

Application of cadmium-doped ZnO for the solar photocatalytic degradation of phenol

Behzad Shahmoradi, Farzaneh Farahani, Shadi Kohzadi, Afshin Maleki, Mohammadamin Pordel, Yahya Zandsalimi, Yuxuan Gong, Jixiang Yang, Gordon McKay, Seung-Mok Lee and Jae-Kyu Yang

ABSTRACT

In this study, photocatalysis of phenol was studied using Cd-ZnO nanorods, which were synthesized by a hydrothermal method. The Cd-ZnO photocatalyst was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy, and Fourier transform infrared (FT-IR) and UV-Vis spectroscopy. XRD patterns exhibit diffraction peaks indexed to the hexagonal wurtzite structures with the P63mc space group. SEM images showed that the average size of the Cd-ZnO nanorods was about 90 nm. Moreover, the nanorods were not agglomerated and were well-dispersed in the aqueous medium. FT-IR analysis confirmed that a surface modifier (n-butylamine) did not add any functional groups onto the Cd-ZnO nanorods. The dopant used in this study showed reduction of the bandgap energy between valence and conduction of the photocatalyst. In addition, effect of various operational parameters including type of photocatalyst, pH, initial concentration of phenol, amount of photocatalyst, and irradiation time on the photocatalytic degradation of phenol has been investigated. The highest phenol removal was achieved using 1% Cd-ZnO for 20 mg/l phenol at pH 7, 3 g/l photocatalyst, 120 min contact time, and 0.01 mole H₂O₂.

Key words | Cd-ZnO, hydrothermal, nanorods, phenol, photocatalyst, sunlight

Behzad Shahmoradi (corresponding author)

Shadi Kohzadi

Afshin Maleki

Mohammadamin Pordel

Yahya Zandsalimi

Department of Environmental Health Engineering,

Environmental Health Research Center,

Research Institute for Health Development,

Kurdistan University of Medical Sciences,

Sanandaj, Iran

E-mail: bshahmoradi@muk.ac.ir

Farzaneh Farahani

Academic Center for Education, Culture and

Research (ACECR),

Alborz Branch, Alborz, Iran

Yuxuan Gong

Kazuo Inamori School of Engineering,

Alfred University,

Alfred, NY, 14802, USA

Jixiang Yang

Chongqing Institute of Green and Intelligent

Technology, Chinese Academy of Sciences,

Chongqing, China

Gordon McKay

Division of Sustainability, College of Science and

Engineering,

Hamad Bin Khalifa University, Education City,

Qatar Foundation,

Doha, Qatar

Seung-Mok Lee

Department of Energy and Environment

Convergence Technology,

Catholic Kwandong University,

Gangneung 25601, Korea

Jae-Kyu Yang

Department of Environmental Engineering,

Kwangwoon University,

Seoul, 01897, Korea

INTRODUCTION

Phenolic compounds constitute an important group of water pollutants mainly generated from chemical, petrochemical, paint, textile, pesticide, food processing, and biotechnological industries (Bazrafshan *et al.* 2016; Gul *et al.* 2017). The

toxicity of phenolic compounds is an important issue since their presence inhibits the activity of microorganisms in the biological treatment of wastewater (Gao *et al.* 2017). Therefore, the presence of phenol strongly reduces the

biodegradation of other wastewater components (Maleki *et al.* 2006; Mahvi & Maleki 2010; Wysocka *et al.* 2018). Decreasing its concentration to a safe level (0.1–1.0 mg/l) in water is difficult because it is stable and soluble in water (Seftel *et al.* 2014). Traditional wastewater treatment methods such as solvent extraction, activated carbon adsorption, and common chemical oxidation are partly effective, non-destructive, inefficient, costly, or often conducted by transferring pollutants from water to another phase resulting in the production of secondary pollutants (Prabha & Lathasree 2014).

Biodegradation is environmentally favorable and cost-beneficial even though it is a time-consuming process (Muhammadi *et al.* 2015). Some organic compounds are not biodegradable, and hence development of a facile and effective method to degrade these compounds is highly necessary.

Among various methods reported in the literature, photocatalytic degradation has been demonstrated as one of the most accomplished, facile, green, cost-effective and innovative methods for the successful degradation of toxic organic compounds (Shahmoradi *et al.* 2018).

Photocatalysis using several kinds of semiconductors has been widely investigated as an environmentally favorable technology for the removal of phenol and phenolic compounds from water (Ahmed *et al.* 2014). Several photocatalysts have been utilized for photocatalytic degradation of environmentally benign organic compounds (Muhd *et al.* 2014; Shahmoradi *et al.* 2017). Using TiO₂ and ZnO as photocatalysts is widely favored due to their better photocatalytic activity, less toxicity, and cost-effectiveness. ZnO is known as a more active photocatalyst than TiO₂ under solar irradiation (Han *et al.* 2012; Salehi *et al.* 2017). As TiO₂ and ZnO have a large bandgap energy of 3.2 eV (~388 nm), photocatalysis is active only in the presence of UV light with wavelengths shorter than 380 nm (Casbeer *et al.* 2012). ZnO is one of the widely used photocatalysts because of its low price, high photocatalytic activity, and non-toxicity. In addition, the use of ZnO for the photocatalytic degradation of organic compounds has received much attention due to its high photosensitivity and stability (Lavand & Malghe 2016). It has been reported that phenol could be photocatalytically degraded using ZnO as a catalyst and oxygen as an electron acceptor (Rajamanickam & Shanthy 2016). Because of the instability of catalytic activity, many kinds of metal oxides are doped onto ZnO to improve its photocatalytic degradation activity (Wang *et al.* 2013; Maleki *et al.* 2015).

