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Degrading two endocrine disrupting chemicals from water by UV irradiation with the presence of nanophotocatalysts

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ABSTRACT

The photocatalytic degradation of two selected endocrine disrupting chemicals (EDCs), namely phenol and resorcinol was investigated in TiO_2 and ZnO aqueous suspensions under UV irradiation. These catalysts were investigated for crystallinity, surface area and optical properties. The effects of various operating parameters including the photocatalyst dosage, solution pH, initial substrate concentration and the presence of second substrate on photocatalytic degradation were studied. Under optimized conditions, ZnO showed greater degradation and mineralization activities as it absorbed more light quanta than TiO_2. Several degradation intermediates were detected using HPLC, which allowed the proposal of tentative pathways for the photocatalytic degradation of phenol and resorcinol. By investigating the effect of various radical scavengers, it showed that the photocatalytic degradation of phenol and resorcinol took place mainly via the hydroxyl radicals. The ZnO photocatalyst was also reused for several times and without considerable loss of activity. Compared to the single solutions, the degradation efficiencies of binary solutions decreased. The difference between the observed rate constants of phenol and resorcinol in binary solutions became lesser compared to the cases in single solutions. Furthermore, the photocatalytic degradation of either single or binary substrates in aqueous solutions satisfactorily obeyed the pseudo-first-order kinetics.

Keywords: Photocatalysis; Phenol; Resorcinol; Endocrine disrupting chemicals; Degradation intermediates; Binary solutions

1. Introduction

Disruption of the endocrine system in wildlife and humans by anthropogenic chemicals has become an issue of worldwide concern due to the recognition of that the environment is contaminated with various endocrine disrupting chemicals (EDCs) that exert hormonal imbalance activity. An endocrine disruptor is defined by the European Commission (1996) as an exogenous substance or a mixture that alters function of the endocrine system and consequently causes adverse health effects in an organism, or its progeny, or (sub) populations [1]. The causative chemicals of endocrine disruption in wildlife populations are wide ranging and include a plethora of industrial chemicals such as phenols, dioxins, pesticides, phthalates, furans, synthetic steroids and some naturally occurring compounds [2–4]. Most of these EDCs are designed to resist biodegradation and are barely removed from effluents using conventional wastewater treatments such as activated sludge, which led to their presence

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in receiving waters where they have the potential to adversely affect the human and animal life even at very low concentrations [5,6]. Therefore, there is a need to develop treatment methods that are more effective in eliminating EDCs from the effluents.

In recent years an alternative to conventional methods, is "advanced oxidation processes" (AOPs) based on the formation of reactive species such as hydroxyl radicals (•OH) that oxidize a wide range of organic pollutants quickly and non-selectively. Particularly, heterogeneous photocatalysis has garnered much attention as a promising destructive technology leading to the total mineralization of most of the organic pollutants including EDCs [7,8]. The photocatalytic process is initiated by the photoexcitation of the semiconductor, followed by the formation of electron-hole pair on the surface of catalyst (Eq. (1)). The electron in the conduction band ($e_{cb}-$) can recombine with the valence band hole ($h_{vb}+$) and suppressing the efficiency of the photocatalytic process (Eq. (2)). In contrast, $e_{cb}-$ can migrate to the surface of the catalyst particle being trapped by adsorbed oxygen molecules, therefore generating the superoxide radical anions ($O_2\bullet-$) and increasing the efficacy of the process (Eq. (3)). In parallel, the h_{vb}^{+} can be trapped on the catalyst surface undergoing charge transfer with adsorbed water molecules or with surface-bound hydroxide species and thus forming strong oxidizing •OH radicals (Eqs. (4) and (5)). Finally, the h_{vb}^{+} in the catalyst can also directly oxidize the adsorbed organic pollutants to reactive intermediates (Eq. (6)) [9].

$$\text{Semiconductor} + hv \rightarrow e_{cb}^{-} + h_{vb}^{+} \quad (1)$$

$$e_{cb}^{-} + h_{vb}^{+} \rightarrow \text{heat} \quad (2)$$

$$e_{cb}^{-} + O_{2(\text{adsorbed})} \rightarrow O_2\bullet- \quad (3)$$

$$h_{vb}^{+} + H_2O_{(\text{adsorbed})} \rightarrow H^{+} + {}^{\bullet}OH \quad (4)$$

$$h_{vb}^{+} + OH^{-}_{(\text{adsorbed})} \rightarrow {}^{\bullet}OH \quad (5)$$

$$h_{vb}^{+} + \text{organicpollutant(OP)} \rightarrow OP^{\bullet+} \rightarrow \text{oxidationofthepollutant} \quad (6)$$

