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Application of enhanced nZnO photocatalytic process with ultrasonic wave in formaldehyde degradation from aqueous solution

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ABSTRACT

This study was performed to evaluate formaldehyde degradation ratio in a batch reactor. For investigation of the synergism effect, formaldehyde degradation by each process (UV photolysis, ZnO catalyst, ultrasonic wave) was tested. In the next step, the influence of important operational parameters, such as pH of the solution (3–8), initial CH_2O concentration (20–100 mg/l), dosage of nZnO (10–60 mg/l), ultrasonic wave power (40–150 W), and reaction time (10–60 min) was investigated. Ultrasonic wave process could slightly degrade CH_2O and had a partial effect as synergism on formaldehyde degradation. Maximum formaldehyde removal ratio occurred with a nZnO dosage of 60 mg/l, pH of the solution of 8, ultrasonic wave power of 40 W, and initial formaldehyde concentration of 50 mg/l with a contact time of 30 min (78%). A comparison of the reaction orders of kinetic studies showed that formaldehyde degradation was in accordance with pseudo-second-order reaction. It could be found that the sonophotocatalytic process may be recommended for the treatment of solutions containing low formaldehyde concentrations.

Keywords: Formaldehyde; Nanoparticle; Photocatalyst; Ultrasonic wave

1. Introduction

Formaldehyde is a colorless, reactive gas with a strong smell at room temperature. It is related to a large family of chemical compounds called volatile organic compounds.

Formaldehyde is manually produced from methanol. This chemical can be produced in liquid (formalin) or solid (para formalin) form [1]. Formaldehyde has important applications in chemical industries for making different types of products, such as those of home furnishing, household cleaners, paints, textiles, landscape, yard products, and pesticides [2]. Also, it is a good preservative because it causes protein denaturation as an antioxidant and microbial growth inhibitor [3].

In 1990, the USA and Japan had the most production of formaldehyde. In 1996, Canadian domestic consumption of formaldehyde was about 191 kilotonnes [4].

China had the maximum formaldehyde consumption in 2007 [5]. In water resources, formaldehyde

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may be formed by oxidation of humic matter during ozonation and chlorination [4]. Also, discharges of formaldehyde from industries can threaten life in the recipient water resources. The exposure of aquatic ecosystem to formaldehyde can lead to impacts such as potential negative effects on the biological balance of environment. Short-term exposure to formaldehyde in drinking water can cause irritation and allergic dermatitis when formaldehyde may be associated with direct skin contact [6]. Direct discharge of this toxic compound into biological wastewater treatment systems causes interference of bacteria activity and failure in system operation as well [7]. According to the report on carcinogens, formaldehyde is the 25th most produced chemical in the US [3]. It is also the most toxic organic product of 45 organic substances that cause adverse environmental impacts [8]. Based on human studies carried out by international agencies for research on cancer, formaldehyde has been classified as a human carcinogen [8,9]. Industrial effluents may have formaldehyde in a wide range of concentration of 100–10,000 mg/l [10,11]. Large-scale formaldehyde consumption will endanger water resources if effluents of chemical industries are not treated or managed well [6]. In general, it will be expected that maximum formaldehyde concentration in drinking water be less than 100 μg/l [4].

Because of formaldehyde degradation, biological processes were frequently performed. But formaldehyde is a chemical compound and adaptation is time consuming. Olivera et al. had adapted micro-organisms to phenol for about one year, and then evaluated formaldehyde biodegradation by injecting formaldehyde into the adapted environment [12]. However, liquid effluents with a high formaldehyde concentration using conventional processes such as biological systems are difficult to treat because formaldehyde can react with DNA and damage cells and cause death of micro-organisms [13].

For formaldehyde degradation in aqueous solutions, various methods are available, such as electrocoagulation, electroflotation, and electroflocculation. However, these methods are traditional and are incapable of removing the contaminant completely. Further, these processes may create by-product compounds that are adverse and harmful to environment [2].

It is recommended that when process kinetics is very short, photocatalyst process be applied [13]. Formaldehyde degradation has been evaluated by following advanced oxidation processes: electrogeneration of H_2O_2, electrochemical, photocatalysis with pt/Fe_2O_3/TiO_2, UV/TiO_2 and UV/H_2O_2, UV/H_2O_2/TiO_2, Fenton and photo-Fenton, and advanced wet oxidation.

TiO_2 and ZnO are known for wide band gap semiconductors that can be used as photocatalysts under UV radiation [14]. ZnO nanoparticles have a band gap of about 3.2 eV and a wavelength of 387 nm [15]. ZnO photocatalyst has less toxicity, is inexpensive, and more active than TiO_2, so it is considered in lieu of TiO_2 [16]. Studies have reported that ZnO powder has more efficiency than TiO_2 in the oxidation process.

