Photocatalysis of formaldehyde in the aqueous phase over ZnO/diatomite nanocomposite

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Abstract: In the present study, ZnO nanostructures were synthesized and immobilized on the surface of diatomite via a simple sonochemical method for the photocatalytic degradation of formaldehyde in the aqueous phase. The characterization of as-prepared ZnO/diatomite nanocomposite was carried out by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). The photocatalysis of formaldehyde was favored at neutral pH. At a ZnO to diatomite ratio of 0.3, increasing the photocatalyst dosage from 0.2 to 1.5 g/L resulted in increasing the photocatalytic removal of formaldehyde from 37.51% to 88.05%. At a formaldehyde concentration of 100 mg/L, the complete removal of formaldehyde was attained within the reaction time of 50 min. A mineralization efficiency of 53% was achieved, thereby confirming a suitable mineralization of formaldehyde within the short reaction time of 60 min.

Key words: Formaldehyde, immobilization, nanocatalyst, photocatalysis, ZnO nanostructures

1. Introduction

Discharging industrial effluents containing hazardous compounds can pollute receiving waters such as rivers and lakes. Formaldehyde is one of the most toxic refractory organic compounds and is widely used in chemical industries and anatomy laboratories. Thus, its discharge into the aqueous environment can cause serious environmental and sanitary impacts.1−3 The carcinogenic effect of formaldehyde has been demonstrated by the International Agency for Research on Cancer (IARC). It is also the most toxic organic substance of 45 organic compounds causing environmental problems.2 There are various industries discharging effluents with formaldehyde concentrations ranging from 100 to 10,000 mg/L, indicating an urgent need for the treatment of such effluents before discharge into the environment.1 One of the promising alternatives for the degradation of refractory organic compounds such as formaldehyde is the application of advanced oxidation processes (AOPs). Among the various AOPs, the application of photocatalytic processes has gained much more attention due to their high potential to degrade toxic organic compounds.4,5 The photocatalysis of gaseous formaldehyde has been studied by many researchers,6−9 but little attention has been paid to the photocatalysis of this organic

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pollutant from the aqueous phase. Among various photocatalysts, ZnO, in nanosize, has been considered an efficient and cost-effective photocatalyst because of its large volume to area ratio, wide band gap (3.37 eV), high potential to absorb UV light irradiation, and low cost.\textsuperscript{10,11} Generally, photocatalysts with smaller particle size possess higher photocatalytic activity. However, it is demonstrated that using suspended nanoparticles leads to the aggregation and inactivation of nanophotocatalysts in the aqueous phase, causing a significant decrease in photocatalytic activity. The difficult separation also limits the application of suspended nanophotocatalysts for the treatment process.\textsuperscript{12,13} Moreover, discharging nanoparticles into the environment must be limited due to their toxic effects on the aquatic and terrestrial environments.\textsuperscript{14} Therefore, suspended ZnO nanoparticles should be immobilized on a suitable support before application as photocatalyst. Different supports have been used for the immobilization of nanosized photocatalysts such as glass plates,\textsuperscript{14,15} ceramic sheets,\textsuperscript{16} and clay-like materials.\textsuperscript{12,17,18} Considering the economical point of view, in the present study, Iranian diatomite was applied as a promising clay-like support for the immobilization of ZnO nanostructures. Diatomite is a sedimentary rock of microfossils of aquatic plants, especially single-celled algae, that is mainly composed of SiO\textsubscript{2}. It is used in many industries as insulation material, filter aid, surface cleaning material, abrasive agent, adsorbent, catalyst support, and silica source in chemical industries. Furthermore, diatomite has high surface area, creating a suitable structure for the immobilization of nanosized photocatalysts.\textsuperscript{19–21} To the best of our knowledge, there is no report on the use of ZnO-coated diatomite for the photocatalysis of formaldehyde in aqueous solutions. Thus, in the present study, ZnO nanostructures were synthesized and immobilized on the surface of diatomite through a simple sonochemical method for the photocatalysis of formaldehyde. After the characterization of as-prepared photocatalyst, the effects of various operational parameters on the photocatalysis of formaldehyde were evaluated. In the following, reusability and mineralization tests were carried out.