Till now many types of semiconductors have been studied as photocatalysts including titanium dioxide (TiO_2), zinc oxide (ZnO), zinc sulphide (ZnS), cadmium sulphide (CdS), stannic oxide (SnO_2) and so on [10–13]. TiO_2 is the most commonly used effective catalyst for a broad range of organic chemicals degradation due to its faster electron transfer to molecular oxygen. However, the extensive use of TiO_2 is uneconomical for large-scale water treatment. Given the drawbacks to the application of TiO_2 in the waste remediation, there is renewed interest to seek for more reliable photocatalysts. ZnO is a kind of semiconductor that has similar band gap as that of TiO_2 and has presented promissory results due to its higher photocatalytic activity in comparison with TiO_2 [10,12,14]. Gaya et al. [11] reported that ZnO was a suitable alternative to TiO_2 for the degradation of 4-chlorophenol since its photodegradation mechanism was proven to be similar to that of TiO_2. In fact, the biggest advantage of ZnO in comparison with TiO_2 is that it absorbs over a large fraction of solar spectrum [15].

In polluted groundwater and effluents from industrial or municipal sources, organic substance mixtures are prevalent. It is important to understand the mixture effect as the photocatalytic degradation of one component can be hindered by other compounds in the mixture owing to the competitive adsorption of the components [16–18]. However, studies on the photocatalytic degradation of multi-component systems of EDCs are scarce. The aim of this present work was therefore to evaluate the photocatalytic degradation of two selected endocrine disruptors, namely phenol and resorcinol using different semiconductors as TiO_2 and ZnO in order to determine the most effective catalyst for the degradation of EDCs. The effects of the photocatalyst dosage, solution pH, initial substrate concentration and the presence of the second substrate on the photocatalytic activity were systematically investigated. The formation of reaction intermediates and roles of various radical scavengers in the photocatalytic degradation of phenol and resorcinol were also studied. Phenol and resorcinol were chosen since they are synthetic chemicals produced worldwide in millions of tons each year and are widely used in the manufacture of adhesives, dyestuffs, pharmaceuticals, cosmetics and agricultural chemicals. Indeed, dose-dependent chromosomal aberrations have been reported in spermatogonia and primary spermatocytes of mice treated with solution of phenol in water in multigeneration studies. Various *in vivo* tests of mice and epidemiological studies of humans have also showed that resorcinol can interfere with tri-iodothyronine (T3) and thyroxine (T4) metabolism, interrupting the normal functioning of thyroid system [19–21].

2. Experimental

2.1. Materials

Titania P25 was obtained from Degussa. ZnO was purchased from ACROS Organics. Phenol and

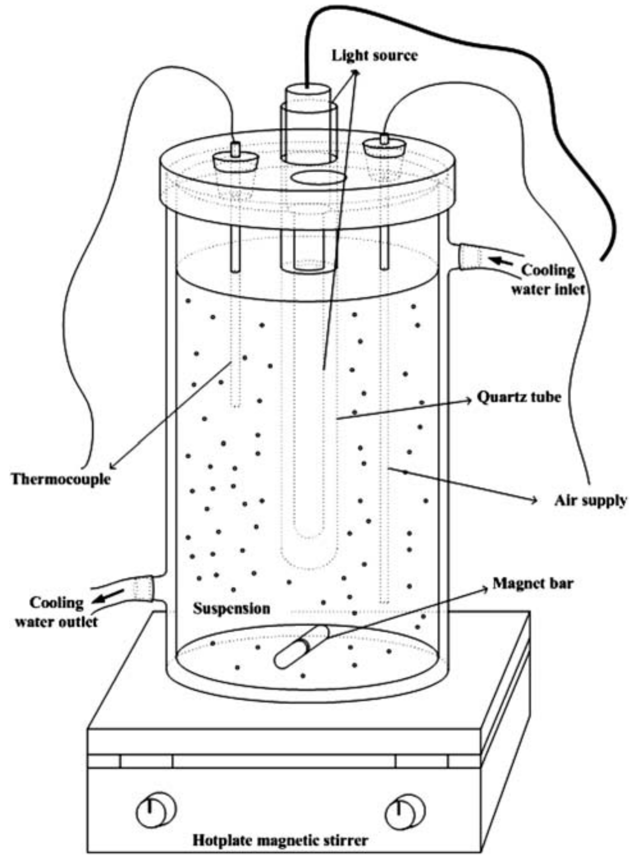

Fig. 1. Schematic diagram of the photoreactor.

resorcinol were purchased from ACROS Organics and were used without further purification. Deionized water was used for preparation of various solutions.

