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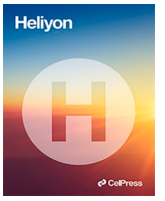

Research article

Optimization of the electro-photocatalytic process for the removal of formaldehyde from water using the Taguchi model

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ABSTRACT

The most significant environmental issue in many nations across the world is industrial wastewater contamination with formaldehyde (a priority pollutant). Any natural water that has had industrial effluent discharged into with formaldehyde concentrations between 100 and 1000 mg/l is deemed toxic to humans. This is an applied analytical research project aimed at examining formaldehyde removal from urban drinking water using a batch electro-photocatalytic (EPC) reactor that uses ultraviolet-A (UV-A) lamp dynode and immobilized ZnO NPs on a zinc sheet-copper electrode. pH, formaldehyde content, lamp intensity, radiation duration, lamp-electrode distance, ZnO NP stacking, and current density are the factors under investigation. They were found to be in the ranges 3–11, 110–330 mg/l, 480–720 mW/cm^2, 8–32 min, 1.5 cm, 1–3, and 4–12 mA/cm^2, respectively. The findings demonstrate the relationship between UV-A lamp intensity, radiation duration, and current density with the elimination of formaldehyde. The experimental data better fit a first-order reaction (R^2 = 0.9982). The most optimal conditions elimination (0 mg/l) of formaldehyde are achieved at pH = 11, radiation period = 8 min, two layers of ZnO NPs, and current density = 8 mA/cm^2 by the Taguchi model. The results show that increasing pH, radiation period, lamp intensity, and current density all increase removal efficiency. The results show that EPC is a practical and efficient method for treating formaldehyde-contaminated drinking water at high concentrations.

1. Introduction

Iran is classified as one of the countries most affected by water scarcity due to a lack of available water resources due to being located in a dry belt with an average annual rainfall of 250 mm and a per capita water level of 1750 cubic meters per person per year. The overall water risk is 3–4 in Tehran city [1]. Water scarcity is one of the biggest challenges of our time. Lack of safe water is a problem worldwide. Water demand is growing rapidly due to population growth and rapid urbanization. As the world's population activities grow and develop in various industries, drinking water quality has become one of the world's most pressing problems [2].

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Water resource contamination by formaldehyde is among the increasingly serious environmental issues, according to recent reports. Inadequate treatment and discharge of these pollutants into the environment can greatly contaminate water resources. The drinking water formaldehyde is often analyzed. Formaldehyde reacts with amino groups proteins [3]. The formaldehyde concentration of tap water, canal water, and textile effluent is 0.0, 2.5, and 8.9 mg/l, respectively in Panjab [4]. The natural sources of aldehydes are their photochemical oxidation reaction in the troposphere and their emission from the plants including terpenoids and isoprenoids [5]. The man-made sources of aldehydes are wooden door manufacturing, types of adhesive substances (urea resin), highly during application of disinfectant substances such as chlorination and ozonation in the drinking water treatment process due to the oxidation of organic matter with them. Also, water treatment processes and leachates from plastic fittings lead to increasing formaldehyde concentration in water. The application of furniture, fabrics, carpets, household cleaning agents, paints, and cosmetic products leads to exposing indoor persons to aldehydes such as formaldehyde due to emitting fumes [6]. The presence of water, aldehydes, carbon dioxide, carboxyl-terminated polyester chains, and terephthalic acid mono-glycol ester attendance in PET-bottled water following sunlight and high-temperature exposure and are reported after exposure to sunlight and high temperature [7]. Formaldehyde-contaminated natural water above the permissible limit of drinking water results in undesirable odor taste problems (taste and odor thresholds are 50 and 25 mg/l, respectively), may be a source of suspected carcinogen, a confirmed human exposure [8], and drinking water standard have been proclaimed as 10 μg/l. There is an environmentally safe threshold of 61.1 mg/l for formaldehyde [9]. Processes like chemical, biological, condensation, absorption, adsorption, membrane, and ion exchange methods are adopted for the removal of formaldehyde and formaldehyde compounds from water or wastewater [10]. Nevertheless, the key drawback of the above processes is low efficiency. The need for precise control of the parameters affecting the system such as pH, temperature, oxygen, and formaldehyde inhibitory effect has limited the application of these systems in treating highly contaminated samples. The physical and chemical methods, also transmit pollution from one phase to another phase, condensing it or producing a new contaminant, that needs more refining. From the aspects of cost, efficiency and maintenance, the selection of formaldehyde removal processes depends on the raw water quality characteristics. Overall, chemical method is more expensive than membrane and membrane is more than ion exchange. Ion exchange method is more efficient than membrane and membrane is more than chemical. In recent years, advanced oxidation processes (AOP_S) including Fenton, Photo-Fenton, photo-catalysis, electrolysis, and ultraviolet-based processes have been used as a suitable replacement for conventional purification processes due to their ease of use, economy, and high efficiency [11–13]. The electro-photocatalytic (EPC) method has been considered a promising, clean, requires too no regents, and innovative technique for organic polluted-water decomposition. This process is a mixture of an external direct electric field and heterogeneous photocatalysis to prevent electron–hole recombination. The photo-catalytic reaction includes heterogeneous catalysis, where a light-absorbing catalyst such as sunlight, or ultraviolet is put in contact with the target reactants such as different pollutants in solution and gas forms. Examples of materials that catalyze the water fission reaction include oxynitrides, titanium oxide, indium oxide, and ZnO. In the H_2 production process, photo-catalysts significantly contribute to the light process, and their structure and electronic properties largely identify the effects of each step on water photolysis. The pollutants may be directly oxidized by producing one or more oxidants, such as hydroxyl radicals and chemisorbed active oxygen species produced during the electrochemical anodic oxidation process (an advanced oxidation process (AOP) for water treatment at room temperature and usual pressure) [14]. AOPs include the application of strong oxidizing materials, catalysts or photo-catalysts, and energy sources (ultraviolet (UV) radiation, ultrasound (US), and electrical) [15]. There are several advantages to thin-film metal surface-stabilized electro-photocatalysts: no need for stirring for a homogeneous mixture, generation of strongly reactive radicals at adequate number limitation, and more homogeneous UV radiation to the catalyst [16]. Their optimal performance is affected by several factors like characteristics of the catalyst, e.g., gap bond, improved photocatalytic efficacy, film thickness, light source/intensity/absorption, charge transfer, and water qualities, e.g., presence of particle-associated (PA) microorganisms [17]. EPC technologies have been demonstrated in recent studies to offer a good chance to eliminate chemical and microbial contaminants. As reported by Omar et al. (2019), Fenton, photo-Fenton, and ozonation/Fenton processes have been applied to remove formaldehyde from water and wastewater [18]. The application of electro-photocatalytic by coating ZnO NPs on zinc-sheet copper electrodes for purification of sulphonamide water is reported by Li et al. (2018) [19]. The application of photo-degradation by copper tungsten oxide NPs with electron sacrificial agents for the purification of dye water is reported by Hosseinzadeh et al. (2021). The efficiency of formaldehyde removal from water through the optimized Fenton process and from wastewater through the ozonation/Fenton process was 75 % and 80 %, respectively [20]. Herein, light-emitting dynode (LED) UV-A lamp coupled with ZnO semiconductor immobilized on Zn electrode has yielded a novel approach to more efficient formaldehyde degradation. It is clear that the research is very important for the development and improvement of existing methods for treating water containing high concentrations of formaldehyde. Research innovations and strengths are as follows: presenting the mechanism, determining the importance degree of variables influencing removal efficiency, reaction kinetics, and application of LED lamp. This research aimed to degrade formaldehyde, a chemical agent-tolerant pollutant (herein, the model pollutant) from potable water by means of thin-film photocatalytic stabilized ZnO NPs on Zn. The following variables are studied: current density, formaldehyde concentration, lamp intensity, ZnO NP layering, pH, and radiation time.