It is crucial to find cheap dopant materials and economical preparation methods for industrial application. Surface properties of ZnO, controlled by various fabrication processes, will influence the photocatalytic property as well as the final degradation efficiency. Hence, applying a surface modifier along with a suitable dopant could possibly overcome such deficiencies.

One potential dopant is chromium, which is known as an excellent candidate in this regard (Wu *et al.* 2011; Nibret *et al.* 2015). In our previous works, we reported successfully doping ZnO with some of the transitional metal oxides including Fe, Ni, Mn, Cr, and Cu (Shahmoradi *et al.* 2011; Maleki & Shahmoradi 2012; Maleki *et al.* 2015; Pirsaeheb *et al.* 2017; Salehi *et al.* 2017). Although some of them are heavy metals, their substitution in the ZnO lattice avoids their release into the environment. Cr-ZnO nanowires synthesized through solvothermal technique were used for the photodegradation of methyl orange as a model dye. However, the effect of operational parameters on the photocatalytic degradation efficiency was not studied. Such information is crucial for scaling up the process and industrial applications. Nibret *et al.* (2015) used the impregnation method for the synthesis of Cr-N co-doped ZnO. In their report, no information on the light source, its intensity and effect of parameters influencing photocatalytic degradation efficiency was reported.

The doping of Cr on ZnO is expected to modify efficiency of absorption, luminescence and photocatalysis in addition to other physical or chemical properties of ZnO (Chang *et al.* 2014).

Hamza *et al.* (2013) evaluated the effect of irradiation time on the degradation of phenol over ZnO and α -Fe₂O₃. The degradation of phenol increased with increasing irradiation time, and reached 52 and 86% for ZnO and α -Fe₂O₃ within 6 h, respectively (Hamza *et al.* 2013). Dewidar *et al.* (2018) evaluated phenol photodegradation using ZnO nanocatalyst and results showed 78.2% chemical oxygen demand reduction at pH = 2 and ZnO loading 1.5 g/l.

Moreover, the previous works have confirmed the suitability of *n*-butylamine as a surface modifier for controlling crystal growth direction and reducing agglomeration of as-prepared nanoparticles (Maleki & Shahmoradi 2012; Maleki *et al.* 2015; Pirsaeheb *et al.* 2016). In this study, cadmium was used as a dopant material. Hence, the aim of this study was to synthesize Cd-doped ZnO nanocatalyst and to compare its effectiveness for solar photocatalytic degradation of phenol under identical experimental conditions.

EXPERIMENTAL

Materials

NH₄OH and HCl (extra pure, Merck, Germany) were used for pH adjustment. ZnO (GaA, Merck, Germany), CdO (extra pure, GaA, Merck, Germany), and KOH (extra pure, Merck, Germany) were used as precursors. Standard grade phenol (C₆H₅OH) (extra pure, Merck, Germany) was used as the model pollutant. *n*-Butylamine (≥99%, for synthesis, Merck, Germany) was used as a surface modifier. All of the chemicals, as analytical grade, were purchased from Merck (Germany) and were used as-received.

Preparation of the Cd-doped ZnO photocatalysts

For the synthesis of ZnO nanomaterials doped with cadmium (Cd-ZnO NPs), a low temperature hydrothermal method was used. In brief, 1 mole of ZnO powder and 0–2 wt% of CdO were mixed and gently stirred for 5 min using a glass rod in a Teflon liner using 10 ml of 1 N KOH solution as solvent, and then 1 ml of the surface modifier (*n*-butylamine) was added dropwise to the mixture. The homogeneous mixture in the Teflon liner ($V_{\text{fill}} = 10 \text{ ml}$) was placed into a general-purpose autoclave, which was sealed using impingers and was later kept in an electric oven at 100 °C for 8 h. After the reaction, the contents of the autoclave were washed with double-distilled water into a clean beaker. The surface modifier was washed out by rinsing several times with double distilled water. Eventually, the product was dried at room temperature (40 °C), and kept in a vacuum desiccator prior to any characterization or testing.

