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Photocatalytic degradation of formaldehyde in aqueous solution using ZnO nanoparticles immobilized on glass plates

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ABSTRACT

In the present study, the application of a photocatalytic process equipped with immobilized ZnO nanoparticles on glass plates was studied for removing formaldehyde in an aqueous phase. According to the obtained data, the removal efficiency of formaldehyde was sharply decreased to 12.96% as the solution experienced strong acidic conditions (pH 2). In addition, the removal efficiency was decreased from 56.41 to 44.02% with increasing pH values from 7 to 10, respectively, indicating a considerable drop in the removal efficiency at basic conditions. As the initial concentration of formaldehyde fed into the reactor was increased from 500 to 4000 mg/L, its removal efficiency decreased from 62.30 to 11.96%, respectively, in a short time of 30 min. The obtained removal efficiency of chemical oxygen demand (41%) demonstrated a considerable mineralization of formaldehyde along with a removal efficiency of 56.41%. The kinetic study was performed and the result indicated a significant reaction rate of the photocatalytic degradation of formaldehyde (k_{app} = 0.0265 1/min), resulting in a removal efficiency of 96.08% by 120 min at an initial formaldehyde concentration of 1000 mg/L. It can be concluded that the photocatalytic process using immobilized ZnO nanoparticles could be an efficient and promising method for treating wastewaters containing formaldehyde.

Keywords: Formaldehyde; Photocatalysis; ZnO nanoparticles; Immobilization; Reaction rate

1. Introduction

The presence of formaldehyde (CH_2O) in aqueous environments can cause severe damages to human health because it has been categorized as a toxic and carcinogen agent based on human studies carried out by the International Agency for Research on Cancer [1,2]. Moreover, formaldehyde has been classified as a "Probable Human Carcinogen" agent according to the USEPA [3]. There are many industries which discharge effluents containing formaldehyde, including synthetic resins, medicines, fertilizers, paints, wood and paper manufacturing, textile processing, fiberboard adhesives manufacturing, and so on [2–6]. Additionally, formaldehyde is one of the major components of anatomy laboratories' wastewaters because of its application as preservative of biological

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pieces against microbial activities [2]. Industrial effluents contain a formaldehyde concentration range between 100 and 10,000 mg/L, indicating the urgent need for treatment prior to discharge into the environment [1]. It is demonstrated that a formaldehyde concentration ranging from 10 to 100 mg/L can be toxic to the microbial community of wastewater treatment plants as a result of the rapid interaction of formaldehyde molecules with DNA and RNA of the microorganisms [3,7]; thus, biodegradation of formaldehyde using biological wastewater treatment technologies is ineffective to achieve a desirable effluent. Various physicochemical techniques have been used to degrade formaldehyde in aqueous solutions, including electrochemical [6,8] and adsorption [2] processes. However, in recent years, the application of advanced oxidation processes (AOPs) has attracted much more attention among environmental researches because of the generation of hydroxyl radical ($OH^{\bullet}$) during AOPs as the most powerful oxidant for decomposition of refractory organic compounds, such as formaldehyde [1]. Among different AOPs, photocatalytic processes have been widely used in recent years due to their high potential to degrade various organic pollutants [9–12]. Compared to TiO_2, which has been most frequently used as photocatalyst in photocatalytic processes, the application of ZnO can be considered as a promising photocatalyst because of its low cost, wide band gap (3.37 eV), and high potential to adsorb UV irradiation with a large exciton binding energy of 60 meV [13–15]. The generation of $OH^{\bullet}$ during a photocatalytic process conducted with ZnO is shown through Eqs. (1) and (2) [16,17]:

$$ZnO + hv \rightarrow ZnO(e^- + h^+) \quad (1)$$

$$h^+ + H_2O \rightarrow H^+ + OH^{\bullet} \quad (2)$$

So far, the application of photocatalytic processes with ZnO as photocatalyst has been considered for the degradation of gaseous formaldehyde [18]. But, to the best of our knowledge, there is no report on the use of ZnO nanoparticles as photocatalysts for the photocatalytic decomposition of formaldehyde in aqueous media. In the present investigation, we used ZnO in nano-size because fine particles possess a higher surface to volume ratio to elevate the density of active sites and electronic structure for the photocatalysis [13]. The toxicity of nanoparticles, such as ZnO, for the aqueous environments has been proven [19]; thus, in the present investigation, ZnO nanoparticles were immobilized on an inert material (glass plate) to avoid releasing nanoparticles into the environment [20,21]. Furthermore, the immobilization of nano-photocatalysts would be beneficial for increasing their photocatalytic activity in comparison with suspended ZnO [22,23]. According to the above-mentioned statements, in the present study, ZnO nanoparticles were immobilized on glass plates for the photocatalytic decomposition of formaldehyde in aqueous phase. In the following, the effect of various operational parameters influencing photocatalytic degradation of formaldehyde was evaluated to reach a better understanding of the efficacy of the process under different operational conditions.

2. Materials and methods

2.1. Immobilization of ZnO nanoparticles on glass plates

ZnO nanoparticles were prepared from US Research Nanomaterials, USA. All chemicals, which were of analytical grade, were purchased from Merck, Germany. But, sodium hydroxide used for functionalizing the surface of glass plates was of industrial grade. To begin the immobilization of ZnO nanoparticles on glass plates, a 3% suspension of ZnO nanoparticles was prepared and thoroughly mixed with a Heidolph magnetic stirrer (Model: MR 3001, Germany) at 300 rpm for 1 h. Then, it was sonicated at 50˚C for 90 min in an ultrasonic bath (Starsonic 18–35, Italy). Before coating, glass plates were immersed in concentrated sodium hydroxide solution for 24 h to reach a suitable coverage of the surface with hydroxyl groups. The functionalization of the surface of glass plates would be effective to avoid detachment of the immobilized ZnO nanoparticles [24]. After pulling out the plates from concentrated sodium hydroxide, they were washed with deionized water and were dried in room temperature. Then, the homogeneous suspension was coated on glass plates (3 cm × 20 cm in size) using a 5-milliliter pipet. After coating, the plates were dried in room temperature for 24 h and then calcined at 450˚C for 3 h in an electric furnace (Exciton Co., Iran). Considering from economical point of view, one layer of catalyst was coated on glass plates. Finally, the glass plates containing immobilized ZnO nanoparticles were placed in the experimental reactor.

2.2. Experimental setup

A bench-scale rectangular experimental reactor was used to carry out the photocatalytic degradation of formaldehyde in aqueous phase (Fig. 1). Three glass plates were placed in reactor in which five 6-W low-pressure UVC lamps with peak intensity at 254 nm (Philips, Holland) were 2 cm above the surface of glass plates. This configuration allows the solution containing formaldehyde to have a larger surface area

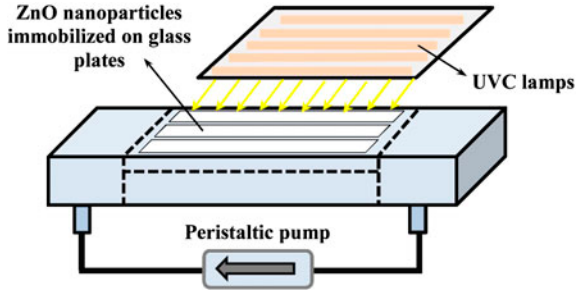

Fig. 1. A schematic flow diagram of bench-scale experimental reactor for the photocatalytic degradation of formaldehyde.

for an efficient photocatalytic reaction. Recirculation of the solution containing formaldehyde was performed via a Heidolph peristaltic pump (Model: 5001, Germany) to keep the solution homogeneous. After each run, the immobilized ZnO nanoparticles were regenerated by recirculating a solution containing a few drops of hydrogen peroxide where UV lamps were turned on. To avoid increasing the temperature and to keep the temperature of the solution at about 25°C during photocatalytic process, the pipes transferring the flow were passed beside the ice packs.