2. Materials and methods

2.1. Materials

ZnO NPs (specific surface area = 50 m^2/g; particle size = 20 nm) were prepared from AMOHR (Germany). H_2SO_4, NaOH, and formaldehyde were supplied from Merck (Germany). 1N NaOH and H_2SO_4 were used to adjust pH [21].

2.2. Preparation of ZnO NPs

100 mL of distilled water were mixed with 5 g of ZnO NPs. ZnO dispersion in distilled water was improved by sonicating the suspension for 22 min at a frequency of 50 kHz in an ultrasonic cleaning bath (MATR. N.B., Italy) after it had been stirred for 30 min using a magnetic stirrer (AIKA, Germany). Once the zinc electrode had been hydroxylated and cleaned with distilled water, its weight was determined [22].

2.3. Electrode preparation

The Zn electrode (Amin Sanat Poya, Iran) was utilized as the substrate to immobilize ZnO NPs [23,24]. To enhance the number of OH groups, a 0.1N NaOH solution and detergent were used to pre-treat the Zn electrode. The electrodes were pre-treated by polishing them with abrasive paper, washing them with tap water and detergent, and rinsing them with deionized water to eliminate any impurities.

2.4. ZnO NP immobilization

ZnO films were prepared using drying methods [25,26]. Herein, a Zn plate was employed for immobilization. Pre-treatment was followed by weighting the Zn electrode, immersing it in a colloidal solution, and drying it in an oven for 28 min at 37 °C (AIKA, Germany). Subsequently, coated particles were calcined for 62 min at 104 °C and 318 °C in a muffle furnace (AIKA, Germany). The immobilized ZnO films underwent thermal treatment, which increased their mechanical stability. The whole procedure was repeated twice for two-layer coatings and three times for three-layer coatings. All free ZnO NPs were eliminated by washing them with distilled water.

