Research Article

Degradation of High Level m-Cresol by Zinc Oxide as Photocatalyst

In this study, the high concentration of m-cresol as a sample of organic pollutants was degraded in the presence of zinc oxide and UV irradiation during 6 h at laboratory scales. The amount of photocatalyst, pH and m-cresol concentration were considered as effective factors on the photodegradation. The demineralization of m-cresol was measured by UV–Vis spectrophotometry while the total organic carbon-analyzer was used to determine the mineralization. The ultrahigh performance LC was used to identify probable intermediates. The results showed optimum condition at pH 7–9, which is the natural pH of industrial wastewater. Moreover, 100% of m-cresol was removed after 5 h of irradiation time, which is quite significant. The detected intermediates were 3,5-hydroxytoluene, 2,5-hydroxy-benzaldehyde, and 3-hydroxy-benzaldehyde after 3 h of reaction time. Reusability of the photocatalyst showed insignificant reduction in the photo-catalytic performance. In conclusion, this investigation indicated high potential of zinc oxide suspension to remove high level concentration of m-cresol under UV irradiation.

Keywords: Advanced oxidation process; Demineralization; Photochemistry; Photodegradation; Wastewater treatment

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1 Introduction

According to the United Nations World Water Development Report 2012, up to 90% of untreated wastewater is flowing into rivers, lakes and highly productive coastal zones. The hazardous wastewater contains high concentration of phenolic compounds, which must be prevented of entering into the environment [1]. The global attention has been focused on the removal of the compounds from the wastewater using several methods, including biological oxidation systems, electrochemical and adsorption methods [2–6]. The methods are limited by a few drawbacks; the drawback of the biological method is the longer retention time, usually measured in days, to oxidize the organic compounds, the adsorption method cannot mineralize the pollutants and the electrochemical method generates the new toxic intermediates [7–10]. On the other hand, advanced oxidation processes (AOPs) mineralize the organics to harmless final products using stable and non-toxic photocatalysts, suitable reaction time, appropriate irradiation wavelength at ordinary temperature and atmospheric pressure [11–13]. The mineralization is carried out on the photocatalyst surface by hydroxyl radicals (·OH) that are powerful and non-selective to oxide pollutants and probable intermediates [14, 15]. The process of the radicals’ generation starts when the valence band electrons are excited to the empty conduction band of the photocatalyst by an appropriate irradiation as the source of the energy. The excited electrons are trapped by adsorbed oxygen molecules over the suspension photocatalyst to produce O$_2^-$ species. The species are converted to hydroxyl radicals by further oxidation [16, 17]. The AOPs usually use TiO$_2$ and ZnO as photocatalysts to degrade the organics to CO$_2$ and H$_2$O that are environmental friendly products [15, 18–20]. However, the inexpensive ZnO photodegrades a broad range of organic compounds in acidic and basic medium as an excellent alternative for TiO$_2$ [21–24]. To the best of our knowledge, AOPs have never degraded m-cresol, one of the phenolic compounds, by ZnO under UV irradiation. In developing countries, m-cresol is extensively used in manufacturing products including cresol-based herbicides, pharmaceuticals, petrochemicals, and surfactants [25–27]. The wastewater of the industries contains a huge amount of m-cresol which easily penetrates into groundwater because its water solubility is very high, 24.4 g L$^{-1}$ at 25°C [28]. On the other hand, m-cresol was classified as persistent, priority, toxic chemical in 1970s because its quantitative structure–activity relationship shows chronic effects at 12 g L$^{-1}$ [29]. Therefore, m-cresol with LC50 could be a significant threat to groundwater and must be controlled as near as possible where they are generated. Obviously, at those places, the concentration of the pollutant is very high therefore an effective method is necessary to remove the m-cresol. In our previous work, m-cresol was removed by ZnO suspension under visible-light irradiation [27]. Despite the fact that utilizing visible-light as a solar energy is quite convenient, there are two drawbacks which must be considered for high concentration contaminant solutions. The first one to mention here is that the removal of m-cresol amount was merely 25 mg L$^{-1}$ in 360 min irradiation time, which is considered to
be insignificant. The second drawback is that it does not mineralize all the organics. In addition, the result of the photodegradation using the modified ZnO was not significant for this level of m-cresol concentration [28]. We, therefore, aimed to investigate the photocatalytic destruction of m-cresol by ZnO under UV irradiation with the expectation of a better mineralization process at laboratory scale. Therefore, the photocatalyst amount, pH and m-cresol concentration were studied as effective factors on the photodegradation. However, this work focused on the degradation of high m-cresol concentrations, 50–250 mg L\(^{-1}\). The demineralization of m-cresol was measured by UV-Vis spectrophotometry. The mineralization was determined by measuring total organic carbon (TOC), which was carried out by TOC-analyzer. The ultrahigh performance LC (UHPLC) was used to identify the probable photoproducts.