2. Results and discussion

2.1. Structural characteristics

Figure 1a shows the scanning electron microscopy (SEM) image of pure diatomite. As shown, diatomite particles have nonuniform size distribution. The porous and rough structure of diatomite particles could be beneficial for the efficient immobilization of ZnO nanostructures. Figure 1b exhibits the morphological structure of ZnO/diatomite nanocomposite. Figure 1b also shows that the immobilization of ZnO nanostructures on the diatomite surface is accomplished well. The stability of immobilized catalyst is of great importance. In fact, the immobilization procedure applied in the present study results in the strong attachment of ZnO to the surface of each siliceous support such as diatomite. According to our previous studies, the release of Zn into the solution after the reaction was not significant due to the useful approach applied for the immobilization of ZnO.\textsuperscript{22,23} XRD analysis was performed to show the crystallite structure of as-prepared ZnO/diatomite nanocomposite. Figure 2 displays the XRD pattern of ZnO/diatomite nanocomposite, together with the XRD pattern of pure diatomite. The XRD pattern of ZnO/diatomite nanocomposite contains peaks of both ZnO and diatomite. Two peaks located at 2\(\theta\) of 21.8° and 26.7° indicated the presence of a crystallite silica structure, which is in accordance with the major peaks of a pure phase of silica in the JCPDS Card no. 00-001-0647.\textsuperscript{24} According to JCPDS Card no. 36-1451, the main peaks of pure ZnO are located at 2\(\theta\) of 32.0°, 34.6°, 36.3°, 47.6°, 56.7°, 62.9°, 66.3°, and 68.0°, corresponding to the (100), (002), (101), (102), (110), (103), (200), and (112) planes of hexagonal wurtzite ZnO, respectively.\textsuperscript{25–27} These main peaks were shifted to 33.0°, 33.8°, 38.0°, 44.8°, 54.0°, 58.6°, 59.8°, and 68.9° in the XRD pattern of ZnO/diatomite nanocomposite. These shifts are significant to confirm the formation of a ZnO pillar in the interlayer space of the diatomite. In addition, the peaks with
high intensity reflect the formation of highly crystallite ZnO nanostructures at a high content incorporated into the diatomite lattice.\textsuperscript{17} The Debye–Scherrer formula was utilized to estimate the crystallite size of as-prepared samples.\textsuperscript{28} Accordingly, the average crystallite size of ZnO nanostructures in immobilized form was calculated to be 43 nm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{SEM_images.png}
\caption{SEM images of pure diatomite (a) and ZnO-coated diatomite (b).}
\end{figure}

Functional groups placed on the photocatalyst surface play an important role in photocatalysis because of the fact that photocatalytic processes take place on the photocatalyst surface. In addition, functional groups can be involved in the immobilization of ZnO nanostructures on the diatomite surface. FT-IR spectra of pure ZnO, pure diatomite, and ZnO/diatomite nanocomposite were recorded in the range between 400 and 4000 cm\textsuperscript{-1} (Figure 3). As shown in Figure 3, a broad peak centered at 3400 cm\textsuperscript{-1} is associated with the stretching

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{XRD_pattern.png}
\caption{XRD pattern of ZnO/diatomite nanocomposite.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{FT-IR_spectra.png}
\caption{FT-IR spectra of pure ZnO, pure diatomite, and ZnO/diatomite nanocomposite.}
\end{figure}
vibrations of the \(-\text{OH}\) groups and free silanol group (\(\text{Si-OH}\)) on the diatomite surface.\textsuperscript{20,29,30} This peak was shifted from 3400 to 3520 cm\(^{-1}\) after the immobilization of ZnO nanostructures. In addition, hydroxyl groups of the catalyst surface react with the photogenerated valence band holes (\(h^+\)) and subsequently the adsorbed water on the catalyst surface to generate hydroxyl radicals.\textsuperscript{14} The peaks located at 1650, 1110, 810, and 480 cm\(^{-1}\) were attributed to the presence of the (\(\text{H-O-H}\)) bending vibration of water retained in the silica matrix, asymmetric stretching modes of the Si–O–Si bond, Si–O stretching of the silanol group, and Si–O–Si bending vibration of the diatomite structure, respectively.\textsuperscript{31–34} The intensity of these peaks decreased after the incorporation of ZnO nanostructures into the diatomite lattice. The results of FT-IR analysis confirmed the important role of functional groups in the immobilization of ZnO nanostructures on the diatomite surface.