Photocatalytic degradation of phenol using Cd-ZnO nanorods

The photocatalytic experiments were conducted to investigate the photocatalytic degradation of phenol in suspension using a batch reactor ($V = 250 \text{ ml}$). Firstly, photocatalytic degradation of phenol under sunlight was investigated at a phenol concentration of 20 mg/l, with 2.5 g of Cd-ZnO nanorods at natural pH. Before illumination, the suspension was stirred continuously in dark condition for 30 min to reach adsorption equilibrium. The mean sunlight irradiation (35°16'55.01"N and 47°0'9.27"E) recorded by model TES-1330, Taiwan, was $670 \pm 100 \text{ lx}$. Its illumination time was 120 min under continuous stirring using a magnetic stirrer

(100 rpm). Then, each sample was centrifuged at 2,500 rpm for 10 min, and filtered to separate the Cd-ZnO nanorods from the suspension. The concentration of phenol in the filtrates was measured using a UV-Vis spectrophotometer at a wavelength of 500 nm (absorption maxima of phenol) using a quartz cell with a path length of 5 cm (Eaton *et al.* 2005). Each experiment was triplicated to ensure the results are reproducible. The degradation percentage was calculated using Equation (1):

$$\text{Degradation \%} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 and C are initial and final concentration of phenol, respectively. Similar experimental analysis was carried out with variation of initial phenol concentration (5, 10, 20, 50, and 100 mg/l), at different concentration of the photocatalyst (0.5, 1, 2, 3, and 5 g/l), at different sunlight illumination time (15, 30, 60, 90, and 120 min), and at different pH of the phenol solution (3, 5, 7, 9, and 11). Finally, effects of scavengers and enhancers (FeSO₄, H₂O₂, CCl₄, CH₃OH, C₂H₅OH, CH₃COOH, EDTA (ethylenediaminetetraacetic acid), and NaCl) on the photocatalytic degradation efficiency of phenol were investigated.

RESULTS AND DISCUSSION

Characterization of Cd-ZnO nanorods

The X-ray diffraction (XRD) patterns (D8 Advanced Bruker AXS, Germany) of reagent grade ZnO and Cd-ZnO nanorods are shown in Figure 1(a). These peaks were indexed as the reagent grade hexagonal phase of wurtzite-type ZnO; all the diffraction peaks are sharp, and match well with the characteristic diffraction peaks of hexagonal wurtzite structured ZnO (space group: P63mc (186), JCPDS No. 36-145) (Wang *et al.* 2013). Pure ZnO and Cd-ZnO nanorods had the identical hexagonal wurtzite structure with minor broadening of resolved (101) diffraction plane. A narrow and strong diffraction peak (002) appeared at the angle of 34.34° for the reagent grade ZnO, and the same peak was observed for Cd-ZnO nanorods at 34.87°. Additionally, an obvious characteristic peak of Cd was observed at 44.03°. Moreover, a slight shift in the diffraction peaks towards higher angles was observed as a result of lattice contraction caused by the Cd substitution for Zn in the wurtzite ZnO. Such a phenomenon is contrary to the findings of Shannon, who attributed the shift of Bragg angle to the fact that the

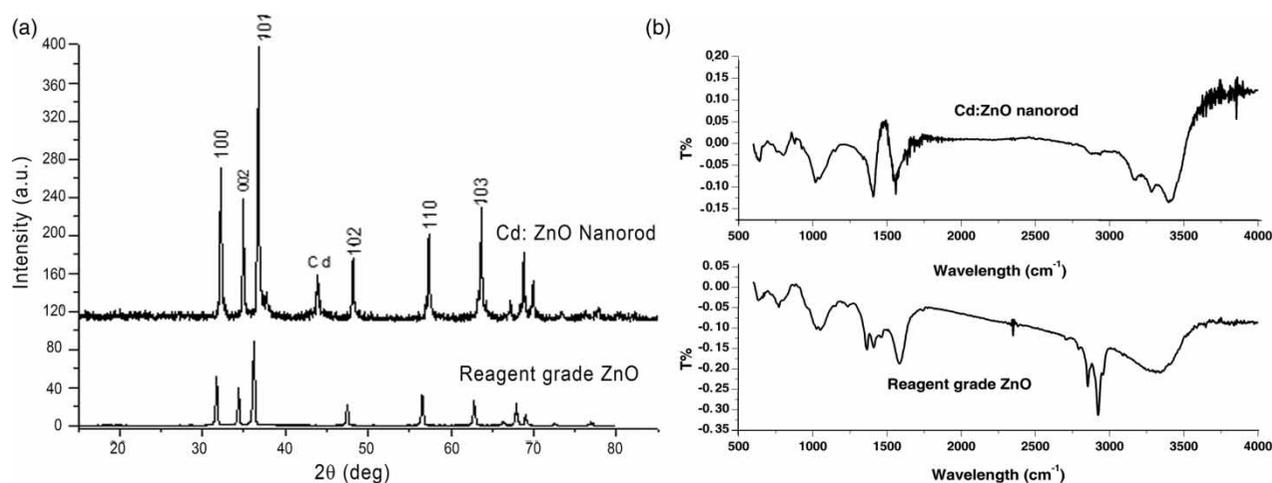


Figure 1 | XRD patterns (a) and FT-IR spectra (b) of reagent grade ZnO and surface-modified Cd-ZnO nanorods.

ionic radius of Cd^{2+} (0.97 Å) is greater than that of Zn^{2+} (0.74 Å) (Shannon 1976).