### 2 Materials and methods

The required chemicals were m-cresol (98%, ASSAY), ZnO (99%), NaOH (99%), and H\(_2\)SO\(_4\) (95–97%), which were obtained from Merck. The ZnO was characterized to measure surface area, 3.3 m\(^2\) g\(^{-1}\), particles size, 0.4–0.5 \(\mu\)m, and band gap 3.02 eV. The used external standards for UPLC were 4-hydroxyl-benzaldehyde (Merck, 98%), 3-hydroxy-benzaldehyde (Merck, 98%), 2-methylresorcinol (Acros, 98%), 2,3-dihydroxy-benzaldehyde (Merck, powder), salicylaldehyde (Acros, 98%), 3,5-dihydroxy-toluene (Merck, powder), 1,4-benzoquinone (Acros, 99%), phenol (99.5%), hydroquinone (Merck, 98%), and methyl-4-hydroxybenzoate (Merck, 98%), acetonitrile (HPLC grade, J. T. Baker). The materials were used, as in our previous work, without further purification [27]. The performance was carried out by various concentrations of m-cresol solution and appropriate ZnO, prepared by de-ionized water. The photodegradation was conducted in a batch photoreactor and was magnetically stirred at 200 rpm [15, 24]. The suspended solution was irradiated in the photoreactor by a 6 W UVA lamp. To determine the residual of m-cresol concentration, the samples were withdrawn from the solution and then filtered through 0.45 \(\mu\)m PTFE membranes [27]. The remaining concentration in filtered solution was detected by UV-Vis spectrophotometry (Shimadzu-UV-1650pc) at maximum wavelength 272 nm. TOC and total inorganic carbon (TIC) were measured by TOC-VCSN analyzer instrument. The used UHPLC was fitted with an ACQUITY BEH phenyl C18 column (10 cm \(\times\) 2.1 mm \(\times\) 1.7 \(\mu\)m) and the detector wavelength was 277 nm. The gradient elution method was applied over a 3-min run time period. The mobile phase was acetonitrile (65%)/water (35%), while a photodiode array spectrometer operated at fixed detection wavelength for each experiment was used as a detector [15]. The GC–MS system consisted a Hewlett-Packard 5890 Series II gas chromatograph fitted with an Elite-5MS 0.25 mm (30 m \(\times\) 0.25 mm id) column, and a Hewlett-Packard 5989A mass spectrophotometer operating in EI mode at 70 eV. The temperature ramp for this column was 40°C for 1 min, 10°C min\(^{-1}\) up to 250°C and held for 1 min) [27]. The photodegradation efficiency (photodegradation %) was calculated by Eq. (1):

\[
\text{Photodegradation} \% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

where \(C_0\) is initial concentration of m-cresol and \(C_t\) is concentration of m-cresol at the end of irradiation time. The experiments were carried out in duplicate and the averages of data were used as responses. As preliminary studies, the photodegradation was performed without photocatalyst and at normal pH 7.63. As observed, only 4% of m-cresol disappeared which might be photolyzed. Therefore, the stability of m-cresol was proved under the irradiation. In the dark, 4% of the concentration decreased possibly adsorbed on the photocatalyst surface [30].

### 3 Results and discussion

The photodegradation was carried out by varying one effective variable and other factors kept constant which is called one variable at a time method. The effective variables on the photodegradation were the photocatalyst amount, pH, and m-cresol concentration. To optimize the variables, photocatalyst loading, pH effect and the concentration of m-cresol as following section were investigated. Finally, the mineralization of m-cresol and the photoproducts were studied.

#### 3.1 Photocatalyst loading

The photocatalyst loading was carried out by keeping pH and m-cresol concentration constant (Fig. 1). As observed, the photodegradation efficiency increased up to 2.5 g L\(^{-1}\) of ZnO because the number of the effective sites directly depends on the amount of the photocatalyst. The sites provide the hydroxyl radicals to the photodegradation. In addition, the amount of the adsorbed m-cresol is increased owing to an increase in surface of the sites [30]. However, the photodegradation decreased when the amount of photocatalyst was enhanced beyond the optimum. The reduction might be due to the excess ZnO particles in the solution that is called screening effect [15, 31]. Moreover, the agglomeration of photocatalyst particles is possible during the stirring process in which a part of the photocatalyst surface becomes inactive for the photon and m-cresol during the photodegradation [27, 32].

#### 3.2 The effect of pH

Photodegradation is carried out on the photocatalysis surface, while the charges of ZnO surface and m-cresol molecules varied with the shift in pH [33–36]. At different pH values, the charge of ZnO surface is ZnO\(^{2+}\), ZnOH\(^+\), and ZnO\(^-\) at pH < pH\(_{zpc}\), pH\(_{zpc}\), and pH > pH\(_{zpc}\), respectively, because the pH of zero point charge (pH\(_{zpc}\)) of ZnO has been reported at pH 9 [37]. On the other hand, as Scheme 1 shows, most m-cresol molecules would tend to be positively charged as, e.g. (3-methylphenyl)oxonium under acidic conditions. However, m-cresol would exist negatively charged as, e.g. 3-methylphenolate.
Therefore, the effect of pH on the photodegradation was investigated in presence of optimum amount of photocatalyst (Fig. 2).