Ultrasounds (sounds with frequencies up to 18 kHz) are able to increase heat and mass transfer reactions. The chemical effects of ultrasound (US) are due to sound production that is passed through a liquid. This can overcome the intermolecular forces bonding the fluid; the molecules are taken apart from each other and tiny microbubbles created. These microbubbles grow during rarefaction, causing the collapse of cavities immediately, with large amount of energy being released. So, the sound waves do not interact with the pollutant directly, but they create shear force. This is sufficient to break chemical bonds. Sonochemical destruction of pollutants in aqueous phase occurs as a result of imploding cavitation bubbles and involves several reaction pathways, such as pyrolysis inside the bubble and hydroxyl radical generation [17]. Above-mentioned mechanisms related to the capabilities of ultrasonic waves, such as accelerating reactions related to oxidation or reduction of many compounds, have causes that have been used for different applications. Application of this process has several benefits, e.g. no requirement of chemical addition and environmental safety [18].

The present investigation aims at studying the possible improvement in an efficient photocatalyst method for the purification of a solution containing formaldehyde with economic and safety concerns. So far, in similar studies, ultrasonic wave synergism effect has not been performed in photocatalyst formaldehyde degradation in aqueous solution whose compatibility has been identified by the application of this process.

2. Materials and methods

The first step was to investigate the synergism effect of ultrasonic wave process and so the formaldehyde removal rate in each process (UV photolysis, ZnO catalyst, ultrasonic) was calculated with an initial CH_2O concentration of 50 mg/l and a reaction time of 60 min. The second step was to investigate the influence of primary operational variables such as pH of the solution (3–8), initial CH_2O concentration (20–100 mg/l), nZnO dosage (10–60 mg/l), ultrasonic wave power (40–150 W), and reaction time (10–60 min) on formaldehyde degradation. Then kinetic studies were concluded.

2.1. Chemical and instruments

In this study, formaldehyde solution 37% (w/w) was used (Table 1). Sulfuric acid and sodium hydroxide (1 N) were used to adjust the pH of the solution [2]. Chemical materials were supplied from Merck Company with high purity.

Zinc oxide nanoparticles (as powder) were supplied from *NANOSAV* Company. Characteristics and structure of ZnO nanoparticles are shown in Table 2.

Ultrasonic homogenizer apparatus (*BANDELIN* Company made in Germany) was used. Also, in the photolysis process, a high-pressure UV lamp with a wavelength of 254 nm and an intensity of 7.3 W/m^2 was used.

2.2. Procedure

The degradation of CH_2O was performed in a batch sonophotocatalytic reactor, as shown in Fig. 1.

A covered cylindrical shape with an effective volume of 2 L was used. A 150-W high-pressure mercury lamp with 254-nm wavelength was used as a light source. An UV lamp was inserted to walled quartz well and located at the reactor. To prevent the lamp from overheating, the reactor was flushed with cooling water. Transcendent probe with 23-kHz frequencies and a maximum 150 W was inserted at the front of the UV lamp in the solution. To establish a uniform mixture, a magnetic stirrer was located in the solution [19].

Table 1
Characteristics of formaldehyde

Chemical name	Formalin
Chemical frame	CH_2O
Solubility in water	400 g/m^3
Density	1.09 kg/l
Melting point	−92°C
Methanol	9–11%

Table 2
Characteristics of ZnO nanoparticles

Characteristics	Unit	Value
Chemical frame	–	ZnO
Purity	%	<99
Particle size	nm	30–50

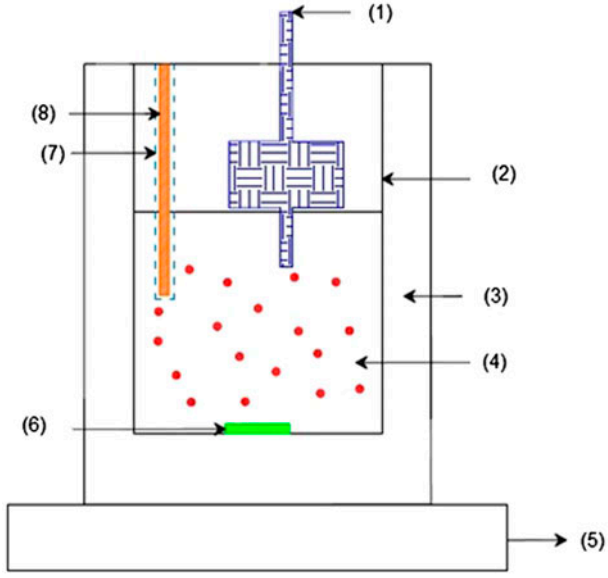

Fig. 1. Schematic diagram of sonophotocatalytic reactor (1—transcendent, 2—sonophotocatalytic reactor, 3—cooling water chamber, 4—sample content nZnO, 5—stirrer, 6—magnet, 7—quartz pipe, and 8—UV lamp).

