols, including 2,4-DCP, enter the body mainly through the skin and breathing and have destructive effects on the body, such as mucus stimulation, skin burning, and irritation, affecting the liver, kidneys, lungs, and vascular system, fatigue, restlessness, muscle weakness, nausea, coma and finally "death" [3,4]. The United States Environmental Protection Agency has recognized these compounds as priority pollutants [5]. Its maximum concentration level in drinking water is 0.9 mg/L and its amount in industrial sewage containing 2,4-DCP is 11.4–89 mg/L that in a concentration of 0.1 mg/L, it leads to drinking water's unpleasant taste, hence its standard limit for drinking water is prescribed as 0.1 mg/L [6]. Several methods are used to remove the 2,4-DCP from industrial wastewater, including biological methods [6], wet oxidation [7], activated carbon adsorption [8] and chemical oxidation [9]. The use of superseded technologies can improve the limitations and shortcomings of these processes and operations. Standard biological methods cannot remove the pollutants such as organic hydrocarbons, due to the toxicity and degradability of these compounds.

In addition, separating methods such as flocculation–filtration, activated carbon adsorption, and reverse osmosis only transmit pollutants from one phase to another. Therefore, advanced oxidation processes have a better performance in the removal of non-degradable organic pollutants than other conventional treatment methods [10,11]. Despite the possibility of forming, the various types of radicals, most of the advanced oxidation processes' results are attributed to hydroxyl radicals, which are strong oxidizers [12,13]. The photocatalytic process is one method for the advanced oxidation process in which organic matter is decomposed by UV ray radiation in the presence of metal dioxides [14]. The sources of UV ray radiation in photocatalytic processes are mercury vapor lamps and light-emitting diode (LED) light. Mercury vapor lamps that are currently used as a source of UV rays in syncretist processes to remove pollutants, have some defects, including large size, low shock resistance, and high sensitivity to temperature changes [14]. These lamps have also recently been identified as major environmental pollutants [14,15]. In recent studies, LED light has been used as a source of UV radiation instead of mercury vapor lamps.

Recently, Ultraviolet-Light Emitting Diode photocatalytic processes have received much attention due to their use in pollution control and air purification. LEDs are light-emitting diodes of semiconductors that emit light of a single wavelength. The benefits of these processes are operating at room temperature and atmospheric pressure and complete oxidizing of pollutants to carbon dioxide and water [14]. UV-LED lamps convert electricity into light more efficiently than older UV mercury lamps and have smaller sizes, so they save more space as well as are more resistant to physical shocks [15]. UV-LEDs have a lifetime of about 100,000 h, while mercury lamps only endure about 8,000 h. These lamps have proper performance in producing ultraviolet rays since they are produced by a process called electro-luminescence that enables the lamp to turn on and off at high frequencies. This feature is too important because according to the results of recent investigations, pulsed light has higher photon efficiency as well as an energy saving of more than 80% compared to wastewater treatment with continuous light affecting [14–16].

These lamps can also emit light at multiple wavelengths and separately and also can be adjusted to the desired wavelength [16].

In the studied process, the zinc oxide catalyst is activated using UV light emitted from UV lamps with a wavelength of less than 400 nm. Zinc oxide is a water-insoluble chemical compound with the formula ZnO [13]. This compound is a semiconductor with a band gap of 2/3 eV that is able to absorb a wide spectrum of electromagnetic waves compared to other metal oxides such as titanium dioxide and its photocatalytic ability under UVA radiation. This semiconductor has desirable properties, including non-toxicity, transparency, high stability, wide energy gap, and higher efficiency in electron production [17–19]. The hydroxyl radical production by ZnO catalyst in the presence of UV ray radiation are shown in Eqs. (1)–(8) [20,21].

$$\mathrm{ZnO} + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$\left(\mathrm{O_2}\right)_{\mathrm{ads}} + e^- \rightarrow \mathrm{O_2^-} \tag{2}$$

$$\mathrm{H_2O} \rightarrow \mathrm{OH^-} + \mathrm{H^+} \tag{3}$$

$$\mathrm{O_2^{-\bullet}} + \mathrm{H^+} \rightarrow \mathrm{HOO^\bullet} \tag{4}$$

$$\mathrm{HOO^\bullet} + e^- \rightarrow \mathrm{HO_2^-} \tag{5}$$

$$\mathrm{HOO^-} + \mathrm{H^+} \rightarrow \mathrm{H_2O_2} \tag{6}$$

$$\mathrm{H_2O_2} + e^- \rightarrow \mathrm{OH^-} + \mathrm{OH^\bullet} \tag{7}$$

$$\mathrm{H_2O} + h^+ \rightarrow \mathrm{H^+} + \mathrm{OH^\bullet} \tag{8}$$

This study was done to investigate the removal efficacy of 2,4-dechlorinate from aqueous media using the UV-LED/ZnO process, due to the specific advantages and features of photochemical processes in the removal of toxic organic compounds.