Figure 1(b) presents the Fourier transform infrared (FT-IR) (Tensor 27 spectrophotometer, Bruker, Germany) spectra of reagent grade ZnO and Cd-ZnO nanorod. As shown in Figure 1(b), the characteristic absorption peak of 1 wt% Cd-doped ZnO nanorods at approximately $3,456\text{ cm}^{-1}$ corresponds to the stretching vibration of the O–H groups. The absorption peak observed at $1,630$ and $1,384\text{ cm}^{-1}$ is due to the O–H bending vibration. The peak at 511 cm^{-1} is the characteristic absorption peak of ZnO (Meng et al. 2015). Meanwhile, no other functional group was observed after the surface modification, indicating that the surface modifier applied has been detached as a result of rigorous washing. Hence, no contamination was detected after introduction of surface modifier.

Figure 2 shows the scanning electron microscopy (SEM) images of Cd-ZnO nanorods at two different concentrations of Cd (1 and 2 wt%; normal values are reported here). Agglomeration is negligible for both Cd concentrations, which could be attributed to the surface modifier (*n*-butylamine) (Shahmoradi et al. 2015). As shown in Figure 2(a) and 2(b), the nanorods are not equal in size; the average nanorod size is 74.7 nm.

The used surface modifier controls the agglomeration and increases dispersibility of nanoparticles in the media. When surface modifier was used, the zeta potential of the Cd-ZnO nanorods was decreased, showing negative charges above pH 4.3. The pH_{zpc} was decreased from 8.6 to 4.3 as a result of adding surface modifier. In addition, the SEM images shown in Figure 2 support such a claim. At pH levels higher than pH_{zpc} , the particles have negative surface

charge, while at pH levels lower than this, the particles have positive surface charge (Saeedi et al. 2015). The electrostatic interaction between the surface of the Cd-ZnO and phenol as well as the affinity of Cd-ZnO nanorods toward phenolate through adsorption under strong alkaline condition is limited, leading to the reduction of phenol degradation rate (Shahamat et al. 2014).

Effect of dopant concentration on the photocatalytic degradation of phenol

Three different weight percentages of dopant (0.5, 1, and 2 wt%) were used for the synthesis of Cd-ZnO photocatalysts. The photocatalytic degradation of phenol using different concentrations of dopant, Cd, is plotted in Figure 3. The maximum efficiency (70%) was found for 1% Cd-ZnO photocatalysts, while an efficiency of less than 10% was observed for undoped ZnO photocatalysts (Figure 3). Moreover, the highest efficiency was observed for 1% followed by 2% and the lowest was achieved for 0.5% Cd-ZnO photocatalysts. This result clearly suggests that the photocatalytic activity of ZnO can be greatly improved with an optimum amount of Cd. Hence, further photocatalytic degradation studies of phenol were conducted using 1% Cd-ZnO photocatalysts.

Effect of pH on the photocatalytic degradation of phenol

One of the key parameters affecting the degradation of organic pollutants such as phenol is solution pH. Thus, photocatalytic degradation of phenol in the presence of Cd-ZnO nanorods was investigated over a pH range from