2.2. Comparative study

A comparative study was performed before conducting the experiments to specify the role of each process involved in the photocatalysis of formaldehyde. As depicted in Figure 4, the adsorption of formaldehyde onto pure ZnO, pure diatomite, and ZnO/diatomite nanocomposite resulted in formaldehyde removal of 15.67%, 27.47%, and 30.21%, respectively. Furthermore, in order to reach the adsorption–desorption equilibrium, the reactor was placed in the dark for 30 min prior to the experiments. Although ZnO/diatomite nanocomposite can adsorb some formaldehyde molecules (Figure 4), most of them will desorb. They will be released into the bulk solution to be more effectively degraded by OH\(^-\), as well as the photocatalysis of formaldehyde molecules adsorbed on the photocatalyst surface via hole oxidation.\textsuperscript{22} Both visible and UV light (photolysis processes) could not significantly remove formaldehyde from the aqueous solution. The visible light and UV light reduced the formaldehyde by 9.11% and 33.95%, respectively. However, visible light/ZnO and UV light/ZnO processes were responsible for formaldehyde removal of 19.22% and 71.87%, respectively. Overall, the photocatalysis of formaldehyde over UV light-induced photocatalyst was efficient in removing formaldehyde compared with photolysis alone. A similar result was reported by Méndez et al. in their study on the detoxification of formaldehyde in aquatic environments.\textsuperscript{35} The oxidation of water and hydroxyl groups on the photocatalyst surface produces OH\(^-\), resulting in the degradation of formaldehyde to form CO\(_2\) and H\(_2\)O as shown in Eqs. (1)–(5):

\[
\begin{align*}
\text{ZnO-diatomite} + h\nu &\rightarrow e^- + h^+ \quad (1) \\
h^+ + \text{OH}^- &\rightarrow \text{OH}^- \quad (2) \\
h^+ + \text{H}_2\text{O} (\text{ads}) &\rightarrow \text{H}^+ + \text{OH}^- \quad (3) \\
\text{CH}_2\text{O} + \text{OH}^- &\rightarrow \text{HCO}_2^- + 2\text{H}^+ \quad (4) \\
\text{HCO}_2^- + \text{OH}^- &\rightarrow \text{H}_2\text{O} + \text{CO}_2 \quad (5)
\end{align*}
\]

The immobilized form of ZnO nanostructures was irradiated with UV light and caused formaldehyde removal of about 80% at an initial formaldehyde concentration of 500 mg/L within a reaction time of 60 min. In accordance with our results, Seftel et al. found that TiO\(_2\)/LDH clay nanocomposite had photocatalytic activity higher than that of pure TiO\(_2\), due to the increased adsorption of the target organic pollutant.\textsuperscript{18} Additionally, it is demonstrated that the immobilization of photocatalyst on the diatomite surface improves the charge, optical properties, and mass transfer efficiency during photocatalysis.\textsuperscript{13,36}
2.3. The effect of ZnO to diatomite ratio
To evaluate the effect of ZnO to diatomite ratio on the photocatalysis of formaldehyde, this ratio was varied between 0.1 and 1.0. As shown in Figure 5, increasing the ZnO to diatomite ratio from 0.1 to 0.7 resulted in increasing the removal efficiency of formaldehyde from 67.35% to 90.06%, respectively. However, increasing the ratio to 1.0 led to a small decrease in removal efficiency (83.56%). In accordance with our results, Saleh et al.\textsuperscript{37} reported that increasing the photocatalyst to support ratio up to a specified value could cause a significant drop in the photocatalytic degradation of the target pollutant. The excessive amount of photocatalyst immobilized on the diatomite results in the accumulation and aggregation of nanostructures. The aggregation of photocatalyst decreases the interfacial area between the bulk solution and the photocatalyst, which reduces the number of active sites on the photocatalyst surface. Moreover, the excess amount of photocatalyst can mask some parts of the photosensitive surface and deactivate the activated molecules caused by the collision with the ground state of the photocatalyst.\textsuperscript{13,38} The application of photocatalyst at optimum amount leads to a better distribution of nanostructures and improved light adsorptive behavior of the photocatalyst, which is helpful for better exciting the photocatalyst to produce OH\textsuperscript{·}.\textsuperscript{11,39,40} Overall, it can be deduced that an optimum ZnO to diatomite ratio is necessary for enhancing formaldehyde removal and avoiding the use of excess photocatalyst.