2.2.1. Synergism effect experiment

The effect of photolysis, ZnO nanoparticle catalyst (nZnO dosage of 20 mg/l), and ultrasonic waves (power of 40 W) on formaldehyde degradation was evaluated separately. The initial concentration of formaldehyde was 50 mg/l with a reaction time of 60 min and at neutral pH.

2.2.2. Kinetic studies experiment

The influences of the pH of the solution (3–8), nZnO dosage (10–60 mg/l), initial CH_2O concentration (20–100 mg/l), ultrasonic wave power (40–150 W), and reaction time (10–60 min) on the degradation of formaldehyde were studied by sonophotocatalytic process. The reactions were continued using optimal variables obtained in the previous stages. For example, in step (1), the basic conditions for the influence of the pH of the solution were as follows: CH_2O concentration: 50 mg/l, nZnO dosage: 20 mg/l, reaction time for each pH value of the solution: 30 min, and ultrasonic wave power: 40 W. The basic conditions for influence of nZnO dosage solution in step (2) of the test were as follows:

CH_2O concentration: 50 mg/l, pH of the solution: optimal value that was obtained in step (1), reaction time for each pH value of the solution: 30 min, and ultrasonic wave power: 40 W. Other steps were

continued through optimal parameters that were obtained before the steps of the sonophotocatalytic test. Upon completion of the designated reaction time, sample contents were filtered through a syringed acetate cellulose filter with 0.2-μm pore size and formaldehyde residues were determined. Finally, the kinetic studies were concluded upon obtaining optimal values. During the experiment, a test as a control sample was performed under similar conditions without interference of processes.

2.3. Analysis methods

In this experiment, to determine formaldehyde residues and formaldehyde degradation, spectrophotometer method (Dr-5000, HACH model) was used in accordance with 8110 colorimetric method with a visible light detector operating at a wavelength of 630 nm [20].

3. Results and discussion

This survey was accomplished with the object of investigating formaldehyde degradation in aqueous solution using enhanced sonophotocatalytic process and also identifying the capability of ultrasound synergism effect for formaldehyde degradation in aqueous solution that has not been accomplished previously. Firstly, the results related to synergism effect of ultrasonic waves were evaluated. Secondly, optimal operational conditions were obtained and then kinetic studies were concluded.

3.1. Ultrasonic synergism effects

This test was performed at the initial concentration of CH_2O of 50 mg/l with the reaction time of 60 min. Also, the pH of the solution was neutral.

3.1.1. Formaldehyde degradation by photolysis process

The effect of UV radiation on CH_2O degradation was investigated. The solution was exposed to the UV-C lamp at 254 nm with the intensity of 7.3 W/m^2. The CH_2O removal rate is shown in Fig. 2.

Efficiency of the photolysis process in the removal of formaldehyde was about 46% with the reaction time of 60 min. Similar results were found by Shiraish who also reported that formaldehyde, while exposed to the photolysis process using a 254-nm wavelength, did not degrade well [21]. Guimarães also found that formaldehyde was not degraded appropriately by using the photolysis process (254 nm as wavelength)

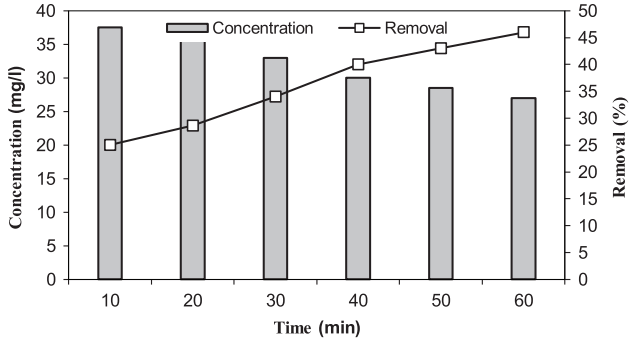

Fig. 2. Effect of UV-C radiation on formaldehyde degradation (formaldehyde concentration: 50 mg/l and neutral pH of the solution).

[3]. Shin et al. [22] reported that only 20% of CH_2O at an initial concentration of 100 mg/l was decomposed during the photolysis process.

3.1.2. Formaldehyde degradation by nZnO catalyst process

ZnO nanocatalyst dosage in the solution was 20 mg/l. The result of the effect of nZnO catalyst process on formaldehyde degradation is shown in Fig. 3.