2. Material and methods

2.1. Experimental setup for degradation of 2,4-dichlorophenol

This experimental study was carried out in the Laboratory of Water and Wastewater Chemistry of School of Public Health, Hamadan University of Medical Sciences. All experiments were carried out in a laboratory scale and in a batch Plexiglas reactor with an inner diameter of 10 cm and a volume of 200 mL. A 100 mL sample of distilled water and 2,4-DCP were prepared in a concentration of 50 mg/L for each test. Sulfuric acid and 0.1 N and sodium hydroxide 0.1 N were used to adjust the pH of the samples, mixing was also performed continuously using a magnetic agitator to poke the solution by magnet. Mixing was also performed continuously using a magnetic agitator to stir the solution by magnet. The source of radiation was 18 UV-LED lamps, 75 GaN semiconductors, made in Seoul, Korea. The specifications of the lamps are given in Table 1. UV-LEDs were mounted on an aluminum plate and the UV-LEDs were coated using a 1 mm diameter quartz flake. The distance of UV-LEDs was 1 cm from the solution surface inside the reactor and a continuous flow of water was used around the reactor to prevent sample evaporation due to the heat generated by the lamps. After inserting the sample into the reactor and adding ZnO as the catalyst, the desired pH was adjusted and the lamps were turned on to begin the process (Fig. 1). At the end of each test, the samples were placed in a centrifuge at 4,000 rpm to precipitate the catalyst sedimentation.

2.2. Synthesis process of catalyst, ZnO nanoparticles

The ZnO sample was fabricated using zinc acetate dehydrate as a precursor based on the sol–gel method. In a typical synthesis, 2 g of zinc acetate dihydrate was dissolved in 200 mL of deionized water to get a mixture. The resultant mixture was agitated vigorously for 1 h, while 2.0 mol sodium hydroxide (NaOH) solution was added dropwise to the mixture to obtain pH 12. At this condition, the white precipitate formed was completely rinsed with deionized water several times and followed by ethanol washing. The precipitate was allowed to age for 3 h in an air oven at a temperature of 105°C. Then, it was kept in an electric furnace at 300°C for 5 h, with a heating rate set at 10°C/min for calcination. The obtained sample denoted as ZnO was applied in the son photolytic reactions [22].

Table 1
UV-LED lamp specifications

Parameter	Feature
Maximum wavelength	390 nm
Maximum intensity	20 mA
Radiant flux	1 mW
Angle	20
Diameter	2.82 ± 0.4 mm
Length	2.7 ± 0.8 mm

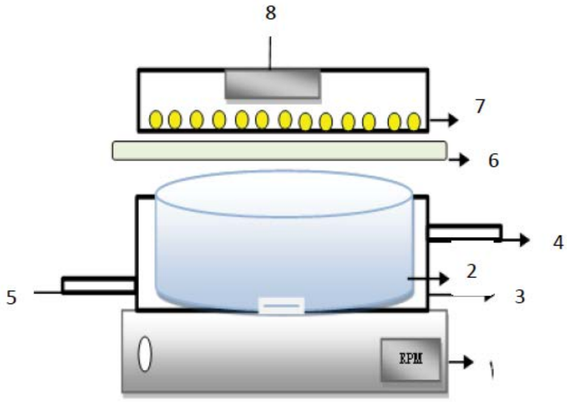

Fig. 1. Schematic of UV-LED reactor. (1) Magnetic stirrer; (2) Plexiglas reactor; (3) Water rotation chamber; (4) Water flow inlet; (5) Water flow outlet; (6) Quartz sheet; (7) UV-LED lamp; (8) Power supply.

2.3. Analytical methods and catalyst characteristics

The concentration of remaining 2,4-DCP was measured by UV-Vis Spectrophotometer DR 5000 at wavelength of 500 nm using the 5,530 colorimetric methods in the standard method. Also, to measure the process efficiency of mineralization, the amount of chemical oxygen demand (COD) reduction was measured according to the standard method book 5,220 [23]. The surface morphology of ZnO catalyst was investigated by a field-emission scanning electron microscopy (FEI Nova NanoSEM 450, USA). The composition of the elements at the ZnO surface was determined by an energy-dispersive X-ray spectroscopy mapping (EDX; Bruker XFlash 6-10, Germany). The crystalline structure of the ZnO was also studied by X-ray diffraction method (XRD, Ultima IV, Rigaku, Japan). Fourier-transform infrared spectroscopy (FTIR, PerkinElmer, Spectrum 65, Waltham, USA) was used to study the functional groups of catalyst.