2.3. Analysis

The concentration of formaldehyde in withdrawn samples was measured spectrophotometerically using the Hantzch reagent [25]. To estimate mineralization of the formaldehyde due to the photocatalytic degradation, chemical oxygen demand (COD) of the solution was measured using open reflux method according to the Standard Methods [26]. Structural characteristics of the immobilized ZnO nanoparticles were analyzed via scanning electron microscopy (SEM) with a Philips microscope (Model: XL 30, the Netherlands). The removal efficiency (%) of formaldehyde was calculated through Eq. (3):

$$\text{Removal efficiency } (\%) = [1 - (C/C_0)] \times 100 \quad (3)$$

where C_0 is the initial concentration of formaldehyde and C is the concentration of formaldehyde after reaction in specified exposure time [9].

3. Results and discussion

3.1. Surface morphology of the photocatalyst

Surface morphology of the pure and immobilized ZnO nanoparticles was analyzed through observing the SEM images which is depicted in Fig. 2. Fig. 2(a) shows a uniform size distribution of purchased ZnO nanoparticles, indicating their suitability for application in photocatalytic system as photocatalyst. As it is obvious from Fig. 2(a) and (b), ZnO nanoparticles are composed of spherical-shaped particles with a consistent size. Besides, cross-sectional SEM image of immobilized ZnO nanoparticles on glass plates exhibited an appropriate and homogeneous coverage of ZnO nanoparticles, which could be due to the suitable procedure used for the immobilization of ZnO nanoparticles (Fig. 2(b)). The calcination of the OH-functionalized glass plates containing ZnO nanoparticles results in a reaction between OH groups of the surface of the photocatalyst and OH groups of the support. As shown results, one molecule water of is lost and one remaining oxygen molecule is bridged leading to a strong adherence between the photocatalyst and support [27]. To vigorously evaluate the adherence between the photocatalyst and support, the photocatalytic reactor was filled with deionized water and the absorbance of effluent water was measured at 370 nm after 30 min to determine the presence of ZnO nanoparticles [27,28]. The results demonstrated no absorbance at specified wavelength.

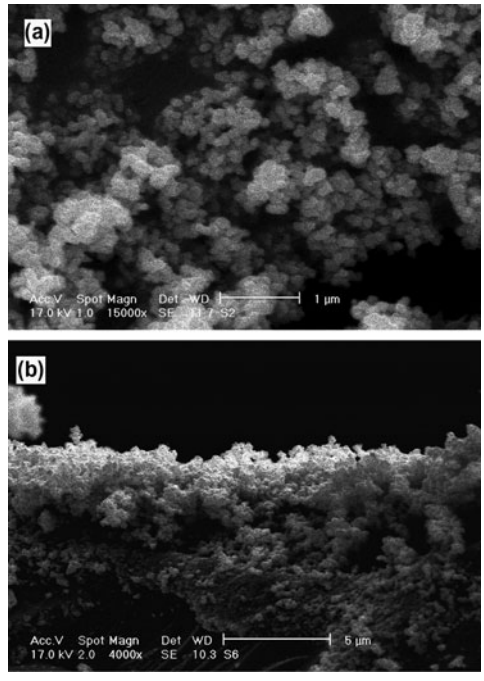

Fig. 2. SEM images of pure ZnO nanoparticles at 15,000× magnification (a) and immobilized ZnO nanoparticles on glass plate taken at 4,000× magnification (b).