Maximum formaldehyde removal efficiency by nZnO nanoparticles was 44% with 60 min as the reaction time. Some assumptions about the main steps in the oxidation of organic compounds containing oxygen in the presence of catalysts oxidation such as Zn oxide can be made. The process may be initiated by adsorption of the substrate onto ZnO nanoparticles and formation of surface complexes. Finally, formaldehyde decomposes to intermediates or is mineralized which can produce CO_2. $OH^{\cdot}$ radicals are released

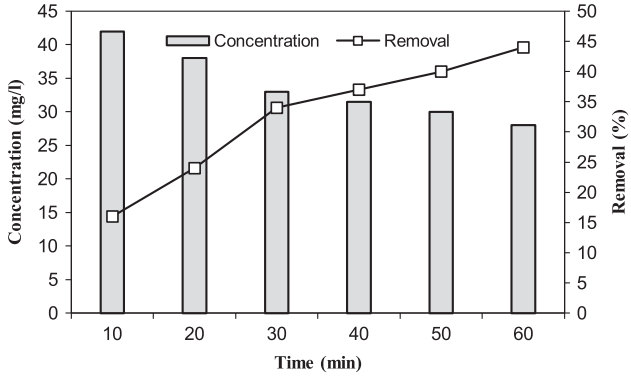

Fig. 3. Effect of ZnO nanoparticle on formaldehyde degradation (formaldehyde concentration: 50 mg/l, ZnO dosage: 20 mg/l, and neutral pH of the solution).

when formaldehyde is adsorbed onto zinc oxide nanoparticles. So, surface ability to have high reactivity increases and oxidation pathways are accomplished. Similar results were reported by Christoskova and Stoyanova, who found that formaldehyde could be mineralized by contact with nickel oxide catalyst and reformed to formic acid and CO_2 molecules [23].

3.1.3. Formaldehyde degradation by ultrasonic wave

The power of ultrasonic waves was 40 W. The results of ultrasonic effects on formaldehyde degradation are shown in Fig. 4.

The diagram shows that formaldehyde degradation efficiency was <34% when ultrasonic waves are only processed for decomposition. Formaldehyde degradation mechanisms by ultrasonic wave performance might be related to sound waves that break chemical bonds in solution using shear force caused by energy release. In aqueous solution, formation of hydroxyl radicals has a more important role for organic pollutant degradation by ultrasonic sounds. Gogate and Pandit [24] studied the effect of ultrasonic waves on wastewater treatment. They reported that the application of ultrasound wave increases the formation of hydroxyl radicals and the degradation of pollutants [24].

3.1.4. Formaldehyde degradation by enhanced nanophotocatalyst process

Photolysis, catalysis, and ultrasonic wave effects on formaldehyde degradation were also investigated (Fig. 5).

Enhanced sonophotocatalytic process decomposed formaldehyde by approximately 50%, but in the control experiments, CH_2O degradation was constant. When ZnO absorbs UV-C light at a higher energy, the electrons of the valence band are excited and transferred. The photogenerated electrons would be able to react with dissolved oxygen in water, and the excited sites reacting with water molecules absorbed onto ZnO nanoparticles lead to the generation of the reactive $OH^{\cdot}$, OH_2, and H_2O_2 species. These photogenerated species are very strong oxidizing agents and correspond to the removal of formaldehyde in the solution. The synergy curve for formaldehyde degradation between UV-C photolysis, nZnO adsorption, and ultrasonic wave was obtained from the following equation [25]:

$$\text{Synergy} = \frac{k_{\text{ZnO + UV-C + Ultrasonic}} - (k_{\text{ZnO}} + k_{\text{UV-C}} + k_{\text{Ultrasonic}})}{k_{\text{ZnO + UV-C + Ultrasonic}}} \quad (1)$$

Eq. (1) gives a synergism result of −1.44. It indicates that the ultrasonic process could not create a synergism effect on formaldehyde degradation. Sonophotocatalytic reactions are partially implemented faster than UV-C photolysis, ZnO nanoparticle adsorption, and ultrasonic process (Fig. 6).

3.2. Effect of pH and the mechanism of formaldehyde degradation

The influence of the pH of the solution in the range of 3–8 on the degradation of formaldehyde in the sonophotocatalytic process was investigated. The operational conditions were as follows: initial CH_2O concentration of 20 mg/l, power of ultrasonic waves of 40 W, ZnO dosage of 20 mg/l, and reaction time

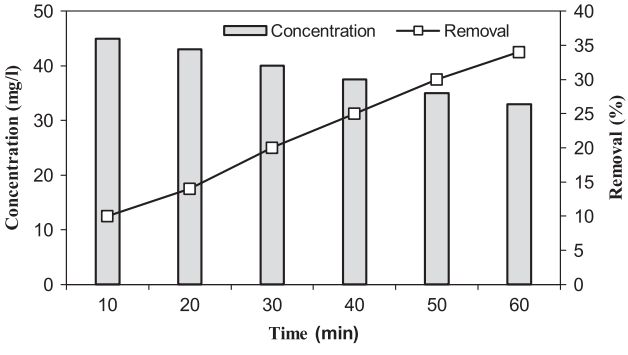

Fig. 4. Effect of ultrasonic wave on formaldehyde degradation (formaldehyde concentration: 50 mg/l and neutral pH of the solution).