3. Results and discussion

3.1. Catalyst characteristics

The characteristics of ZnO catalyst were analyzed by scanning electron microscopy, EDX, XRD and FTIR analyses. Fig. 2a shows that ZnO nanoparticles are aggregates of irregular quasi-spherical particles with a particle size range of 25–75 nm. The composition of the elements at the ZnO catalyst surface were investigated by EDX-mapping analysis. Fig. 2b shows that the chemical composition of the ZnO catalyst consists of zinc (53.6% wt.) and oxygen (46.4%) [24]. The XRD spectra of ZnO nanoparticles are shown in Fig. 2c. In the XRD spectrum of ZnO, the three sharp characteristics peak at $2\theta = 32°$, 34.5°, and 36°, as well as characteristics peak at 47.5°, 56.3°, 62.9°, 68°, and 69° belong to [100], [002], [101], [102], [110], [103], [112] and [201] crystalline planes (JCPDS Card ID 36-1451) [25]. All of these characteristic peaks belong to the ZnO structure. Fig. 2d shows the FTIR spectrum of the ZnO. Four major peaks were observed at 3,418; 1,632; 804 and 458 cm^{-1}. The peaks appearing at 3,418 and 1,632 belong to O–H stretching and O–H bending vibrations of the water molecule, respectively. The peaks observed at 804 and 458 cm^{-1} are related to the weak vibration and the symmetric bending vibration of Zn–O, respectively [23,27,28].

3.2. Influence of pH on efficiency of UV-LED/ZnO process

Samples were placed in the reactor with an initial concentration of 2,4-DCP l equal to 50 mg/L and a dose of zinc oxide equal to 0.006 mol/L for 90 min, to investigate the effect of pH changes on the efficiency of the UV-LED/ZnO process. At pH 3, 7 and 11, removal efficiency was 46.94%, 98.2% and 100%, respectively. As it is shown in Fig. 3, in this process, with increasing pH, the removal efficiency of