![Figure 4](image1.png)  
**Figure 4.** Contribution of each process involved in the photocatalytic degradation of formaldehyde (formaldehyde concentration = 500 mg/L, photocatalyst dosage = 1 g/L, ZnO to diatomite ratio = 0.3, and initial pH = 7).

![Figure 5](image2.png)  
**Figure 5.** The effect of photocatalyst to support ratio on the photocatalytic degradation of formaldehyde (formaldehyde concentration = 500 mg/L, photocatalyst dosage = 1 g/L, and initial pH = 7).

2.4. The effect of initial pH
Figure 6 displays the effect of initial pH on the photocatalytic degradation of formaldehyde in the pH range between 3 and 11. As can be observed, both acidic and basic conditions are unfavorable for the photocatalysis of formaldehyde over ZnO/diatomite nanocomposite. Decreasing the initial pH from neutral value of 7 to 3 and 11 resulted in decreasing the removal efficiency from the optimum value of 80.07% to 23.45% and 50.79%, respectively. At basic pH values, formaldehyde is converted to methoxide (\(\text{CH}_3\text{O}^-\)) and formate anions,\textsuperscript{41} leading to electrostatic repulsion between the produced anions and the negative surface charge of the photocatalyst (the zero point charge of pure ZnO nanostructures is about 9.0). This can restrain the efficient photocatalytic reaction on the photocatalyst surface.\textsuperscript{1}
2.5. The effect of photocatalyst dosage

In order to avoid the application of excess photocatalyst, it is essential to find out the optimum photocatalyst dosage for efficient photocatalysis. The effect of photocatalyst dosage on the photocatalysis of formaldehyde was investigated (Figure 7). As illustrated in Figure 7, a high amount of catalyst enhanced the photocatalysis of formaldehyde over ZnO/diatomite nanocomposite. With increasing photocatalyst dosage from 0.2 to 1.5 g/L, the photocatalytic removal of formaldehyde increased from 37.51% to 88.05%, respectively. This can be as a result of enhanced absorption of photons and subsequently increased photogeneration of OH·. However, increasing the photocatalyst dosage beyond 1.0 g/L did not influence the photocatalysis of formaldehyde. A further increase in the photocatalyst dosage can cause the screening effect. Moreover, the aggregation of nanostructures may also decrease the photocatalytic activity at high loadings of the photocatalyst. Therefore, a photocatalyst dosage of 1 g/L was chosen as the selective value for performing the rest of the experiments.

![Figure 6](image1.png) ![Figure 7](image2.png)

**Figure 6.** The effect of initial pH on the photocatalytic degradation of formaldehyde (formaldehyde concentration = 500 mg/L, photocatalyst dosage = 1 g/L, and ZnO to diatomite ratio = 0.3).

**Figure 7.** The effect of photocatalyst dosage on the photocatalytic degradation of formaldehyde (formaldehyde concentration = 500 mg/L, ZnO to diatomite ratio = 0.3, and initial pH = 7).

2.6. The effect of initial formaldehyde concentration

Obviously, the effect of initial pollutant concentration can be one of the most important parameters in the treatment of various organic and inorganic pollutants. For this reason, the effect of the initial formaldehyde concentration was assessed in the range of 100–2000 mg/L, where the other operational parameters were constant. The result of this set of experiments showed that increasing the initial formaldehyde concentration from 100 to 2000 mg/L led to a significant drop in the photocatalysis of formaldehyde (Figure 8). At formaldehyde concentration of 100 mg/L, the complete removal of formaldehyde was achieved within the reaction time of 50 min, while the removal efficiency of formaldehyde was insignificant (19.82%) at an initial concentration of 2000 mg/L. The higher the initial formaldehyde concentration, the longer the time needed for its photocatalysis. Moreover, at high pollutant concentrations, photonic efficiency decreases and the photocatalyst surface becomes saturated, resulting in photocatalyst deactivation.
2.7. Mineralization

The success of each advanced oxidation process in the degradation of target organic pollutants depends on the rate of mineralization. To assess the mineralization of formaldehyde during photocatalysis, COD analysis was performed and its removal was compared with the removal efficiency of formaldehyde. Figure 9 reveals a mineralization efficiency of 53.12% within the reaction time of 60 min. The possible reaction between the photogenerated hydroxyl radical and formaldehyde is depicted by Eq. (6):

\[ CH_2O + OH^- \rightarrow 3H^+ + 3e^- + CO_2 \]  