2.5. Batch EPC reactor

Fig. 1 displays the experimental setup. The 360 mL 100 × 60 × 60 mm glass vessel served as the batch reactor. Two electrodes with thin-film ZnO NPs immobilized on Zn (i.e., anode) and a copper electrode (i.e., cathode) were the electrodes' properties. Each of the electrodes had an active surface area of 3600 mm^2 (90 × 40 × 1 mm). The electrodes were positioned 10 mm from the reactor's bottom, and the Zn/ZnO electrode was placed 15 mm from the LED UV-A lamp (OSRAM, Germany). With a maximum electrical power (60 W), the direct current (DC) power source (Iran Jahesh, Iran) produced electrical energy at a rate of 1000–5000 mA. The electrical power, radiation intensity, wavelength, and voltage of the LED UV-A lamp (Osram, Germany) were 1000 mW, 120 mW/cm^2, 395 nm, and 3.4 V, respectively. Samples were treated with LED UV-A lamps (at 480, 600, and 720 mW/cm^2) using an electrode comprising thin-film ZnO NPs immobilized on Zn (1.5, 3, and 4.5 mg/cm^2) with varying current densities (4, 8, and 12 mW/cm^2), radiation times (at 8, 16, and 32 min), and pHs (3, 7, and 11). The aim was to assess the impact of the catalyst, UV light, and current densities on

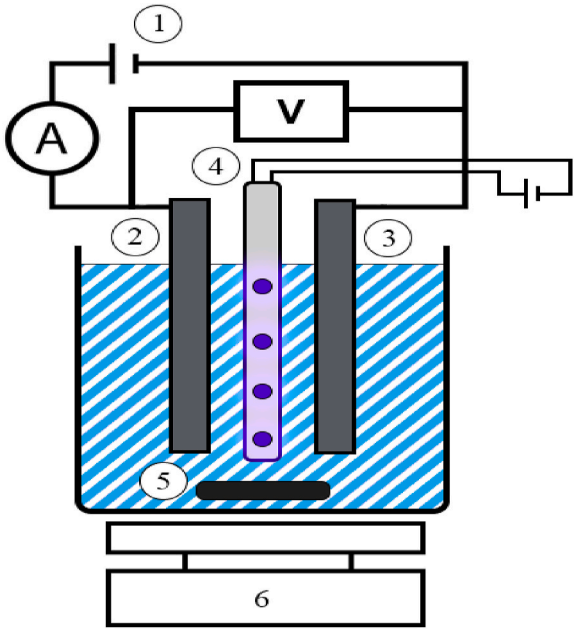

Fig. 1. Thin-film immobilized ZnO NPs on Zn within a batch EPC reactor (1. Power supply; 2. Cu electrode; 3. Zn/ZnO electrode; 4. LED UV-A lamp; 5. Magnetic stirring bar; 6. Magnetic stirrer).

degradation. Contaminated water samples were mixed homogeneously using a magnetic stirrer.

2.6. Analytical methods

Every test was run three times to determine the average data values. Water samples were tested for formaldehyde (Unico UV-2100 spectrophotometer (Germany)), ORP (CG ORP meter (Malesia)), temperature, and pH (Hack pH meter (USA)) following EPC. Formaldehyde content was measured through common standard processes (6252 at 400 nm).

Formaldehyde removal percentage was measured as follows (1) [25]:

$$\text{Removal}\ (\%) = \left(1 - \frac{C_t}{C_{t0}}\right) \times 100 \tag{1}$$

where R represents the formaldehyde removal percentage. Besides, C_{t0} and C_t denote average pre- and post-treatment formaldehyde concentration (mg/l). Following the completion of all tests, the electrodes were rinsed for 1 min with distilled water to remove any deposits from their surface.

Kinetic reaction models were evaluated using Eqs. (2) and (3) [27,28],:

$$\ln C_t = \ln C_0 - K_1 t \tag{2}$$

$$\frac{1}{C_t} = K_2 t + \frac{1}{C_0} \tag{3}$$

where C_0 and C_t represent formaldehyde concentrations at the start of the reaction and time t, respectively. Besides, K_1 and K_2 denote first- and second-order reaction constants, which can be measured from the slope of plots ln C_t vs t and $1/C_t$ vs t, respectively. In addition, the relationship between three removal efficiency levels as arraies and six operational variables was represented by the Taguchi model. The selection levels of each of the studied parameters as Taguchi data were given in Table 2.

2.7. Water sample preparation

Water samples contaminated with formaldehyde utilized in EPC experiments were procured from an urban distribution system located near a laboratory of the Islamic Azad University Tehran Medical Sciences Branch in Tehran. The primary physicochemical properties of the samples were examined by testing. Table 1 displays mean values for certain water properties. Synthetic formaldehyde solution 1000 mg/l was prepared by dissolving 2.7 ml of formaldehyde in 1000 ml of double distilled water. By diluting (with a ratio of 1–9.09, 4.54, and 3.03) formaldehyde concentrations of 110, 220, and 330 mg/l of water were obtained. The formaldehyde was measured by colorimetric method with chromotropic acid [26,29]. The removal efficiency was assessed by selecting and analyzing reactor water at the end of each research cycle. The test control was an EPC reactor devoid of formaldehyde and an electro-photo. Every sample was analyzed in triplicates, and every EPC experiment was at least duplicated.

3. Results

The following are the findings of this investigation, including the impacts of formaldehyde concentration, current density, lamp intensity, ZnO NP layering, pH, and various radiation times on the EPC reactor performance in formaldehyde removal from urban drinking water contaminated with formaldehyde.

3.1. Initial concentration of formaldehyde effect

Fig. 2 depict the effect of formaldehyde initial concentration and pH on EPC removal efficiency. As shown, removal efficiency is reduced by increasing concentration from 110 mg/l to 330 mg/l. With 8 min of radiation, the EPC reactor demonstrates that the

Table 1
Major physical/chemical properties of urbane water contaminated with formaldehyde (in 2024 year).