3.2. Comparison of different processes involved in the photocatalytic process

Before evaluation of the effect of operational parameters influencing photocatalytic degradation of formaldehyde, the role of adsorption, photolysis, and photocatalytic processes was determined separately to achieve a better understanding of the efficiency of the photocatalytic process alone. Fig. 3 displays the removal efficiency of different processes involved in the photocatalytic process for the removal of an initial formaldehyde concentration of 1,000 mg/L within a short reaction time of 30 min. A little contribution of the adsorption process to the removal of formaldehyde can be observed from Fig. 3. Fig. 3 shows that adsorption of formaldehyde onto the immobilized ZnO nanoparticles can be responsible for only 8.69% of removal efficiency. But, longer reaction time of up to 15 min led to no significant increment in the removal efficiency of formaldehyde via adsorption. The results showed that photolysis process carried out by UV lamps alone can degrade formaldehyde with removal efficiency of 17.50% within 30 min. Comparatively, Kajitvichyanukul and colleagues reported about 1.5% photo-degradation of formaldehyde using a 10-W UV lamp alone with peak intensity at 254 nm [29]. Different reported results may be attributed to the different experimental conditions in various investigations. There should be identical conditions to meaningfully compare the results obtained in various studies. A short reaction time of 30 min was enough for photocatalytic process over immobilized ZnO nanoparticles to degrade 56.41% of formaldehyde in aqueous solution. Shafaei et al. reported that UV light alone is not efficient enough to degrade terephthalic acid, while addition of photocatalyst resulted in acceleration of the photo-degradation [30].

3.3. Effect of initial pH

The pH of the solution plays an important role in the removal of formaldehyde from aqueous solutions [2]. The effect of initial pH was evaluated by varying the initial pH values between 2 and 10. As depicted in Fig. 4, increasing initial pH from 2 to 5 resulted in a rapid increase in the removal efficiency of formaldehyde from 12.96 to 52.17%, respectively, while the increase in initial pH values up to neutral value of 7 caused a little increment in the removal efficiency of formaldehyde (4.24%). As the pH values increased and reached basic conditions, a significant decrease in the removal efficiency of formaldehyde happened. At the pH value of 10, the removal efficiency of formaldehyde decreased to 44.02%. Therefore, an initial pH of 7 was chosen as selective value for the subsequent experiments because of higher removal efficiency of formaldehyde at this value and considering the fact that pH of the wastewater is often about 7. A significant decrease in the removal efficiency at strong acidic conditions has been observed and reported by Araña et al. for the photocatalytic degradation of formaldehyde over TiO_2 as photocatalyst compared to higher pH values of 5 and 7 [1]. The pH

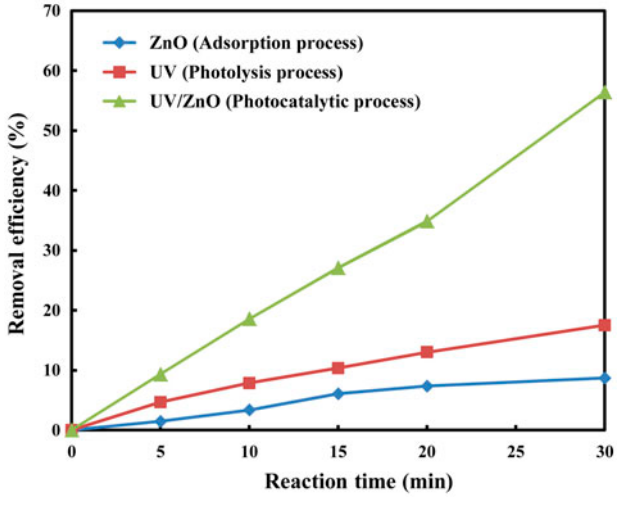

Fig. 3. Removal efficiency of different processes involved in photocatalytic degradation of formaldehyde. Initial formaldehyde concentration = 1,000 mg/L, initial pH 7, reaction time = 30 min.