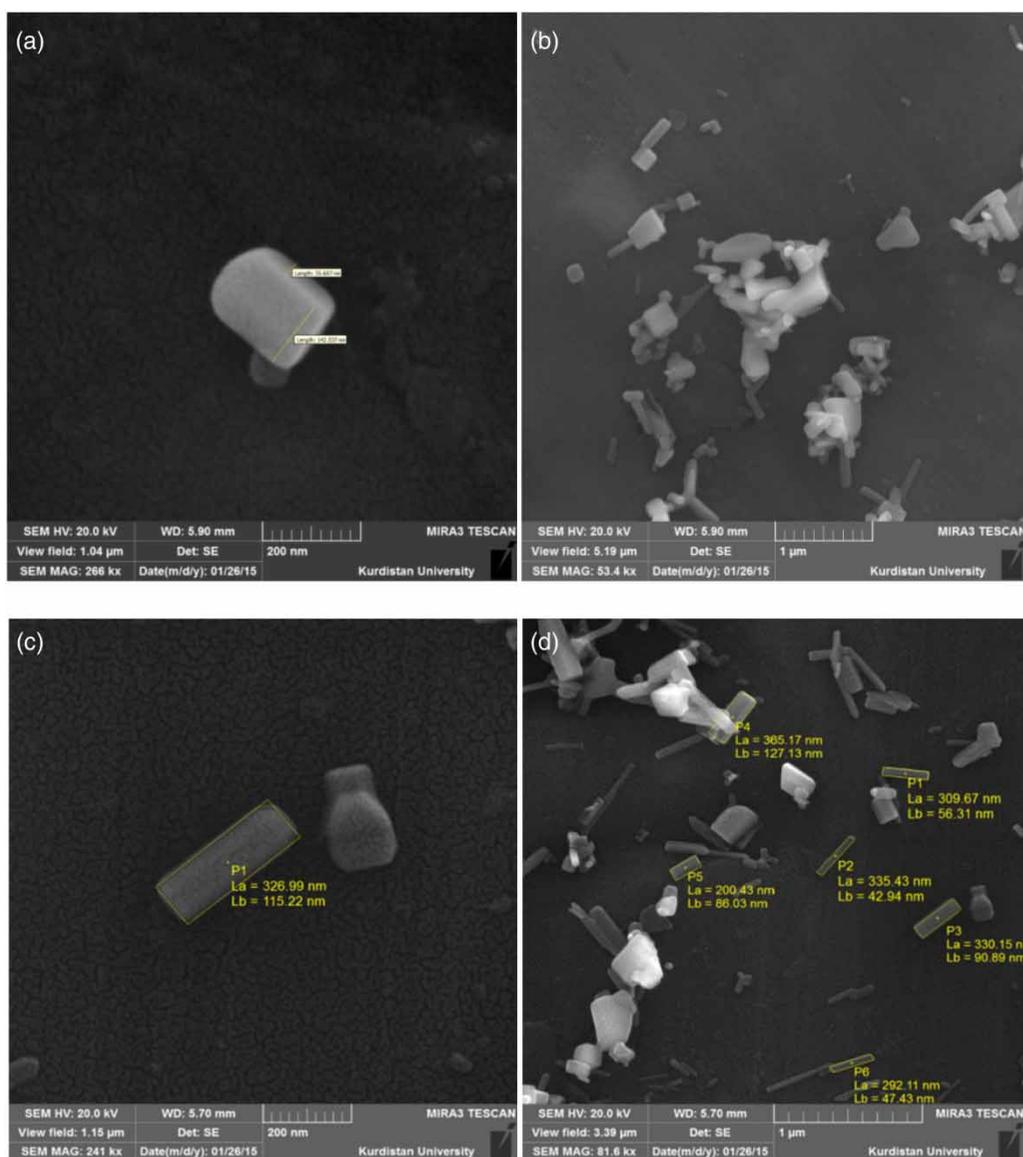


Figure 2 | Characteristic SEM images of (a) and (b) 2% Cd-ZnO and (c) and (d) 1% Cd-ZnO nanorods.

3.0 to 11.0. The influence of solution pH depends on the type of contaminants as well as on the zero-point charge (zpc) of the photocatalyst (Barka *et al.* 2013; Wahab & Hussain 2016). The solution pH indeed influences the surface charge properties of the photocatalyst, affecting electrostatic interaction between photocatalyst surface and pollutant molecules. Figure 4 illustrates the effects of pH on the photocatalytic degradation efficiency of phenol in the presence of Cd-ZnO photocatalysts. It was found that the degradation percentage of phenol increased with the increase of pH from 3 to 7. In the pH lower than pH_{zpc} of ZnO, its surface will be more positively charged. Hence adsorption power between the ZnO surface and phenol will

be strong, leading to more phenol degradation (Yusoff *et al.* 2017). In contrast, Prabha & Lathasree (2014) reported that phenol degradation decreased with increase in pH; however, it was almost the same (15–18%) at mildly acidic and neutral pH. At higher pH values, phenol exists in the solution as negatively charged phenolate species. Therefore, the adsorption of phenol on the catalyst surface decreases due to electrostatic repulsion. It has to be noted that higher pH causes more formation of carbonate ions, which helps in inactivating OH radicals, thus resulting in decreased degradation efficiency (Feng *et al.* 2015). Therefore, phenol degradation is more favorable in mild acidic or neutral pH, where phenol can attach onto the surface of ZnO more favorably.

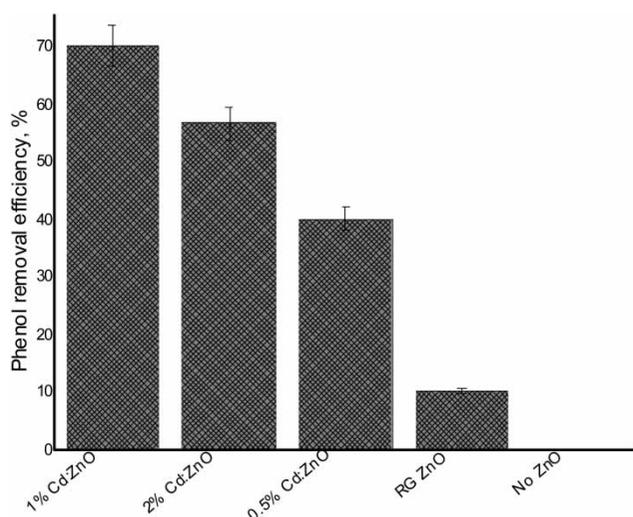


Figure 3 | Effect of dopant concentration on the photocatalytic degradation of phenol.

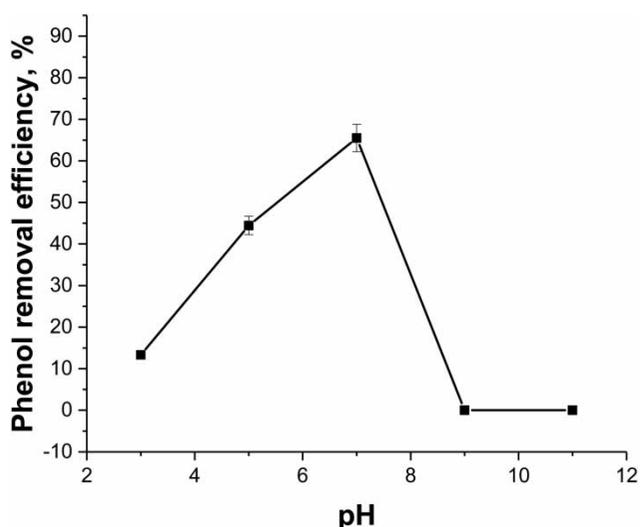


Figure 4 | Effect of pH on the photocatalytic degradation of phenol using 1% Cd-ZnO nanorods.