Parameter	Unit	Value
Calcium	mg/l as $CaCO_3$	160
Dissolved oxygen	mg/l	8.08
Formaldehyde	mg/l	0.00
Nitrate	mg/l	9.2
ORP	mV	275
pH	–	7.13
Sulfate	mg/l	94.3
Temperature	°C	20
Total Alkalinity	mg/l as $CaCO_3$	120

Table 2
Arrays and levels selected for the removal of formaldehyde using the EPC process.

Effective parameters	Levels		
	1	2	3
Current density	4	8	12
Formaldehyde concentration	110	220	330
Lamp intensity	480	600	720
ZnO NP concentration	1.5	3	4.5
pH	3	7	11
Radiation time	8	16	32

removal percentage of formaldehyde (110 and 330 mg/l) increases from 85 to 100 % and 65–85 %, respectively, as pH rises from 3 to 11. The degradation effect highly depends on pH—a key operating variable influencing the EPC process efficiency—and is amplified when it rises.

3.2. pH effect

In order to check and determine pH, formaldehyde samples were prepared at a constant concentration of 330 mg/l. In this study, the effect of pH changes in the range of 3–11 in EPC method with current intensity of 12 mA/cm^2, 16 min of radiation, lamp intensity of 720 mW/cm^2, and ZnO concentration of 3 mg/cm^2 is studied that the results can be seen in Fig. 3. The highest removal of formaldehyde in EPC process is obtained at pH 11 equal to 100 %.

3.3. Lamp intensity effect

Fig. 4 shows the impact of LED UV-A lamp intensity on the photo-reactor process's removal efficiency including EPC and photo-electro (PEC). Formaldehyde removal percentage significantly increases in the presence of LED UV-A lamp. With 16 min of radiation, a pH of 11, and an LED UV-A lamp intensity increased from 480 to 720 mW/cm^2, the removal percentage of formaldehyde (330 mg/l) rises from 83 to 100 % in EPC reactor and from 50 to 61 % in PEC reactor.

3.4. ZnO concentration effect

Fig. 5 displays the effects of ZnO concemtrations on the EPC process's removal efficiency. Formaldehyde removal percentage significantly increases in the presence of photo-catalyst ZnO NPs. With 16 min of radiation, UV-A lamp intensity of 720 mW/cm^2, and a ZnO concentration increased from 1.5 to 4.5 mg/cm^2, the removal percentage of formaldehyde (330 mg/l) rises from 55 to 65 % in pH 3, from 65 to 75 % in pH 7, and from 80 to 100 % in pH 11.

3.5. Current Density Effect

The applied current density is one of the main variable parameters influencing the EPC process's oxidation capacity as it controls the quantity of produced OH radicals that function as oxidizing agents. Fig. 6 illustrates the impact of current density on the EPC process's removal efficiency. With a pH of 11, an LED UV-A lamp intensity of 720 mW/cm^2, an LED UV-A lamp intensity of 720 mW/cm^2, and current density of increased from 4 to 8 mA/cm^2, the removal percentage of formaldehyde (330 mg/l) rises from rises from 75 to 86 % in radiation time of 4 min, from 85 to 91 % in radiation time of 8 min, and from 90 to 100 % in radiation time of 12 min.

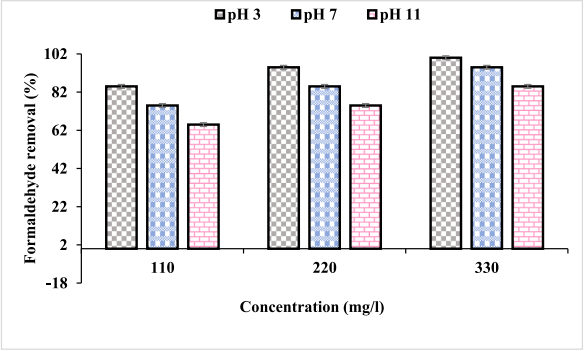

Fig. 2. Impact of formaldehyde initial concentration and pH on formaldehyde removal efficiency (Experimental conditions: pH = 3–11; Temperature = 20 °C; Radiation time = 8 min; UV-A lamp intensity = 720 mw/cm^2; Initial concentration = 110–330 mg/l; Current density = 8 mA/cm^2; ZnO concentration = 3 mg/cm^2).

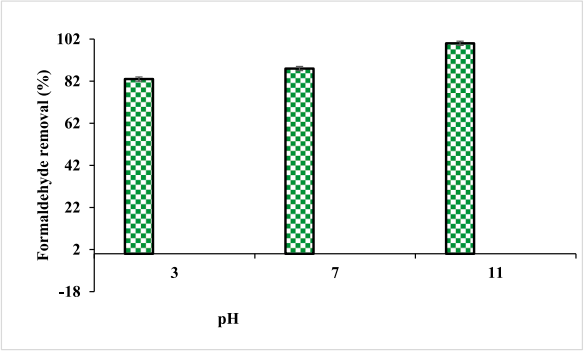

Fig. 3. Impact of pH on formaldehyde removal efficiency (Experimental conditions: pH = 3–11; Temperature = 20 °C; Radiation time = 16 min; UV-A lamp intensity = 720 mw/cm^2; current density = 12 mA/cm^2, Initial concentration = 330 mg/l; ZnO concentration = 3 mg/cm^2).