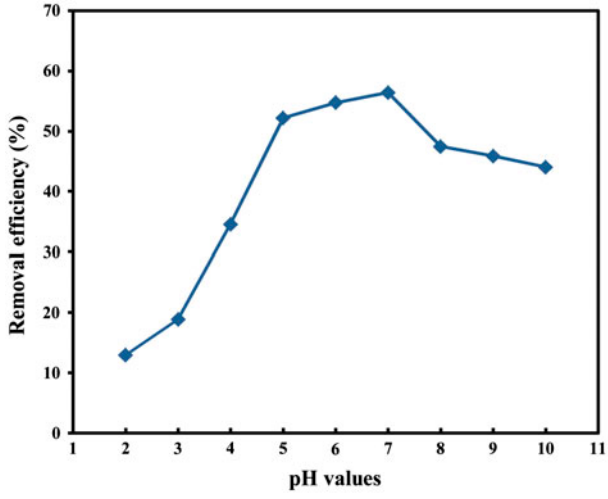

Fig. 4. Variations in the removal efficiency of formaldehyde vs. initial pH values. Initial formaldehyde concentration = 1,000 mg/L and reaction time = 30 min.

of the solution can change the surface charge of the photocatalyst; thus, photocatalytic processes are mostly pH-dependent [9,30]. At acidic pH values, the photocatalysis of formaldehyde was hindered as a result of protonation of the surface of photocatalyst which subsequently caused a significant adsorption of hydroxyl anion (OH^-), preventing the generation of $OH^{\cdot}$. It could be explained by the fact that the zero-point charge of pure ZnO nanoparticles is about 9.0, which lower pH values lead to a positive charge on the surface of ZnO nanoparticles [22]. One of the routes for the generation of $OH^{\cdot}$ during a photocatalytic process is the reaction between hydroxyl anions and the valence band hole of the photo-excited ZnO nanoparticles as shown through Eq. (4) [16]:

$$h^+ + OH^- \rightarrow H^+ + OH^{\cdot} \quad (4)$$

For the generation of $OH^{\cdot}$ through above-mentioned reaction, free hydroxyl anions are required [9] in which there is no free hydroxyl anions to form hydroxyl radicals at acidic pH values. The decrease in photocatalytic degradation of formaldehyde, when the solution experienced basic conditions, may be due to the conversion of formaldehyde to methoxide (CH_3O^-) and formate anions at basic pH values, resulting in a significant decrease in the removal efficiency of formaldehyde [2]. Increasing the pH values up to basic conditions results in the coulomb repulsion between the produced anions and the negative surface charge of the photocatalyst which can restrain an efficient photocatalytic reaction [31], because the photocatalytic reactions mainly occur on the surface of the photocatalyst [32].

3.4. Effect of initial formaldehyde concentration

Initial formaldehyde concentrations of 500, 1,000, 2000, 3,000, and 4,000 were selected to evaluate the efficacy of the photocatalytic process with immobilized ZnO nanoparticles under different formaldehyde concentrations. As shown in Fig. 5, the removal efficiency of formaldehyde declined as the initial concentration of formaldehyde increased. Increasing the formaldehyde concentration from 500 to 1,000 mg/L resulted in a little decrease in the removal efficiency from 62.30 to 56.41%, respectively, while increasing the concentration to 4,000 mg/L led to a removal efficiency of about 12% within a short reaction time of 30 min. This indicated the need for more time to achieve the appropriate removal efficiency of formaldehyde at higher concentrations. The higher the initial formaldehyde concentration, the longer the time needed to reach acceptable removal efficiency [1]. Decreasing removal efficiency with increasing initial concentration may be due to the limited number of active sites for the subsequent generation of hydroxyl radicals to degrade high initial concentrations at specified short reaction time [17]. Additionally, the amount of formaldehyde removed via photocatalytic process is directly corresponding to the probability of the generation of $OH^{\cdot}$ and subsequently the probability of the interaction between $OH^{\cdot}$, and the formaldehyde molecules [33]. Therefore, increasing the initial concentration of the formaldehyde caused an evident decrease in the interaction of $OH^{\cdot}$ with formaldehyde molecules.