As observed, the photodegradation efficiency was at maximum value, 100%, in a broad range of pH 7–9. The efficiency may be due to interactions between m-cresol and the photocatalyst surface because ZnO surface is positive and most of m-cresol molecules are transformed to 3-methylphenolate (negative species) [39]. Moreover, when solution shows pH 8–9, OH is easily generated by oxidizing available hydroxyl ions [32]. However, the photodegradation was insufficient before and after the optimum (pH 7–9). This could be attributed to a reduction in the amount of adsorbed m-cresol on the ZnO surface at pH 6 and 10 [27] because (3-methylphenyl)oxonium exists at pH 6 and 3-methylphenolate at pH 10 while ZnO surface was covered by similar charge at both pH values [37, 39].

### 3.3 Determining the level of the contaminants

The photodegradation of several levels of m-cresol concentrations was carried out at optimum condition of photocatalyst and pH (Fig. 3). As observed, the efficiency was 100% for concentrations ranging between 50 and 100 mg L\(^{-1}\), which was quite significant. To evaluate the behavior of the photodegradation around the optimum, the removal concentration of m-cresol as a function of irradiation time was studied (Fig. not shown). According to the studies, the removal rate constant was calculated for different concentrations of m-cresol. The rate constants were plotted versus m-cresol concentration (Fig. 4). The plot indicates that the efficiency sharply increased with increasing m-cresol concentration up to optimum, 100 mg L\(^{-1}\). The reason for this behavior is related to the probability interaction between m-cresol and ZnO surface, which increased with increasing m-cresol concentration [27, 32, 40, 41]. However, the rate gradually decreased as the concentration increased to >100 mg L\(^{-1}\). It may be due to the fact that m-cresol molecules can compete with H\(_2\)O to attract the hole for direct degradation on the photocatalyst surface at high concentrations [27, 42]. The other possibility is that with increasing concentration, the amount of ZnO remains constant [15, 43]. A similar observation was made in our previous work on the photodegradation of m-cresol by manganese doped ZnO nanoparticles under visible-light irradiation[15, 42].

### 3.4 Mineralization

Mineralization of m-cresol is the main aim of the photodegradation that followed under optimum condition by GC–MS, TOC, TIC, and UHPLC. The UHPLC histogram at the beginning and at the end of the photodegradation showed that removal of m-cresol was 100% after 5 h of irradiation (Fig. 5). As Fig. 5a shows, the only m-cresol peak sharply appeared before irradiation while the peak disappeared completely at 300 min of the irradiation time (Fig. 5b). Moreover, the GC–MS of the similar condition confirmed the UHPLC results (Fig. not shown). However, TOC steadily decreased with increasing irradiation time, up to 72% (Fig. 6). In addition, TIC was generated in the first hour of the irradiation time and then was constant at 8%. The constancy is due to...
some organic carbon converting to inorganic carbon such as carbonate ions, which easily transformed into CO₂ and H₂O [15, 42, 44]. Hence, the residual value of TOC and TIC, 19.56%, indicates the presence of other photo-products (intermediates) identified by UHPLC.

Figure 7 shows the detected intermediates including 3,5-hydroxytoluene (1.7 mg L⁻¹), 2,5-hydroxybenzaldehyde (0.2 mg L⁻¹), and 3-hydroxy-benzaldehyde (0.3 mg L⁻¹) at 180 min of irradiation time. The intermediates were reported earlier by GC–MS for hydroxyl radical reactions [45]. Therefore, the proposed mechanistic pathway for the photodegradation is provided in Fig. 8. Thus, 3-hydroxybenzaldehyde, 3,5-hydroxytoluene and 2,5-hydroxy-benzaldehyde could be produced by steps (2), (3), and (4) in Fig. 8, respectively. It is believed that the carboxylic acids such as oxalic acid (HOOC–COOH) are formed by steps (8) and (10) in Fig. 8 [44]. At the last stage, oxalic acid is easily transformed to CO₂ and H₂O (step (11)). As the final study, the fresh photocatalyst was reused five times to indicate stability of photocatalyst. The results showed that the photocatalytic
performance of fresh and used ZnO at optimum condition was not significantly reduced.

4 Concluding remarks

In this study, the high concentration of m-cresol was degraded in presence of ZnO under UV irradiation during 6 h. The ZnO amount, pH and m-cresol concentration were considered as effective factors on the photodegradation. The demineralization of m-cresol was measured by a UV-Vis spectrophotometer while the TOC-analyzer was used to determine the mineralization of the pollutant by the end of the irradiation time. The UHPLC was used to identify the probable intermediates. The results showed that the optimum condition happens at pH 7–9. Moreover, 100% of m-cresol was removed at fifth hour of irradiation time that is quite significant. However, the removed TOC was 80%, which confirms generated intermediates during that time. The intermediates were detected after 3 h of the reaction time. The intermediates were 3,5-hydroxytoluene, 2,5-hydroxy-benzenaldehyde, and 3-hydroxy-benzenaldehyde. Reusability of the photocatalyst showed insignificant reduction in the photodegradation. In conclusion, this investigation indicated high potential of ZnO to remove high level concentrations of m-cresol under UV irradiation.

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References