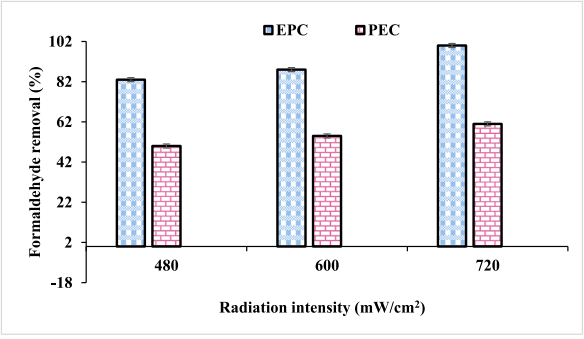

Fig. 4. Impact of catalyst and UV radiation on formaldehyde removal efficiency (Experimental conditions: pH = 11; Temperature = 20 °C; Radiation time = 16 min; UV-A lamp intensity = 480–720 mw/cm^2; Initial concentration = 330 mg/l; Current density = 8 mA/cm^2).

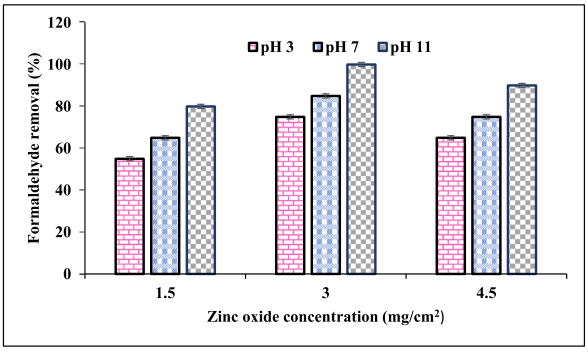

Fig. 5. Impact of catalyst layer on formaldehyde removal efficiency (Experimental conditions: pH = 3–11; Temperature = 20 °C; Radiation time = 16 min; UV-A lamp intensity = 720 mw/cm^2; Initial concentration = 330 mg/l; Current density = 12 mA/cm^2).

3.6. Kinetic studies and optimization

Fig. 7 (a, b) demonstrates the plots of the kinetic 1st- and 2nd-order reaction models fitted with experimental data (better fitted with the 1st-order reaction ($R^2 = 0.9982$)) of formaldehyde removal in the batch EPC reactor, respectively. The half-life period ($t_{1/2}$) and apparent rate constant (K_2) were measured as 2.6 min and 0.31 min^{-1}, respectively. The optimal values for operating variables were ascertained by applying the Taguchi model. Effective parameters in EPC decomposition of formaldehyde based on software analysis are shown in Fig. 8. According to Fig. 8, it can be seen that the percentage of effective factors are concentration, pH, current density, lamp intensity, layering ZnO, radiation time, respectively. It should be noted that the relative standard deviation (RSD) or coefficient of variation (CV) of less than 1.4 indicated the high reproducibility of the data obtained during the experiments.

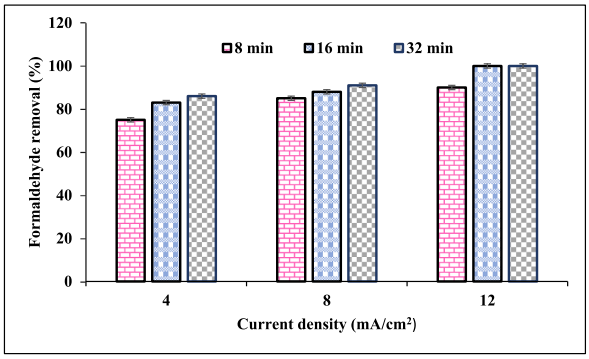

Fig. 6. Impact of current density on formaldehyde removal efficiency (Experimental conditions: pH = 11; Temperature = 20 °C; Radiation time = 8–32 min; UV-A lamp intensity = 720 mw/cm^2; Initial concentration = 330 mg/l; Current density = 4–12 mA/cm^2; ZnO concentration = 3 mg/cm^2).

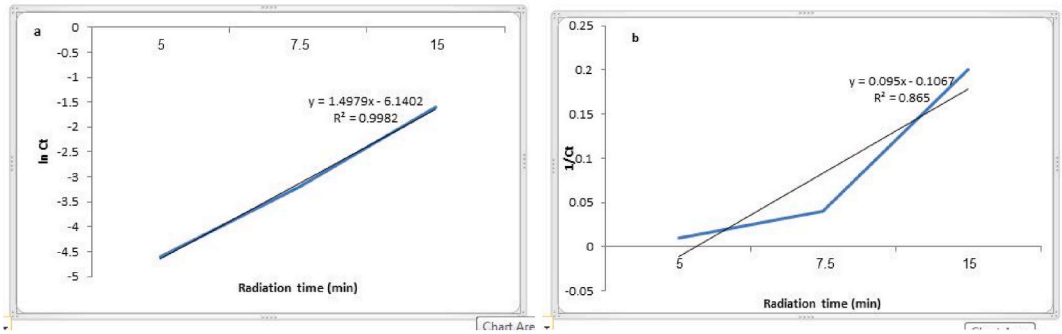

Fig. 7. Plots of 1st (a)- and 2nd (b)- order reaction models fitted with formaldehyde removal in the batch EPC reactor (Experimental setup: Temperature = 20 °C, pH = 11, Radiation time = 0–15 min).