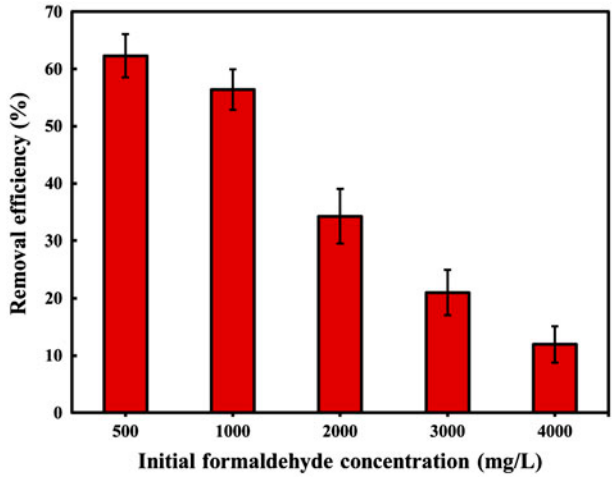

Fig. 5. The effect of initial formaldehyde concentration on its photocatalytic degradation. Reaction time = 30 min and initial pH 7.

3.5. Elimination of COD

The estimation of the COD parameter would be an appropriate approach to estimate the organic strength of the samples, because this test measures the amount of oxygen needed for the conversion of organic compounds, such as formaldehyde, to water and carbon dioxide [4]. Therefore, to evaluate the degree of mineralization of formaldehyde during photocatalytic process, the reduction in COD parameter was measured at an initial formaldehyde concentration of 1,000 mg/L. Fig. 6 shows the removal efficiency of formaldehyde and COD as the photocatalytic process was prolonged for 30 min. Although a removal efficiency of 56.41% was achieved for the photocatalytic removal of formaldehyde during a short reaction time of 30 min, the removal of COD was only about 41% which was slightly lower than the removal efficiency of formaldehyde. This is indicative of an

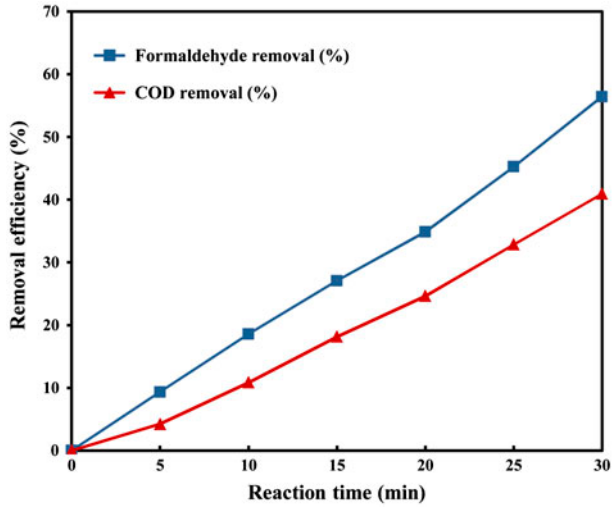

Fig. 6. The efficiency of photocatalytic process for the removal of formaldehyde and COD. Reaction time = 30 min and initial pH 7.

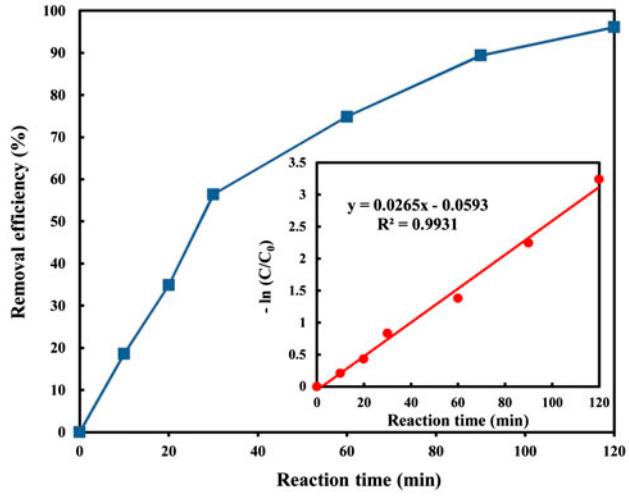

Fig. 7. The effect of exposure time on the photocatalytic degradation of formaldehyde and corresponding kinetic plot. Initial formaldehyde cocentration = 1,000 mg/L and initial pH 7.