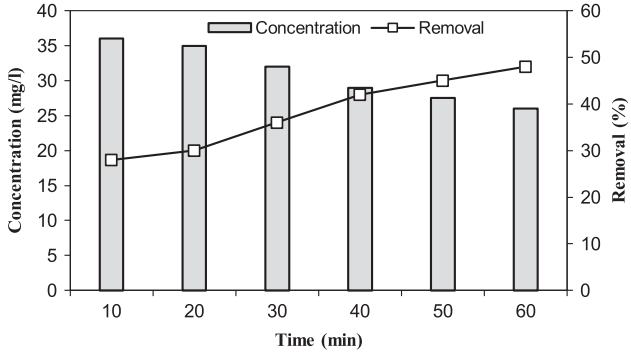

Fig. 5. Effect of ZnO catalyst, UV-C radiation, and ultrasonic wave process on formaldehyde degradation (formaldehyde concentration: 50 mg/l, ZnO dosage: 20 mg/l, and neutral pH of the solution).

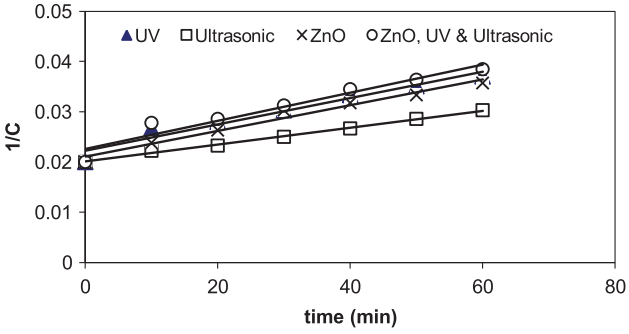

Fig. 6. Kinetic variances of UV-C photolysis, nZnO catalyst, ultrasonic, and enhanced nanophotocatalyst with ultrasonic wave (sonophotocatalytic process).

of 30 min. The results of formaldehyde degradation as a function of the pH of the solution are shown in Fig. 7.

As seen in Fig. 7, formaldehyde degradation increased from 22 to 64% for pH 3 and 8, respectively. It shows that CH_2O degradation increased when the pH of the solution increased. The pH of the solution is one of the most operational parameters which can influence pollutant removal rate by influencing pollutant ionization and surface properties of the system using catalyst. The results may be related to the pH effects on surface properties of ZnO nanoparticles and pollutant properties [25]. On the other hand, the increase in pH can increase the reaction rate, namely a reduction in the particle size of ZnO and the increase in band gap by increasing the pH value. Therefore, ZnO nanoparticle surface area of the powder became more active. Bagheri also found that the performance of electro-Fenton process in alkaline pH could increase formaldehyde degradation rate from industrial wastewater [26].

3.3. Effect of nZnO catalyst dosage and the mechanism of formaldehyde degradation

The influence of ZnO nanoparticle catalyst dosage (range of 10–60 mg/l) on the sonophotocatalytic process was studied. The operational conditions were as follows: initial CH_2O concentration of 20 mg/l, power of ultrasonic waves of 40 W, and optimal pH of 8 that was obtained before stage and a reaction time of 30 min (Fig. 8).

As seen in Fig. 8, the increase in the nanoparticle catalyst amount from 10 to 60 mg/l causes an increase in formaldehyde oxidation efficiency from 49 to 78%. Oxidation mechanisms of ZnO have been described in previous stages. It could be clearly understood that increasing the catalyst amount leads to increasing formaldehyde removal efficiency due to the creation of more surface area and active sites in nanoparticles. As a result, more oxidation agents such as hydroxyl radicals were formed and removal efficiency was increased. In other studies, ZnO catalyst has shown that with increasing photocatalyst dosage, its positive sites became more [27,28]. Lorenz et al. reported that formaldehyde and methanol can reform to CO_2 and H_2O by ZnO catalyst. Moreover, using ZnPd catalysts could increase formaldehyde degradation rate [28].