4. Discussion

- **Formaldehyde initial concentration effect:** This effect can be explained by reduced path length of photons entering the EPC reactor as well as higher formaldehyde concentrations. Thus, a smaller number of photons reach the surface of the catalyst, thereby reducing the generation of OH radicals and degradation rate. This phenomenon is the same as humic acid (HA). The impact of electrochemical degradation on HA is explored. The experiments are conducted under the following conditions: initial HA concentration = 0–5 mg/l, pH = 4, reaction time = 15 min, aluminum electrode spacing = 2 cm, current density = 9 mA/cm^2, and H_2O_2 concentration = 120 mg/l. The efficiency decreases with increasing concentrations [30]. Due to pKa of >12.79 in 20 °C, the rate of decomposition increases in the sample with low concentration. The maximum efficiency (i.e., 100 %) is obtained by the EPC reactor under the following conditions: pH = 11, radiation time = 8 min, and concentration = 110 mg/l. This outcome is in line

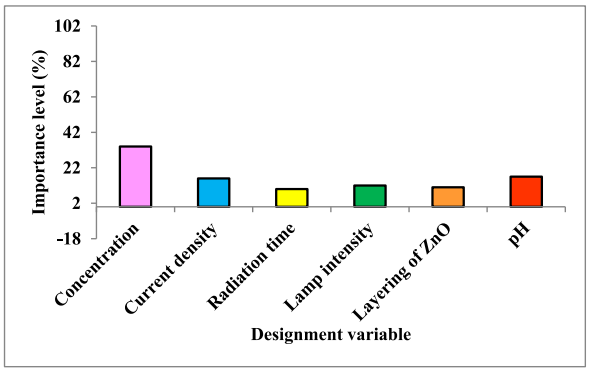

Fig. 8. Taguchi model (Experimental conditions: Temperature = 20 °C; pH = 3–11; Radiation time = 8–32 min, Initial concentration = 110–330 mg/l; ZnO concentration = 1.5–4.5 mg/cm^2, UV-A lamp intensity = 480–720 mw/cm^2; Current density = 4–12 mA/cm^2).

with data that has been released before. Photocatalytic tests are conducted under the following circumstances: initial Acid blue 113/Acid red 88 concentrations = 0–200 mg/l range, pH = 3, TiO_2 concentration = 1 g/l, irradiation time = 90 min, and radiation intensity = 60 W [31]. Increasing the concentration of the studied pollutant with decreasing efficiency the process has been accompanied. Degradation of formaldehyde using UV/$S_2O_8^{2-}$ is reported. They indicate that reduction of formaldehyde removal efficiency at 48 min from 94.08 % to 46.16 % by increasing formaldehyde concentration from 1000 to 10000 mg/l [32].