Comparatively, Guimarães et al. reported a mineralization efficiency of 46% in the case of the application of the UV/H\textsubscript{2}O\textsubscript{2} process for the degradation of 400 mg formaldehyde/L,\textsuperscript{2} and Kajitvichyanukul et al. found that the complete mineralization of formaldehyde in the effluent after a reaction time of 240 min.\textsuperscript{43} In addition, the linearized pseudo-first-order kinetic model was applied in order to evaluate the reaction rate constant of the photocatalysis of formaldehyde over ZnO/diatomite nanocomposite (Figure 9). As can be observed in Figure 9, a relatively straight line of \(-\ln(C/C_0)\) versus reaction time was obtained \((R^2 = 0.961)\), which indicated the suitability of the applied model for predicting the rate of photocatalytic removal of formaldehyde. According to the obtained regression line and its slope, the reaction rate constant of the photocatalysis of formaldehyde was 0.0122 1/min. The reaction rate constant obtained in our previous study regarding the photocatalysis of formaldehyde over commercial ZnO nanoparticles immobilized onto glass plates was higher than that of obtained in the present work (0.0265 1/min). It could be due to the lower particle size of commercial ZnO nanoparticles, creating more reaction sites for the photocatalysis of formaldehyde.
3. Materials and methods

3.1. Photocatalyst preparation

All chemicals, which were of analytical grade, were purchased from Merck, Germany. In a typical manner, the ZnO to diatomite mass ratio was set to 0.3. ZnO/diatomite nanocomposite was prepared as follows: 10 mM ZnCl$_2$ was prepared in 50 mL of deionized water. Afterwards, 1 M NaOH solution was added dropwise to the above solution under magnetic stirring until the pH reached 10. After the formation of precipitate, 2.724 g of the diatomite was slowly added to the resulting precipitate under magnetic stirring. The mixture was sonicated in an ultrasonic bath (Elmasonic E30H, Elma-Hans Schmidbauer GmbH & Co.KG, Germany) at 50 °C for 120 min to achieve homogeneity of ZnO nanostructures. The suspension was filtered and washed with deionized water and ethanol repeatedly to obtain a salt-free sample. Finally, the solid sample phase was dried in an oven at 80 °C for 48 h.

3.2. Experimental procedure and analysis

To carry out the experiments, a quartz-made batch flow mode cylindrical reactor equipped with four 6-W low-pressure UVC lamps with peak intensity at 254 nm (Philips, the Netherlands) was used (working volume of 700 mL). The visible light source was four 6-W visible lamps with peak intensity at 544 nm. Working solutions of formaldehyde were prepared by the dilution of stock solution (1000 mg/L). A magnetic stirrer was applied to mix as-prepared photocatalyst and formaldehyde molecules in the bulk solution. The residual concentration of formaldehyde was measured spectrophotometrically by Nash’s method. The mineralization of formaldehyde during the photocatalysis was determined by means of chemical oxygen demand (COD) according to the standard methods for the examination of water and wastewater. The surface morphology of the samples was analyzed via a scanning electron microscope (TESCAN, Mira3, Czech Republic). X-ray diffraction (XRD) patterns of pure ZnO nanostructures, pure diatomite, and ZnO/diatomite nanocomposite were taken via a PANalytical diffractometer (Model: X’Pert Pro MPD, the Netherlands) at current intensity = 30 mA, voltage = 40 kV, λ = 1.54056 Å, step size = 0.026°/s, measurement temperature = 25 °C, and scanning angle = 10–80°. Fourier transform infrared (FT-IR) analysis was conducted on KBr pellets to show the role of functional groups in the immobilization of ZnO nanostructures (Tensor 27, Bruker, Germany) at wavenumbers ranging from 400 to 4000 cm$^{-1}$.

4. Conclusions

ZnO-loaded diatomite irradiated by UV light lamps was applied for the photocatalysis of formaldehyde in the aqueous phase. As a result, the adsorption and photolysis processes did not remove formaldehyde from the solution reasonably well. The immobilization of ZnO nanostructures improved the removal efficiency of formaldehyde. Increasing the photocatalyst dosage and decreasing the initial dye concentrations enhanced the photocatalysis. Efficient COD removal was attained by applying the reaction time of 1 h for an initial formaldehyde concentration of 500 mg/L. It could be concluded that ZnO/diatomite nanocomposite can be efficiently used for the photocatalysis of formaldehyde in the aqueous environment.

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