3.4. Effect of initial CH_2O concentration on formaldehyde degradation

Influence of initial formaldehyde concentrations (20–100 mg/l) on the sonophotocatalytic process was investigated. Operational conditions were as follows: ZnO nanoparticle dosage of 60 mg/l (optimal range that was obtained in Section 3.3), power of ultrasonic waves of 40 W, pH of the solution of 8 (optimal obtained value in Section 3.2), power of ultrasonic

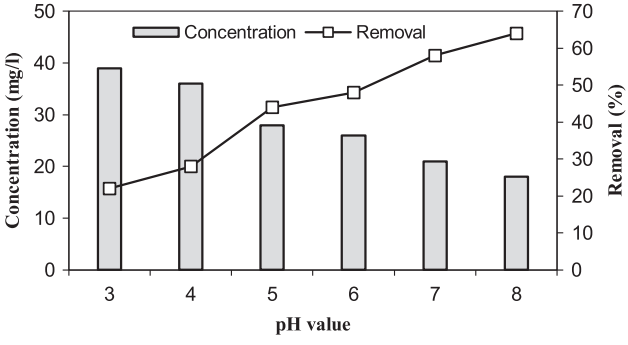

Fig. 7. Effect of pH of the solution on formaldehyde removal efficiency by sonophotocatalytic process (formaldehyde concentration: 50 mg/l, ZnO dosage: 20 mg/l, and contact time: 30 min).

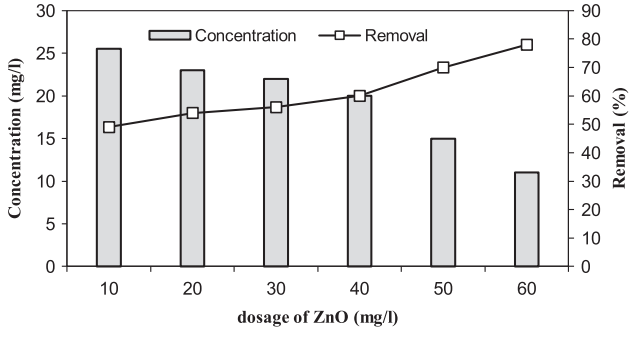

Fig. 8. Effect of ZnO dosage on formaldehyde removal efficiency by sonophotocatalytic process (formaldehyde concentration: 50 mg/l, pH of the solution: 8, and contact time: 30 min).

waves of 40 W, and reaction time of 30 min. The effects of CH_2O variations on formaldehyde degradation rate are plotted in Fig. 9.

It can be seen from Fig. 9 that formaldehyde degradation rate increased from 41.5 to 58% with increasing initial CH_2O concentration from 20 to 80 mg/l, respectively. Upon increasing the formaldehyde concentration to more than 80 mg/l, formaldehyde removal efficiency decreased partially to 56%.

Maximum formaldehyde removal efficiency was 58% (initial CH_2O concentration = 80 mg/l). It could be related to formaldehyde structure since formaldehyde is a hydrophilic and polar compound and at low concentrations, has less access to ZnO catalyst for reforming. Upon increasing CH_2O concentrations, formaldehyde is more soluble in solution and therefore ZnO nanoparticles could reform it better [28]. The fact that formaldehyde removal efficiency decreased to 56% (for >80 mg/l initial concentration) might be explained by active sites of catalyst surface area that completely filled in 80 mg/l formaldehyde concentration and for more initial formaldehyde concentrations, more Zn oxide nanoparticles may be needed.

3.5. Effect of ultrasonic power on formaldehyde degradation

At this stage, the effect of ultrasonic wave power (ranges of 30–150 W) on formaldehyde degradation was evaluated. The operational conditions were as follows: ZnO nanoparticle dosage of 60 mg/l (optimal range that was obtained in Section 3.3), initial concentration of formaldehyde of 80 mg/l (optimal range that was obtained in Section 3.4), and the pH of the solution of 8 (optimal obtained value in Section 3.2) (Fig. 10).

Ultrasonic waves, by cleavage of formaldehyde in the solution through the generation of $OH^{\cdot}$ radical, could be promoting formaldehyde degradation rate. As a result, water and carbon dioxide molecules are produced as follows:

$$CH_2O + 2OH^{\cdot} \rightarrow CO_2 + 2H_2O$$

More $OH^{\cdot}$ radical generation could reform formaldehyde faster. It can be seen from Fig. 10 that the removal efficiency of formaldehyde increased from 40 to 66% as ultrasonic wave power increased from 30 to 100 W. But the degradation rate was constant and partially decreased from 66 to 59% for an ultrasonic wave power of 100–150 W, respectively. This can be explained by the fact that regardless of the amount of dissolved air in the solution degassed during the period of sonication, the amount of hydroxyl radicals generated decreased and consequently, the degradation rate was affected. It could be found that due to increased ultrasonic wave power, dissolved air in the solution degassed faster and $OH^{\cdot}$ radical generation in reduced time decreased. Therefore, in this study, the power of 100 W with a reaction time of 30 min was useful and more effective for formaldehyde degradation. However, Maleki et al. found that the increase in ultrasonic pulse to 8 and power to 85% was more effective for phenol degradation in aqueous solution by ultrasonic wave process [17].