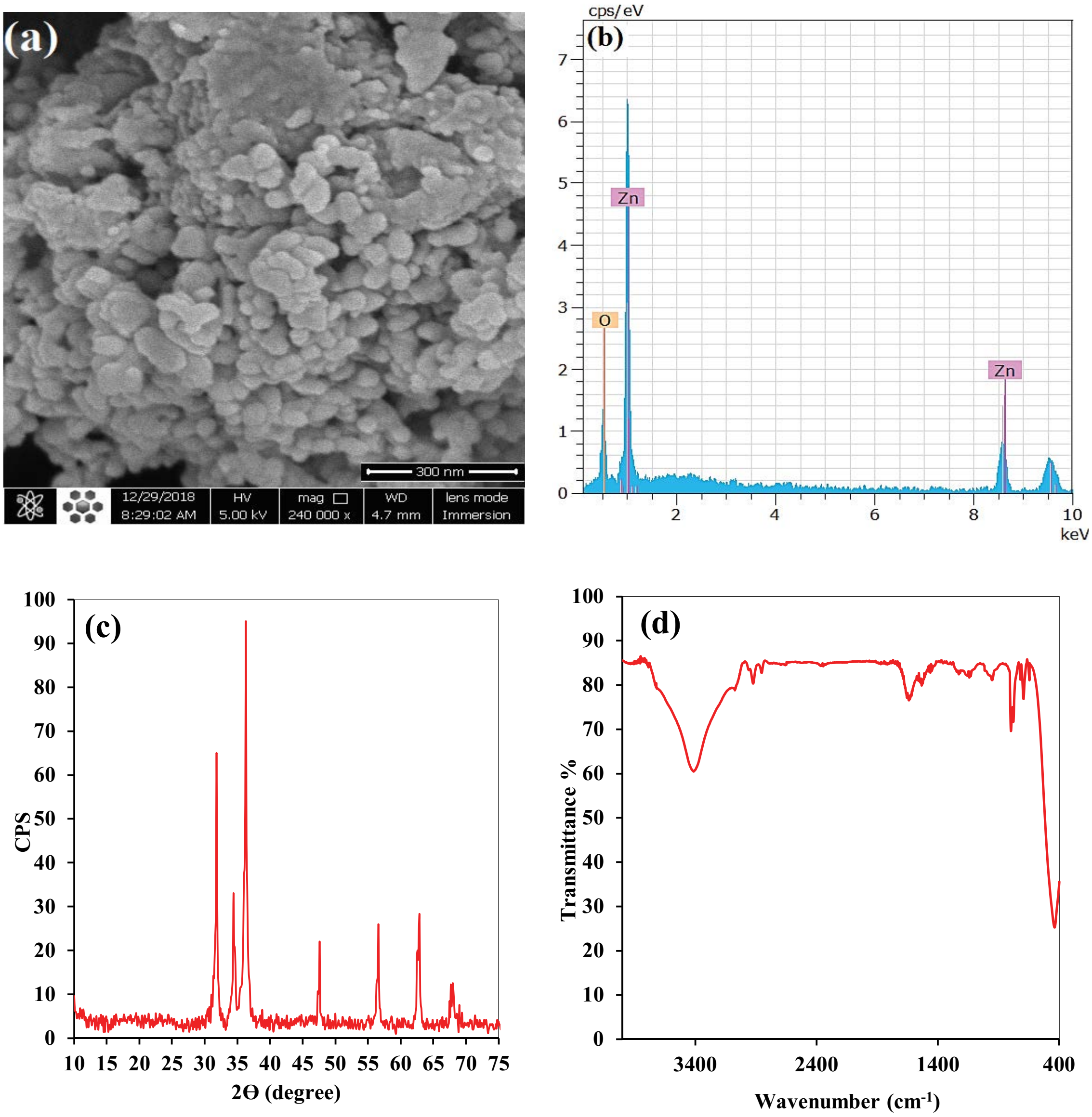

Fig. 2. Field-emission scanning electron microscopy (a), EDX (b), XRD (c) and FTIR (d) of ZnO catalyst.

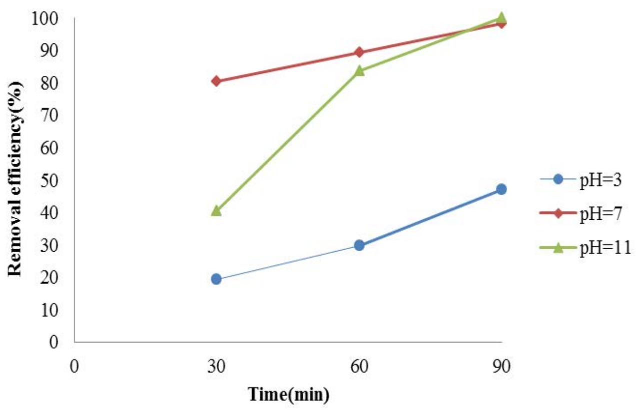

Fig. 3. Effect of pH on the UV-LED/ZnO process (ZnO dosage: 0.006 mol/L; concentrations of 2,4-DCP: 50 mg/L).

2,4-DCP increased. Process efficiency increased rapidly and significantly with increasing pH from 3 to 7, but after pH = 7 from 7 to 11 the removal efficiency increased very little. Although the removal efficiency at pH = 11 was 100%, because this process is often recommended for the treatment of industrial effluents that have an almost neutral pH and that the alkalization of the effluent and bringing it to pH = 11 requires alkalis and the use of alkalis is costly, so for above reasons the appropriate pH for this process was expressed as pH = 7. In fact, in this study, like previous studies, the maximum efficiency of the photocatalytic process was confirmed at alkaline pH [29], but in the following, we have noted a slight difference in process efficiency at neutral pH and alkaline pH. Finally, the audience is advised to choose this pH because of this small difference and in exchange for reducing the costs and benefits of performing the process at a neutral pH.

The pH of the solution is an essential variable in photocatalytic reaction since it governs the surface charge properties of the semiconductor photocatalyst. As the results in Fig. 3 shows the maximum removal efficiency was in neutral and alkaline conditions. Hydroxyl radical production reaches maximum rate with increasing pH from acidic to alkaline, so these radicals with strong oxidation potential decompose organic compounds at a faster rate. Changing the pH of the solution results in a positive or negative charge of the zinc oxide nanoparticles, thus affecting the degradation performance of the nanoparticles. The behavior of zinc oxide is different at alkaline pH values from that of acidic ones. When zinc catalysts are exposed to photons with energy equal to or greater than the vacancy hole energy, electron pairs are formed. The released electrons have the ability to react with the oxygen atom (as the electron receiver) at neutral and alkaline pH, hence converting the oxygen atom from O_2 to O_2^- form. The formed electron-hole separates an electron from organic matter molecules and converts it to R^+ or reacts with existing H_2O or molecules to produce free hydroxyl radical ($OH^•$), hence causing the decomposition of organic matter [30].

An important factor controlling the process of photocatalytic degradation chlorophenolic compounds is the pH of the solution. Chlorine derivatives of phenol are weak organic acids, so the pH affects their degree of ionization and charge. For a pH value lower than the pKa, chlorine derivatives of phenol are present in the solution in molecular form (non-ionic, undissociated). On the other hand, the deprotonated form (dissociated, anionic) is formed if the pH is higher than their pKa. There are two possible reasons for the formation of these anions. First, there is a shift in the dissociation equilibrium of DCP in favor of chlorophenoxide [Eq. (9)] because the pKa of DCP is overestimated. Secondly, the deprotonation of the ZnO surface above its pzc [Eq. (10)] leads to the formation of ZnO^-. On the other hand, the decrease in the reaction rate at a very high pH may be partially attributed to the alkaline dissolution of zinc oxide shown in [Eq. (11)] [31].