- **pH effect:** The effect of the initial pH of the environment varies greatly depending on the type of process used and the type of pollutant. The pH affects the amount of OH· radical formed in water during the EPC process, which significantly contributes to formaldehyde removal. Formaldehyde has a pH range of 3–3.5 and is acidic in nature. Protonation and deprotonation of formaldehyde is dependent on pH. The photocatalytic efficiency of zinc oxide semiconductor depends on pH and its surface charge property changes with pH change. This can be associated with increasing OH^- anion availability at higher pH values that generates a larger number of OH· radicals, which is in line with previous research findings [33]. The oxidizing agents in the EPC reactor according to the alkalinity of the environment are OH· radical and H_2O_2 due to the alkalinity of the reaction medium and the substance under the effect (formaldehyde). Therefore, with increasing pH, the removal efficiency increases. Herein, the initial pH and final pH are calculated to further explore its effect. Therefore, the EPC process performs better in an alkaline environment than in an acidic one due to forming OH· radical and H_2O_2 as oxidizing agents. The mechanism of producing OH· radical takes place from the reactions of hydrogen peroxide with hν (λ = 390 nm) and hydroxide anion (OH^-) with $h^+_{(VB)}$ in the EPC reactor. In other words, with the increase in pH, the production of H_2O_2 and OH^- anion and as a result the creation of OH· radicals in the treated sample increases, and the increase in the production of the amount of OH· means an increase in the efficiency of formaldehyde removal. The results indicate an increase in the initial pH in EPC research (with formaldehyde concentration of 330 mg/l, current intensity of 12 mA/cm^2, 16 min of radiation, lamp intensity of 720 mW/cm^2, and ZnO concentration of 3 mg/cm^2, the increase in pHs are 3.45, 7.57, 11.69, respectively). The maximum efficiency (i.e., 100 %) is reached by the EPC reactor under the following conditions: pH = 11, radiation time = 16 min, ZnO NPs = 3 mg/cm^2, LED UV-A lamp-Zn/ZnO electrode spacing = 15 mm, LED UV-A lamp intensity = 720 mw/cm^2, current density = 8 mA/cm^2, and formaldehyde concentration = 110 and 220 mg/l pH = 11 (optimum pH for standard formaldehyde (10 μg/l)) needs a current density lower than the other two ones. The functional group present in the formaldehyde may undergo protonation and deprotonation based on the sample pH. It is expected that a strong electrophile agent of formaldehyde can affect the solution pH during photocatalytic oxidation. As reported by Haddad et al., OHs formed at pH 7 during the UVC/VUV photo-reactor process [34].
- **Lamp intensity effect:** Formaldehyde removal efficiency directly correlates with LED UV-A lamp intensity, which aligns with information released before. This observation aligns with previously released information. Once exposed to UV radiation, 10 mg/l trichloroethylene concentration in primary samples dropped gradually from 2.85 to 1.14 mg/l when the power of the UV-C lamp increased from 4.2 to 8.4 mW/cm^2 [35]. The current density and exposure time start to drop at highest lamp intensity. The optimal UV-A lamp intensity for standard formaldehyde (10 μg/l) is 720 mw/cm^2. This increasing optical activity can be attributed to greater generation of reactive oxygen species (ROS), e.g., electron-donating OH· radical from water's OH^- anion and O_2^- radical anion. This observation aligns with photocatalytic tests conducted by utilizing silicon dioxide (SiO_2), TiO_2, and SiO_2-TiO_2 composite semiconductors [36]. The minimum energy required to excite ZnO NPs is 3.4 eV and light with a maximum wavelength of 390 nm can provide this energy. Changing the intensity of radiation by changing the lamp intensity causes a change in the excitation rate of photocatalyst electrons and can affect the efficiency of photocatalytic pollutant removal.
- **ZnO concentration Effect:** A maximum ROS concentration capable of participating in the reaction at the outer surface of the film will form by the photo-catalyst at a fixed lamp intensity, indicating the presence of an optimal catalyst amount. The optimal quantity of ZnO catalyst solution and LED UV-A lamp intensity for standard formaldehyde (10 μg/l) are 3 mg/cm^2 and 720 mW/cm^2, respectively. The removal efficiency declines at the one- and three-layer ZnO NP films, but it reaches its maximum value of 100 % at the two-layer ZnO NP film. This can be due to increasing surface area for degradation of formaldehyde concentrations. When the number of ZnO NP films exceeds two films, there will be non-uniform dispersion of ZnO NP in the electrode. The number of more ZnO NP films causes the ZnO NPs to be attracted to each other, clumping of NPs, and eventually weakening the photocatalytic properties. This observation is in line with photocatalytic tests conducted by utilizing TiO_2 thin films. The film thickness was shown to be directly correlated with the red sulphonyl 3BL decay rate constants. Nonetheless, in thick films, a limiting value is seen because of increased light scattering and opacity, which reduces the amount of radiation passing through the film [37]. Formaldehyde removal efficiency decreases with increasing catalyst loadings (above two layers). This can be due to reduced UV penetration into the film's outer layers and declining cluster protection against UV reaching the surface of the catalyst. The presence of UV-A and photo-catalyst ZnO NPs has resulted in increased formaldehyde removal efficiency due to OH· radical formation. Talaiekhozani et al. reported that 10–70 mW/cm^2 UV power significantly affected the removal of the Reactive Blue 203 (RB203) dye [38]. OH· radicals lead to the oxidizing of formaldehyde. Photocatalytic degradation can also be aided by $O2^-$, hydrogen peroxide (H_2O_2), and hydroperoxyl (HO_2) radicals produced when the anode's dissolved oxygen content is reduced. They are in charge of formaldehyde degradation. Pre-tests show that OH· radicals are more effective than O_2^- in formaldehyde degradation. The photocatalytic degradation of emerging concerns contaminants in water has been reported [39].
- **Current Density Effect:** Formaldehyde removal efficiency starts to drop at lower radiation times and current densities. Besides, radiation time starts to decline at higher current densities. due to the increase in the occurrence of reactions on the surface of anode and cathode electrodes in the direction of producing OH· radicals which affects the speed of the reaction. Therefore, it is necessary to determine the opthmum current density in EPC reactor. The optimal current density for standard formaldehyde (10 μg/l) is 12 mA/cm^2. According to the experimental findings, the electrode current density improved the resultant gradient-separated electron-hole that accelerated the degradation by reducing its recombination rate and increasing the photocurrent rate. The anode's direct/