Effect of photocatalyst dosage and initial phenol concentration on the photocatalytic degradation of phenol

The amount of photocatalyst strongly influences the rate of photocatalytic reaction. To avoid excess usage of catalyst and to ensure efficient introduction of photons on the surface of photocatalyst, an optimum catalyst dosage must be determined (Tan *et al.* 2011; Prabha & Lathasree 2014). Different photocatalyst dosages were used to investigate their effect on the photocatalytic degradation of phenol while solution pH, initial phenol concentration, and reaction time were kept constant at 7, 20 mg/l, and 120 min,

respectively. As shown in Figure 5(a), the greatest efficiency of phenol degradation was obtained at the photocatalyst dosage of 3 g/l. This observation can be explained by the fact that there is an adequate amount of photocatalyst to enhance photocatalytic degradation (Khairy & Zakaria 2014; Ye *et al.* 2015). However, excessive photocatalyst dosage may lead to a decrease in light transmittance, and an increase of light scattering in the solution; hence, an excessive photocatalyst dosage resulted in a lower absorption of light for initiating photocatalysis (Zhang *et al.* 2013). Principally, the photocatalytic degradation rate of pollutants is not only affected by the active sites but also influenced by the photo-absorption of the photocatalyst.

It is well known that the initial concentration of reactant plays an important role in the photocatalytic degradation of

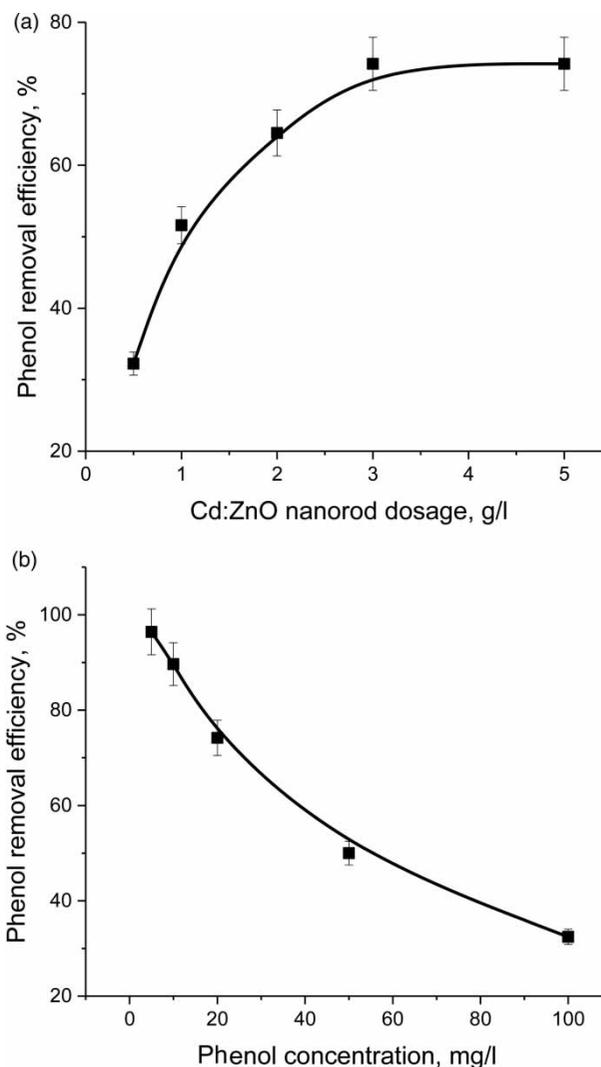


Figure 5 | Effect of photocatalyst dosage (a) and phenol concentration (b) on the photocatalytic degradation of phenol.

organic compounds (Hemmati *et al.* 2014). The influence of initial phenol concentration on photocatalytic degradation was investigated at five levels (5, 10, 20, 50, and 100 mg/l) while initial pH, photocatalyst dosage, and reaction time were kept constant at 7, 3 g/l, and 120 min, respectively. As shown in Figure 5(b), the photocatalytic degradation decreased from 96.42 to 32.43% with increasing initial concentration of phenol from 5 to 100 mg/l. At higher concentrations, the light absorbed by phenol is more than that of the Cd-ZnO nanorods, causing decreased degradation efficiency. Thus, absorbed light is not sufficient to trigger the degradation of phenol (Yang *et al.* 2008). As a result, competitive adsorption of OH^- on the same site decreases, and consequently the amount of $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ attached to the surface of the catalyst decreases. For all our investigations at different initial phenol concentrations, the photocatalyst dosage, irradiation time and intensity of light were kept constant. Since the generation of $\cdot\text{OH}$ does not increase, the probability of phenol molecules reacting with $\cdot\text{OH}$ decreases; hence, a decrease in the degradation efficiency might be observed (Kashif & Ouyang 2009). In fact, with the progression in the degradation reaction at high initial concentrations, some intermediate compounds can be formed. These intermediates may be competitively adsorbed on the photocatalyst surface, and subsequently react with oxidant species. Moreover, the oxidized intermediate could react with the reducing species (e.g. electrons), reverting back to phenol, which finally results in a decrease of the degradation efficiency (Guo *et al.* 2006).