$$\mathrm{PhO(Cl)_2} \xrightleftharpoons{H^+} {}^-\mathrm{OPh(Cl)} \tag{9}$$

$$\mathrm{ZnOH_2^+} \xrightleftharpoons{OH^-} \mathrm{ZnOH} \rightleftharpoons \mathrm{ZnO^-} \tag{10}$$

$$\text{Acidic pH} \rightarrow \mathrm{pH_{pzc}} \rightarrow \text{Basic pH} \tag{11}$$

$$\mathrm{ZnO} + 2\mathrm{OH^-} \rightarrow \left[\mathrm{Zn(OH)_2}\right]^{2+} \tag{12}$$

At acidic pH values (Eq. 4), zinc oxide loses its oxygen in reaction with and is soluble in water and finally loses its photocatalytic nature [29]. Goulart et al. [30] found that the photocatalytic degradation efficiency of levofloxacin in the presence of zinc oxide catalyst depends on the efficiency of pH, in a way that the process increased with increasing pH efficiency and the highest removal efficiency for alkaline was obtained at neutral pH level. Also in a study by Mohsin et al. [32] on the enhanced photocatalytic for dye degradation with Fe/ZnO ceramic fabrication, similar results were obtained that confirm the above results.

3.3. Influence of ZnO dosage on the efficiency of UV-LED/ZnO process

In order to investigate the effect of different dose of ZnO on samples with constant concentration of 2,4-DCP equal to 50 mg/L, the optimum pH obtained from the previous step and different dose of ZnO in the range (0.003, 0.006, 0.009, 0.0012, 0.015, 0.018, 0.021 and 0.025 mol/L) were prepared and placed in the reactor for 90 min. As the results of Fig. 4 show the efficiency of the UV-LED/ZnO process increased by raising zinc oxide dose from 0.003 to 0.006 mol/L and reached 98.2%, but at dosage above 0.006 mol/L, the efficiency decreased as removal efficiency reached 87.39% by increasing the catalyst's dose.

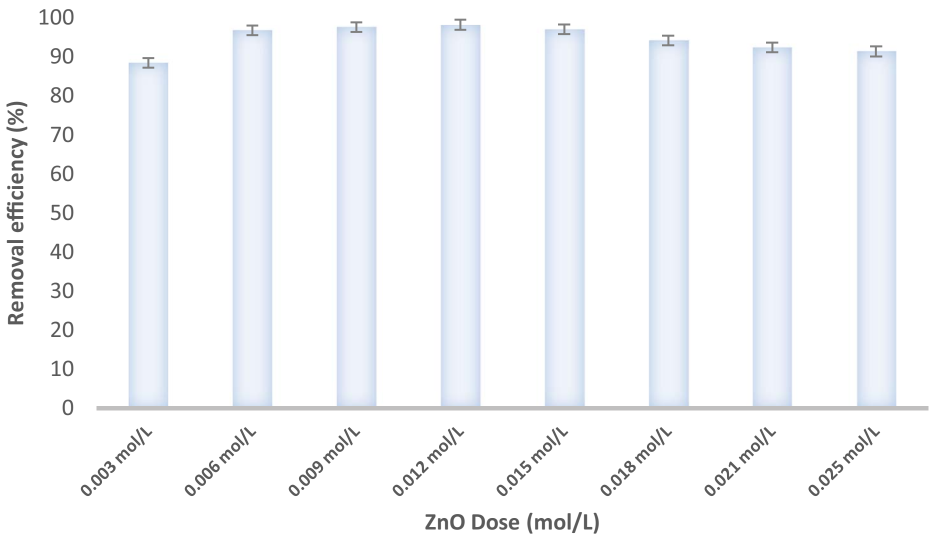

Fig. 4. Effect of ZnO dosage on UV-LED/ZnO process (pH: 7; concentrations of 2,4-DCP: 50 mg/L; 90 min).

Increasing efficiency by raising the catalyst dose up to 0.006 mol/L can be justified since by increasing the catalyst dose, the number of active sites of adsorption goes up and thus this increases the impact of nanoparticles and 2,4-DCP [31,32]. On the other hand, increasing the catalyst dose will increase the number of adsorbed photons and thus it will increase the number of adsorbed 2,4-DCP molecules [33]. The appropriate catalyst dose increases the rate of hole production of electron pairs and hydroxyl radicals, thereby enhancing the rate of photocatalytic process. However, increasing the turbidity of the solution and thus reducing the penetration and dispersion of UV ray from the catalyst surface at doses greater than 0.006 mol/L (0.009–0.025 mol/L) decrease the efficiency [34]. This reduces the activated volume of the ray and also a small amount of ZnO will be activated. Coagulation and sedimentation also occur at high dosage of the catalyst [35]. Taie et al. [33], confirms that increasing the dose of the catalyst has achieved faster destruction rates and higher overall decomposition of trimethoprim. Thus, the efficiency of removal was 87.49% when 50 mg/L of ZnO was used, whereas 90.4% was achieved by increasing the catalyst dose to 250 mg/L and 92.38% when 500 mg/L of catalyst was used.