acceptable mineralization of formaldehyde within 30 min. This indicates no formation of long-lived byproducts having low reaction rate constants to react with produced OH· [31]. It can be concluded that the formaldehyde molecules can be mainly converted to water and carbon dioxide. The possible reaction between formaldehyde molecules and OH· is shown through Eq. (5) [1]:

$$CH_2O + OH^{\cdot} \rightarrow CO_2 + 3H^+ + 3e^- \quad (5)$$

3.6. Effect of reaction time and kinetic study

A reaction time of 120 min was applied to study the effect of exposure time on the photocatalytic degradation of formaldehyde. Fig. 7 displayed the increase in the removal efficiency of formaldehyde as exposure time was continued to 120 min. As can be observed from Fig. 7, an increment in reaction time to 30 min resulted in a significant removal efficiency of about 56%, while a threefold increase in reaction time caused a 40% increment in the removal efficiency of formaldehyde. Obviously, increasing the removal efficiency of formaldehyde with increasing reaction time could be attributed to more OH· generated as the process was continued to prolong [34]. Farzadkia et al. in their study, demonstrated that photocatalytic removal of metronidazole and COD over ZnO nanoparticles has a direct correlation with irradiation time [35]. To assess the rate of the photocatalytic degradation of formaldehyde, the linearized pseudo-first-order kinetic model was used according to Eq. (6):

$$\ln(C/C_0) = -k_{app}t \quad (6)$$

where C (mg/L) is the concentration of formaldehyde at time t. A straight line of $-\ln(C/C_0)$ vs. t indicates the suitability of the model for describing photocatalytic formaldehyde removal. The slope of the line is the apparent rate constant (k_{app}) as 1/mim [15]. The result of kinetic study is shown through a smaller figure which is depicted on Fig. 7. The obtained correlation coefficient (R^2 = 0.9931) for the pseudo-first-order kinetic model indicated the suitability of the model for predicting the rate of photocatalytic degradation of formaldehyde. Moreover, the slope of the equation (k_{app}) was found to be 0.0265 1/min. This indicated the relatively high rate of photocatalytic degradation of formaldehyde. In another study on the degradation of formaldehyde carried out by Kajitvichyanukul and coworkers, the rate constants of Fenton and photo-Fenton processes were obtained as0.0114 and 0.0145 1/min, respectively [29]. Even the reaction rate of the photocatalytic degradation of formaldehyde obtained in the present study was higher than the reaction rate of the photocatalytic degradation of other refractory compounds. For instance, El-Kemary et al. reported a reaction rate constant of about 0.0048 1/min for the photocatalytic degradation of ciprofloxacin drug in water using ZnO nanoparticles at an initial pH of 7 [9], and Fu et al. reported a reaction rate of 0.0083 1/min for the photocatalytic degradation of methyl orange dye when they used ZnO nanoparticles [15].

4. Conclusions

The efficacy of the photocatalytic process using immobilized ZnO nanoparticles on glass plates was evaluated to degrade formaldehyde in an aqueous medium. The results showed lower photocatalytic degradation of formaldehyde at strong acidic and basic conditions. Increasing the initial formaldehyde concentration resulted in a sharp decrease in the removal efficiency, especially at higher concentrations. Mineralization of the formaldehyde was evaluated by measuring COD, so that the results indicated an acceptable reduction in COD (41%) within a short reaction time of 30 min. A reaction rate of 0.0265 l/min was found for the photocatalytic removal of formaldehyde, which was comparatively significant. Conclusively, the results of the present study demonstrated high potential of the photocatalytic process over immobilized ZnO nanoparticles for removing and also degrading formaldehyde in wastewaters with suitable mineralization as the process proceeded.

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