3.6. Effect of reaction time on formaldehyde degradation

The effect of reaction time on formaldehyde degradation was evaluated. The operational conditions were as optimal as those parameters obtained in Sections 3.2–3.5 with a reaction time of 60 min (Fig. 11).

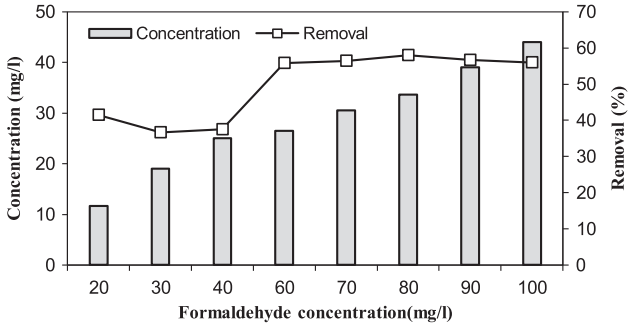

Fig. 9. Effect of initial concentration of formaldehyde on sonophotocatalytic process (ZnO dosage: 60 mg/l, pH of the solution: 8, and contact time: 30 min).

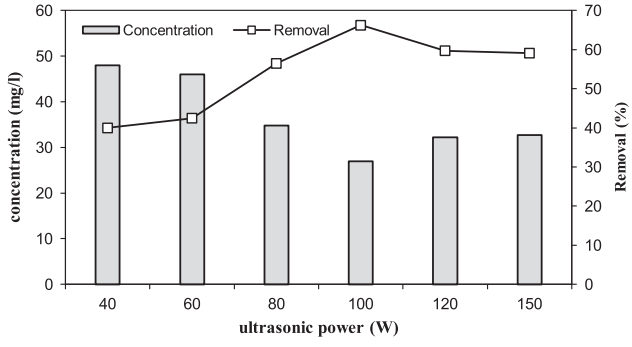

Fig. 10. Effect of ultrasonic wave power on sonophotocatalytic process (formaldehyde concentration: 80 mg/l, ZnO dosage: 60 mg/l, pH of the solution: 8, and contact time: 30 min).

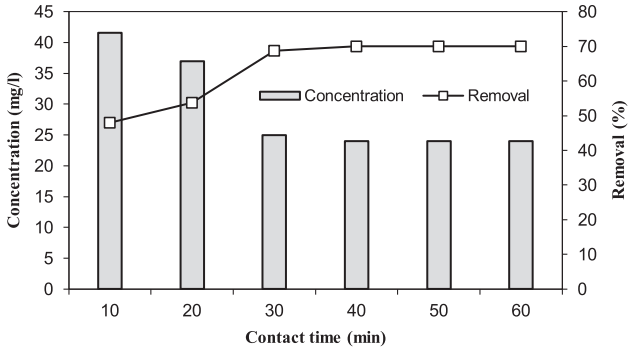

Fig. 11. Effect of contact time on formaldehyde removal efficiency by sonophotocatalytic process (CH_2O concentration: 80 mg/l, ZnO dosage: 60 mg/l, pH of the solution: 8, and ultrasonic intensity: 100 W).

As seen in Fig. 11, increasing the contact time from 10 to 30 min increased formaldehyde degradation efficiency from 48 to 70%, respectively. In reaction time of more than 30 min, CH_2O removal efficiency was constant (70%).

At this stage, the ZnO photocatalyst positive sites' access to pollutants increased and could reform formaldehyde for a longer period of time. Also, a ultrasonic homogenizer produces more $OH^{\cdot}$ radicals that react with formaldehyde and reform it more than before. Gaya also reported that the contact time has an important role in nZnO photocatalytic process so by increasing the reaction time, 4 chlorophenol would be able to degrade faster [29].

Table 3
Equations and results of kinetic calculations

Kinetic model	Equation	Linear form	Constant	Value
Zero-order	$r_c = \frac{dC}{dt} = k_0$	$C - C_0 = -k_0 t$	k_0	1.29
			R^2	0.79
First-order	$r_c = \frac{dC}{dt} = k_1 C$	$\ln \frac{C}{C_0} = -k_1 t$	k_1	0.03
			R^2	0.90
Second-order	$r_c = \frac{dC}{dt} = k_2 C^2$	$\frac{1}{C} - \frac{1}{C_0} = k_2 t$	k_2	0.0007
			R^2	0.95