3.4. Influence of initial 2,4-dichlorophenol concentrations on efficiency of UV-LED/ZnO process

In order to investigate the effect of different concentrations of 2,4-DCP with initial concentrations of 2,4-DCP in the range (25, 50, 75, 100, 150 and 200 mg/L) at the optimum pH and dose of zinc oxide obtained in the previous steps, It was placed inside the reactor and the removal efficiency was evaluated for 90 min. Based on the results of Fig. 5, the removal efficiency decreased with increasing initial concentration of 2,4-DCP, so the highest removal efficiency was 98.87% and 98.2% at concentrations of 25 and 50 mg/L, respectively and by increasing the initial concentration of 2,4-DCP to 200 mg/L removal efficiency was reduced to 84.88%. Investigation of the influence of pollutant concentration shows that by increasing the concentration of 2,4-DCP, UV ray adsorption is increased compared to ZnO, while light adsorbed by 2,4-DCP is ineffective in decomposition. Also, by increasing the concentration of 2,4-DCP, its adsorption on ZnO surface increased, while during the competitive adsorption, the adsorption rate of $^{\bullet}$OH and $^{-}O_2^{\bullet}$ formed on the nanoparticle surface decreased. On the other side, as the concentration of 2,4-DCP increases, the number of its molecules adsorbed on the surface of ZnO increases, while the number of produced hydroxyl radicals is constant. Therefore, a few number of 2,4-DCP molecules are affected by the $^{\bullet}$OH radical [28,34]. On the other hand, the production of intermediate products that are more reactive than 2,4-DCP can react with existing radicals and reduce the number of radicals used to oxidize pollutants. Gharagozlou et al. [35] increasing the concentration of organic pollutants (dye) from 10 to 50 g/L led to a decrease in removal efficiency and the highest efficiency was obtained at a dye concentration of 10 g/L.

3.5. Influence of ionic strength of calcium chloride on UV-LED/ZnO process efficiency

Calcium chloride with concentrations of 0.25, 0.5 and 1 mg/L was used in order to determine the effect of ionic strength on the removal efficiency of 2,4-DCP in optimum operating conditions and concentration of 2,4-DCP of 50 mg/L and pollutant removal rate were evaluated over a period of 90 min. Based on the results of Fig. 6, the removal rate of 2,4-DCP was 92.82%, 96.11% and 99.31%, respectively, at concentrations of 0.25, 0.5, and 1 g/L. while the efficiency removal was 98.2% without calcium chloride in same condition.

Natural water and all wastewater had a number of various compounds and ions and if electric pons are created in these aquatic environments, the existing ions will transmit electrical current between these pones. The higher the ionic strength of these ions, the higher the current transfer. The effect of ions on the removal efficiency of 2,4-DCP was investigated in present study. Based on the results of Fig. 7, the removal rates of 2,4-DCP at sodium chloride concentrations of 0.25, 0.5 and 1 g/L, during 90 min and under optimum test conditions were 92.82%, 96.11% and 99.31%, respectively. However, in the same conditions and without calcium chloride, the efficiency removal was 98.2%. Therefore, it was

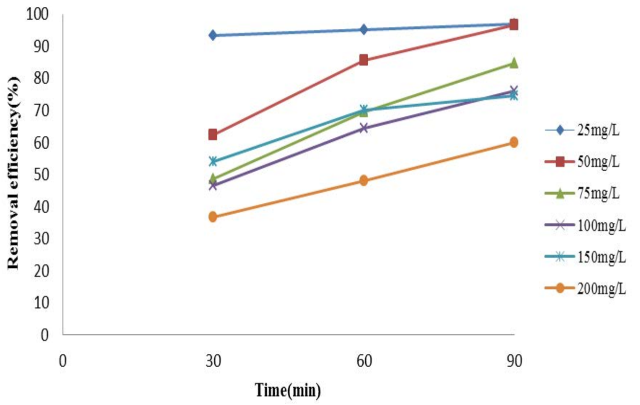

Fig. 5. Effect of initial concentrations of 2,4-DCP on ZnO/UV-LED process (pH: 7; ZnO dose: 0.006 mol/L; duration: 30, 60 and 90 min).