Effect of illumination time on the photocatalytic degradation of phenol

The effect of illumination time on photocatalytic degradation efficiency of phenol was studied at five time periods (15, 30, 60, 90 and 120 min) while initial pH, photocatalyst dosage, and initial phenol concentration were kept constant at 7, 3 g/l, and 20 mg/l, respectively. During these photocatalytic degradation experiments, samples were illuminated with sunlight (mean light intensity = 670 ± 100 lx). As plotted in Figure 6, degradation of phenol with Cd-ZnO under sunlight was increased with increasing illumination time (75% after 120 min illumination).

Effect of scavengers and enhancers on the photocatalytic degradation of phenol

Industrial wastewater is a mixture of different organic and inorganic compounds, which makes it crucial to study the

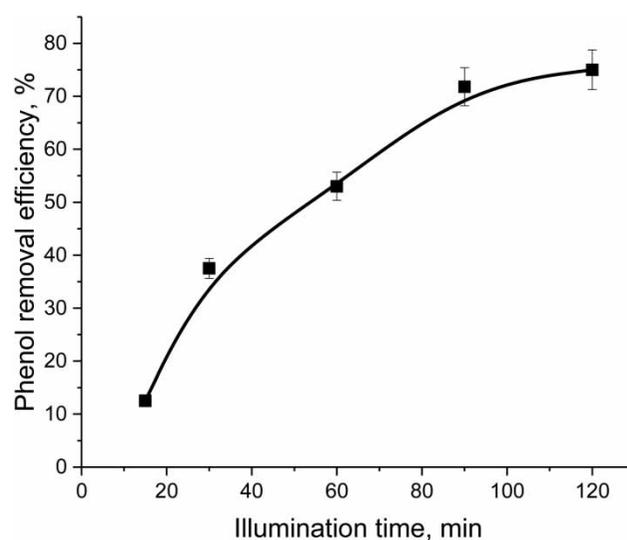


Figure 6 | Effect of sunlight illumination time on photocatalytic degradation of phenol.

effect of scavengers and enhancers on photocatalytic degradation efficiency of a synthetic pollutant. Hence, under optimum conditions, the effect of scavengers and enhancers was evaluated on the photocatalytic degradation efficiency of phenol using Cd-ZnO nanorods. For this purpose, the effect of 0.01 M FeSO_4 , H_2O_2 , CCl_4 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CH_3COOH , EDTA, and NaCl (Shin & Kim 2008; Lim *et al.* 2014; Wu *et al.* 2015; Uddin *et al.* 2016) on the photocatalytic degradation efficiency of phenol (1% Cd-ZnO) was studied by keeping other parameters constant (pH 7, irradiation time 120 min, Cd-ZnO nanorod 3 g/l, phenol concentration 20 mg/l). As shown in Figure 7, the removal efficiency of phenol increased from 75% to 89.56 and 86.2% with adding H_2O_2 and ethanol, respectively. Other

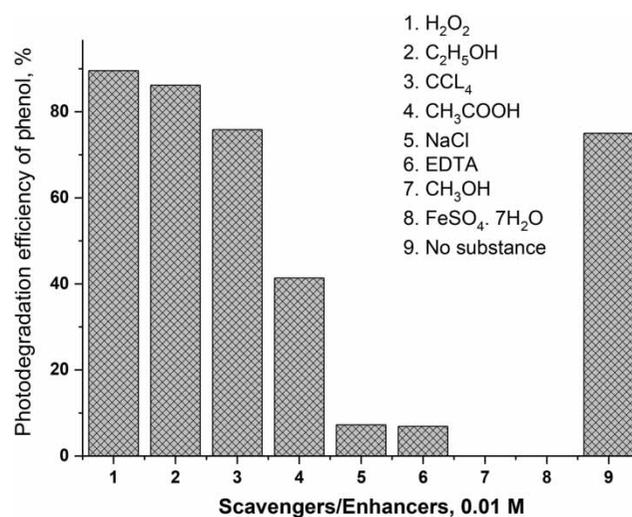


Figure 7 | Effect of scavengers and enhancers on the removal efficiency of phenol.

researchers also reported that phenol removal increased with addition of 0.1 M of H_2O_2 (Yusoff *et al.* 2015). Such an observation could be attributed to the fact that phenol has a high solubility and low octanol–water partition coefficient (K_{ow}); the retention of phenol in the aqueous phase gives a greater probability of reaction between phenol and H_2O_2 (Lim *et al.* 2014). However, addition of FeSO_4 , CH_3OH , EDTA, and NaCl decreased the phenol degradation efficiency from 75% to 0, 0, 41.37, 6.89 and 7.24%, respectively. By generating free electrons, H_2O_2 has an oxidant property and prevents pairing of electrons. H_2O_2 also has the capacity for attracting the electrons, thus generating free radicals that can degrade phenol molecules. It indicates that addition of organic compounds such as CH_3OH and EDTA can clearly confirm their scavenger role in photocatalytic degradation of another organic compound. Chloride ion is a substance that acts as an electron donor like HO_2 and H_2O_2 , but Cl^- sometimes hinders and reduces catalytic activation by adsorption to the active sites (Saratale *et al.* 2014). Saratale *et al.* (2014) found that NaCl had no effect on the photocatalytic degradation of phenol. However, we found it brought about 90% reduction in photocatalytic degradation efficiency. It is in contrast to the findings of Ye *et al.* (2016) in which they reported that common organic compounds (sucrose, urea, EDTA, and sodium formate) did not show a distinct inhibition effect on the catalytic oxidation of hydroquinone. However, CCl_4 had no effect on removal efficiency (Ye *et al.* 2016).