indirect electro-oxidation reactions are improved by the external electric field at higher current densities applied. Because the number of OH is inversely correlated with the electron–hole recombination rate and proportionate to the particular surface area of photo-catalysts, degradation efficiency corresponds to both the quantum yield and specific surface area of the photocatalytic system. Mass transfer is accelerated by photo-electro-catalysis through formaldehyde electromigration toward the electrode. This observation is consistent with electrochemical tests conducted utilizing Cu-U@T/T electrodes [40]. The experimental findings demonstrated that formaldehyde degradation proceeds more quickly the more intensely the radiation penetrates the photocatalytic electrode. As anticipated, the formaldehyde removal efficiency increases as a result of increased exposure time and current density. As reported by Nisa et al. the optimal removal percentage was obtained under the following optimized circumstances: RT = 150 min and current density = 43.28 mA/cm^2 [41]. Increased exposure time and current density help products of electrolysis (e.g., OH^- anion) to be quickly generated in the cathode electrodes. These products are in charge of formaldehyde degradation. The primary driver of electrochemical processes is an increased drift force on the electrode surface as a result of increased current density. As anodic oxidizing agents, the generated OH radicals' quantity is controlled by the current density applied. This observation is consistent with tests conducted by employing the boron-doped diamond (BDD) anode [42]. The generated oxygen in the anode electrode leads to a higher degradation effect against formaldehyde as the O_2 molecule has a significant contribution in photo-catalysis, where it is converted to O_2^- radical in the photo-catalyst ZnO NP capacity bond. This is consistent with photocatalytic tests carried out utilizing ZnO [43]. The efficiency of formaldehyde absorption by a ZnO NP-layered Zn electrode as a positive pole (i.e., anode) is proportional to increased exposure time and current density. As the current density increases, the time required for the reaction is reduced which increases the removal efficiency. The removal efficiency decreases after 8 min due to the consumption of the OH radicals with increasing time and the reason for the decrease in removal efficiency with increasing time is the increase in the ambient temperature of the treated sample. The time of photocatalytic exposure needed for total formaldehyde degradation starts to lessen.

- **Kinetic studies and optimization:** The electrophile agent of formaldehyde can be oxidized by an OH radical/positive hole or reduced by an electron in the conduction band. This electro-photocatalytic mechanism is illustrated in the following equations:

$$ZnO + h\nu\ (\lambda = 390\ nm) \dashrightarrow ZnO\ (e^-_{(CB)} + h^+_{(VB)}) \quad (4)$$

$$O_2 + H_2O \dashrightarrow O_3 + 2H^+ + 2e^- \quad (5)$$

$$e^-_{(CB)}\ (ZnO) + O_{2ads} \dashrightarrow O_{2ads}^- + ZnO \quad (6)$$

$$O_{2ads}^- + H^+ \dashrightarrow HO_{2ads}^- \quad (7)$$

$$HO_{2ads}^- \dashrightarrow O_2 + H_2O_2 \quad (8)$$

$$H_2O_2 + h\nu \dashrightarrow 2\ OH \quad (9)$$

$$h^+_{(VB)} + OH^- \dashrightarrow OH \quad (10)$$

$$\bullet OH + \text{Formaldehyde} \rightarrow \text{Formaldehyde degradation} \quad (11)$$

This finding is not consistent with photo-catalytic experiments conducted utilizing UV lamps. Formaldehyde degradation under UV light was found to follow the second-order degree [44].

Considering all the possible combinations between these 6 3-level factors, $6^3 = 729$ tests are necessary to cover all possible moods (full factorial or factorial method), but in the method.

Taguchi using statistical methods among 729 experiments, 18 experiments that have the most effect of 4 relevant factors are identified. Reaction time is identified as the most significant variable based on the formaldehyde removal efficiency obtained by the Taguchi model, which is inconsistent with experiments conducted by utilizing iron electrodes [45].

5. Conclusion

The results of the experiment indicate that immobilizing thin-film ZnO NPs on Zn during the EPC process is a viable technique for formaldehyde degradation. The process is influenced by various factors such as pH, formaldehyde concentration, radiation time, lamp intensity, current density, and number of ZnO NP catalyst layers. The tests yielded the following results:

- A lower concentration of formaldehyde, improves the removal efficiency.
- A higher pH, improves the removal efficiency.
- A higher LED UV-A lamp intensity improves the removal efficiency.
- Experimental conditions for producing the maximum concentration of ROS are ZnO catalyst solution (3 mg/cm^2), and optimal LED UV-A lamp intensity (720 mW/cm^2).
- Removal efficiency is improved by a higher current density.
- A first-order rate equation governs the reduction of formaldehyde during reactor operation.
- From the point of view of the Taguchi optimization model, reaction time is considered the most effective variable in formaldehyde removal in the EPC reactor.

- Optimum conditions for reducing formaldehyde are: initial formaldehyde concentration 110 mg/l, pH 11, intensity LED UV-A lamp 720 mW/cm^2, ZnO catalyst solution (3 mg/cm^2), current density 12 mA/cm^2, reaction time less than 20 min.
- Prior to being used as a safe water purification technique on a global scale, this process still needs to be further researched and optimized. Its limitations are that it failed to examine the EPC reactor's removal efficiency for water quality chemical variables. Thus, future research is recommended to explore the impact of the above variables on removal efficiency as well as the strengthening effect of batch and continuous EPC reactors with other electrodes and catalysts.
- EPC is a practical and efficient technique to reduce a high quantity of formaldehyde from potable water in batch/monopolar electrode connection modes. It is also a viable approach for treating potable water contaminated with formaldehyde.

Data availability statement

Data will be made available on request.

Additional information

No additional information is available for this paper.

CRediT authorship contribution statement

Amir Mohammad Farhoodi: Writing – review & editing, Writing – original draft, Methodology, Investigation. **Amir Hessam Hassani:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Giti Kashi:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation. **Amir Hossein Javid:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Nabiollah Mansouri:** Writing – review & editing, Writing – original draft, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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