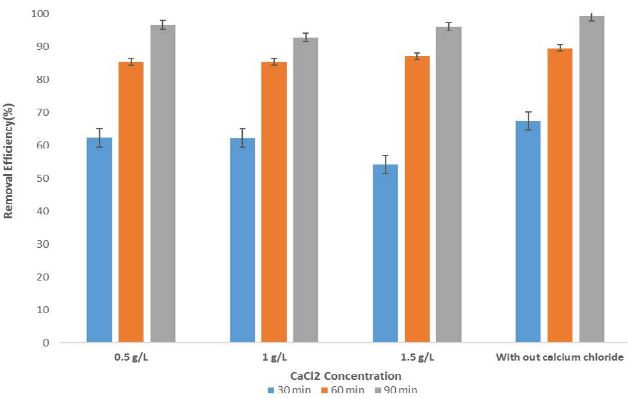

Fig. 6. Effect of ionic intensity of calcium chloride on UV-LED/ZnO process (pH: 7; ZnO dose 0.006 mol/L; concentrations of 2,4-DCP: 50 mg/L; time: 30, 60 and 90 min).

indicated that the ion strength changes have a little effect on the UV-LED/ZnO process. Seid Mohammadi et al. [36] investigate the 2,4-DCP removal using ultrasound waves, found, the presence of calcium chloride ion has no effect on the degradation of 2,4-dichlorophenol.

3.6. Influence of UV-LED/ZnO process on mineralization

Samples at a constant concentration of 2,4-DCP = 50 mg/L were exposed to UV-LED and zinc oxide for 90 min in order to determine the efficiency of the UV-LED/ZnO process in reducing COD after obtaining optimal conditions and as shown in Fig. 7, the UV-LED/ZnO process reduced 51.55% of the initial COD during this time and required a higher reaction time for higher removal, thus the removal efficiency reached 64.45% after 180 min. In addition to eliminating the contaminant in question, reducing the amount of organic contamination load is also important in evaluating the process efficiency at environmental scale. There are several experiments to determine the degree of mineralization of the process. Determining the amount of mineralization, is one of rapid, inexpensive and rather precise tests in this field. According to Fig. 7, the reason for the COD removal rate not being equal to the removal efficiency of 2,4-DCP is that during the photochemical oxidation process 2,4-DCP is not completely converted into water and carbon dioxide, but it is first converted into catechol [Eq. (12)] and then converted into water and carbon dioxide. Therefore, the catechol intermediate matter consumes the oxygen and increases the COD of solution. It should be noted that the complete conversion of this intermediate into carbon dioxide and water required more time, so the removal efficiency reached 60.64% after 150 min. Accordingly, the process of mineralization is able to mineralize the organic pollutants, but requires more time to complete mineralization [37]. Kubiak et al. [31] found similar results that confirm the present results.

$$\begin{aligned}&2,4-\text{dichlorophenol} \rightarrow \text{Catechol}\\&\quad \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O\end{aligned} \tag{12}$$

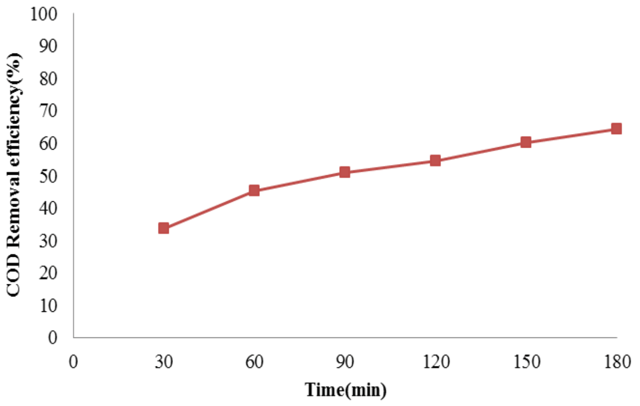

Fig. 7. UV-LED/ZnO process efficiency in COD reduction (pH: 7; ZnO dose: 0.006 mol/L; concentrations of 2,4-DCP: 50 mg/L).

3.7. Effect of zinc oxide and UV-LED alone on the removal of 2,4-dichlorophenol

After obtaining the optimum conditions, the samples at a constant concentration of 2,4-DCP = 50 mg/L were once exposed to UV-LED alone and once to zinc oxide alone for a period of 90 min in order to indicate the efficiency of zinc and UV-LED, separately. As the results of Fig. 8 show, the removal efficiency of 2,4-DCP in the use of UV ray emitted by UV-LED lamps alone was 32.11% under optimum operating conditions (pH = 7, 2,4-DCP concentration 50 mg/L over 90 min). As has been proven in past studies such as Gryglik et al. [38], following reactions occur during photosensitized oxidation of 2,4-DCP [38].

$$\text{RB} + \text{hv} \rightarrow {}^1\text{RB} \rightarrow {}^3\text{RB} \tag{13}$$

$$3\text{RB}^* + {}^3O_2 \xrightarrow{k_\Delta^{O_2}} {}^1O_2 + \text{RB} \tag{14}$$

$${}^1O_2 + 2,4\text{DCP} \xrightarrow{K_r} {}^3O_2 + \text{Product} \tag{15}$$

*RB was a photosensitizer.