Reusability test of photocatalyst material

The reusability of the photocatalyst is a key issue concerning the long-term application. Thus, the effect of reused Cd-ZnO photocatalysts on the removal efficiency of phenol was evaluated. After the first cycle, the Cd-ZnO nanorods were separated, dried, and then put into 1 M HCl for 24 h; after HCl treatment, the nanorods were washed several times with deionized water, and dried at ambient temperature.

Figure 8 depicts the results of the reusability test of the Cd-ZnO nanorods in three consecutive runs. As shown in Figure 8, the photocatalytic degradation efficiency of phenol decreased from 75 to 32.14% within three consecutive experimental runs, indicating almost 50% reduction of degradation efficiency. It can be ascribed to the adsorption of some byproducts of the target pollutant in the pores and cavities of the catalyst, which resulted in the reduction of the active sites for the adsorption and generation of $\text{OH}\cdot$ (Nezamzadeh-Ejhih & Khorsandi 2014). This is one

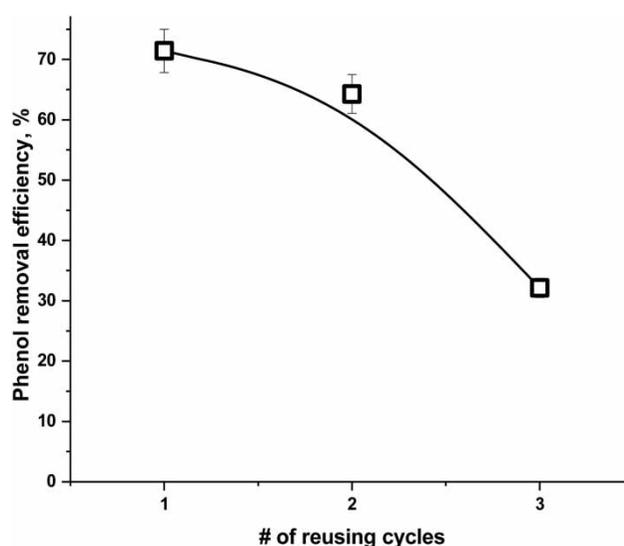


Figure 8 | Effect of reusability of Cd-ZnO nanorods on the photocatalytic degradation efficiency of phenol.

of the limitations of the application of nanomaterials in photocatalytic degradation of pollutants, which can be overcome via immobilizing the photocatalysts on supporting media; however, an attempt to improve the reusability of ZnO as photocatalyst is beyond the scope of this study, and has been more informatively discussed in various literature sources (Zhang *et al.* 2013; Pourshamsian 2015).

Although photodegradation of phenol using Cd-ZnO nanorods gave excellent removal efficiency, it is noteworthy that the light intensity, sunlight angle and the reactor size are important factors, limiting the photodegradation scaling-up. On the other hand, the sunlight illumination, as a free energy driving source, has different angles and intensities during different hours of day and seasons of the year. It is suitable for tropical areas, where sunny days are much more frequent compared with mountainous areas such as Sanandaj city, Iran. In addition, the mineralization of phenol is incomplete in this process.

CONCLUSIONS

Photocatalytic degradation of phenol was carried out using 1% Cd-ZnO (prepared by the low temperature hydrothermal method) under sunlight. Cd-ZnO nanorods were characterized using XRD, FT-IR, and SEM techniques. XRD and FTIR analysis showed that the doping process was achieved successfully. The as-prepared Cd-ZnO nanorods had a hexagonal wurtzite structure, and no contamination resulting from the surface modifier was detected using FT-IR.

SEM images indicated that the average nanorod size was about 74.7 nm with negligible agglomeration. Moreover, effect of solution pH, catalyst dosage, initial phenol concentration, illumination time, existence of scavengers and enhancers on degradation efficiency has been investigated. The highest degradation efficiency was observed at pH 7, Cd-ZnO dosage of 3 g/l, phenol concentration of 20 mg/l and illumination time of 120 min. Experimental results showed that the degradation rate increased with addition of H₂O₂ enhancers. However, the photocatalytic degradation efficiency of phenol reduced remarkably after three repeated cycles.

ACKNOWLEDGEMENTS

The authors acknowledge the support of this work by Kurdistan University of Medical Sciences, Sanandaj, Iran, and Academic Center for Education, Culture and Research (ACECR), Alborz Branch, Alborz, Iran.

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First received 3 July 2018; accepted in revised form 4 February 2019. Available online 14 February 2019