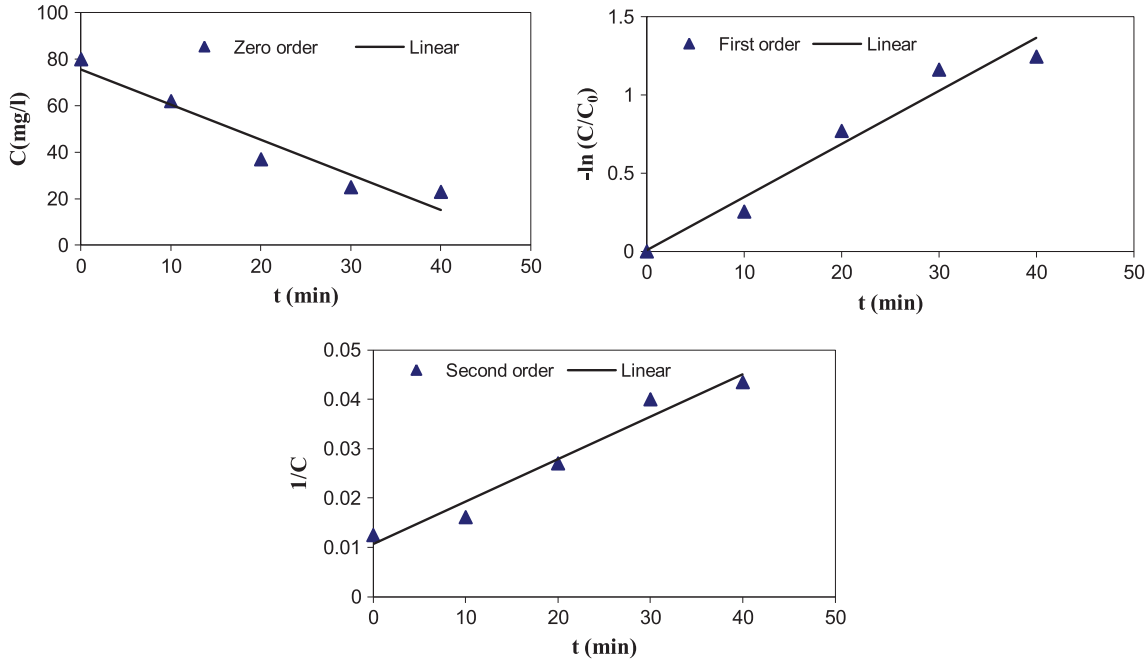

Fig. 12. Kinetic variances of photolysis, nZnO catalyst, ultrasonic wave, and sonophotocatalytic process.

3.7. Kinetic studies of sonophotocatalytic process

To clarify the influence of the sonophotocatalytic process on formaldehyde degradation in aqueous solution, the kinetics of formaldehyde degradation was obtained (Table 3).

As seen in Table 3, the second-order reaction model had a degree of fitness, $R^2 > 0.95$. Also, the kinetics of sonophotocatalytic reactions is shown in Fig. 12.

4. Conclusion

Formaldehyde degradation by an enhanced nZnO photocatalytic process with ultrasonic waves in a low-concentration solution was assayed. The ultrasonic synergism effect, process conditions, and kinetic equations were obtained. The conclusions are as follows:

The UV-C photolysis process could not effectively degrade formaldehyde in aqueous solutions. Also, the application of ultrasonic waves as the process for formaldehyde degradation could slightly degrade low concentrations of CH_2O, but had partially positive effect as synergistic method.

The sonophotocatalytic process was affected by the operational conditions of pH, initial formaldehyde concentration, nZnO catalyst dosage, power rate of ultrasonic waves, and reaction time, which were the main factors investigated in this study. The conditions including initial concentration of CH_2O solution of 50 mg/l, pH 8 of the solution, nZnO photocatalyst dosage of 60 mg/l, 40 W as the power of ultrasonic rate, and reaction time of 30 min were suitable for formaldehyde treatment and the sonophotocatalytic process could degrade around 78% of CH_2O. The oxidations by nZnO photocatalyst and hydroxyl radicals were the main mechanisms for formaldehyde degradation. However, there also was residual CH_2O, in that complete decomposition of residues was difficult. Preferably, increasing nZnO dosage more than 60 mg/l could be effective.

The kinetics of formaldehyde degradation was studied through fitting data from experiments on formaldehyde degradation in the sonophotocatalytic system. The reaction orders were 1.29, 0.03, and 0.0007, respectively. The comparison of reaction orders showed that formaldehyde degradation by the sonophotocatalytic process was in accordance with the pseudo-second-order reaction.

Finally, it could be found that the sonophotocatalytic process is a method for CH_2O degradation in aqueous solution and may be recommended as a supplement with other processes for treatment of solutions containing low formaldehyde concentrations.

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