Under the same conditions at ZnO dose of 0.006 mol/L removal efficiency of 2,4-DCP 2,4-dichlorophenol by ZnO process alone was 30.93% and UV-LED/ZnO process was obtained 98.2%. Therefore, based on the results of current study, the role of UV waves in activation of ZnO catalyst in photocatalytic degradation of 2,4-DCP is too important. These results also showed that the use of UV radiation alone was not very effective even for the decomposition of phenolic compounds such as 2,4-DCP which have high UV molar coefficients, and it is suggested to use of UV radiation and a catalyst such as ZnO, simultaneously [33].

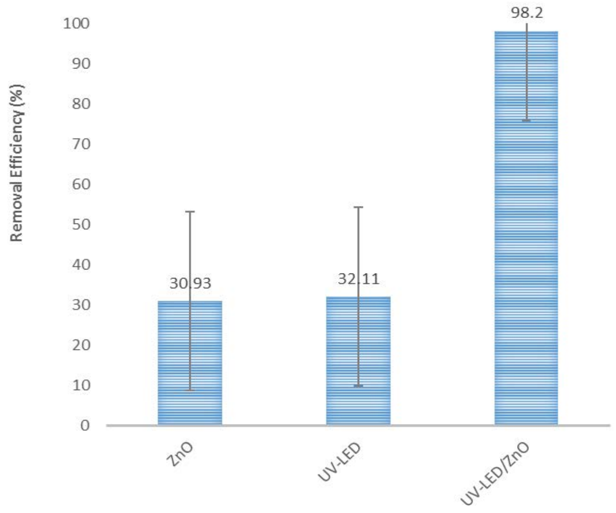

Fig. 8. Efficiency of UV-LED, ZnO and UV-LED/ZnO processes (pH: 7; ZnO dose: 0.006 mol/L; concentration of 2,4-DCP: 50 mg/L).

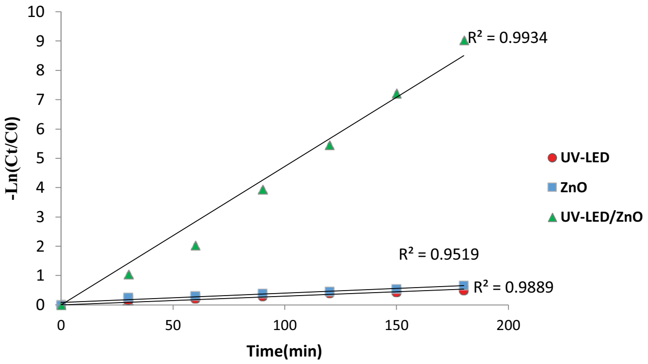

Fig. 9. Kinetic of photocatalytic degradation of 2,4-dichlorophenol UV-LED, ZnO, and UV-LED/ZnO processes (pH: 7; ZnO dose: 0.006 mol/L; concentrations of 2,4-DCP: 50 mg/L).

3.8. Kinetic of photocatalytic degradation of 2,4-dichlorophenol UV-LED, ZnO, and UV-LED/ZnO processes

Predicting the reaction speed of the decomposition process is one of the important parameters in the design of systems. As can be seen in Fig. 9, the decrease in the concentration of 2,4-DCP with the passage of time follows a linear pattern. Determining the optimal kinetics is based on the decomposition coefficient parameter (R^2) in such a way that R^2 was obtained in UV-LED, ZnO, and UV-LED/ZnO processes as 0.95, 0.95, and 0.98, respectively, so the kinetics of decomposition in all three the process is first-order kinetics and follows Eq. (1). where C and C_0 are the concentrations of 2,4-DCP at zero and T times and K is the reaction constant.

$$-\ln\left(\frac{C}{C_0}\right) = KT \tag{16}$$

4. Conclusion

This study was conducted to evaluate the efficiency of the UV-LED/ZnO process in the removal of 2,4-DCP and the effect of operating conditions. The general results of this study are as follows: The results of this study indicated that with increasing pH, the removal efficiency of 2,4-DCP increased. Process efficiency increased rapidly and significantly with increasing pH from 3 to 7, but after pH = 7, from 7 to 11, the removal efficiency rose very little. Although the removal efficiency at pH = 11 was 100%, this process is often recommended for the treatment of industrial effluents that have an almost neutral pH and that the alkalization of the effluent and bringing it to pH = 11 and the use of alkalis are costly, so given the above reasons, the appropriate pH for this process was expressed as pH = 7. The concentration of oxidizing agent was another factor affecting the performance of the process in the removal of organic matter, although with growing the concentration of oxidizing agent more than the optimal value (0.006 mol/L), the removal efficiency decreased. The rate of removal of organic matter depended on the initial concentration of organic matter and gradually decreased with increasing organic matter. The effect of ion intensity changes due to the presence of calcium chloride on the removal efficiency of 2,4-DCP by UV-LED/ZnO process, was reported to be ineffective.

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