2.2. Photocatalytic experiments

All experiments were carried out in an immersion well photoreactor (Fig. 1). The photoreactor is made of Pyrex glass with dimensions of 200 × 100 × 60 mm (height × outer diameter × inner diameter). In the center of cylindrical photoreactor, a 15 W UV Pen-Ray (UVP) lamp with a maximum emission at about 365 nm was used as UV source. The total UV output intensity at distance 10 mm away from UV light, measured by radiometer (Cole Parmer, Series 9811) was 0.840 mW/cm^2. In a typical experiment, the reaction mixture was prepared by adding desired amount of catalyst into the photoreactor containing 350 mL of the substrate solution. Where required, pH adjustment was done using equimolar NaOH and HCl solutions. Prior to the photoreaction, the mixture was maintained under stirring for 5 min in the dark until the adsorption–desorption equilibrium was reached; then it was irradiated and bubbled with air at a constant flow rate of 4 mL/min. All experiments were carried out in batch mode and the temperature of the test solution was maintained constant at 26 ± 2°C using a water circulation.

Scavenger addition method was used to explore the mechanism of photocatalytic degradation of phenol and resorcinol over ZnO. The whole process was almost the same as that of the above photocatalytic activity measurement except with the presence of different scavengers: 1 mM ethanol as •OH radical scavenger, 1 mM sodium iodide (NaI) as h_{vb}^+ scavenger and acetonitrile was used instead of water in order to confirm the roles of •OH radical in the photocatalytic systems.

2.3. Analyses

At specific time intervals, 5 mL of the solution were drawn. The liquid samples were centrifuged at 5600 rpm for 10 min and subsequently filtered through 0.2 μm Millipore filters to remove the particles. The concentrations of phenol and resorcinol in the filtrates were analyzed by HPLC (Perkin Elmer Series 200) using *C18* column (length 150 mm × inner diameter 4.6 mm × particle size 5 μm) with a mobile phase mixture of water 70% (v/v) and acetonitrile 30% (v/v) at a flow rate of 1 mL/min. The wavelength of detector was set at 238 nm. To monitor the extent of mineralization during the phenol and resorcinol degradation, changes in total organic carbon (TOC) were measured using a TOC analyzer (Shimadzu, TOC-V_{CPH}). In order to determine the reproducibility of the results, at least duplicated runs were carried out for each condition for averaging the results, and the experimental error was found to be within ±4%. The degradation and mineralization efficiencies of each sample were calculated using Eqs. (7) and (8).

$$\%\,\text{degradation} = 100 \times \frac{c_o - c_t}{c_o} \tag{7}$$

$$\%\,\text{mineralization} = 100 \times \frac{\text{TOC}_o - \text{TOC}_t}{\text{TOC}_o} \tag{8}$$

where C_o and TOC_o are the equilibrium concentrations of substrates after 5 min dark adsorption, C_t and TOC_t are the concentrations of substrates at irradiation time *t* (min). The intermediates were confirmed by injecting standard chemicals of the compounds. The crystalline phases of the catalysts were analyzed using a Philips PW1820 X-ray diffractometer (XRD) employing Cu-Kα radiation under a scan range of 20–80°. The Brunauer–Emmett–Teller (BET) surface areas of the catalysts were determined by nitrogen adsorption–desorption method (Micromeritics ASAP 2020). In order to study the optical absorption properties of the catalysts, UV–Vis absorption spectra in the range of 350–600 nm were performed using a UV–Vis spectrometer (Perkin Elmer Lambda 35) with $BaSO_4$ as reference.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the catalysts are shown in Fig. 2. As shown in Fig. 2(a), TiO_2 P25 is a mixture of anatase and rutile. Based on the respective peak intensities, the rutile content in the TiO_2 powder can be determined using the following equation [22]:

$$x = \left(1 + 0.8\frac{I_A}{I_R}\right)^{-1} \tag{9}$$

where x is the weight fraction of rutile in the powders, while I_R is the intensity of rutile peak at $2\theta = 27.5^\circ$ and I_A is the intensity of the anatase peak at $2\theta = 25.3^\circ$. The average of anatase to rutile ratio was determined to be 78:22. Fig. 2(b) shows that ZnO has a hexagonal structure. According to the half-peak width using the Scherrer equation [23], the average crystallite sizes were about 30 nm and 182 nm for TiO_2 and ZnO, respectively. Furthermore, the BET surface area of TiO_2 ($47.3\,m^2/g$) and ZnO ($5.9\,m^2/g$), revealing that TiO_2 has smaller crystal size with larger surface area than ZnO. As shown in Fig. 3, ZnO possessed higher absorption than TiO_2 in UV and visible regions, inferring a higher efficiency for the generation of electron-hole pairs than TiO_2. The band gap energies of the samples were determined by extrapolating the steep lines of the absorption spectra to the axis of wavelength [24]. The intersection represents the optical band gap of the samples according to the formula:

$$E_g = \frac{1240}{\lambda} \tag{10}$$

The measured band gap energies of the catalysts were 3.16 eV for TiO_2 and 3.20 eV for ZnO, respectively.

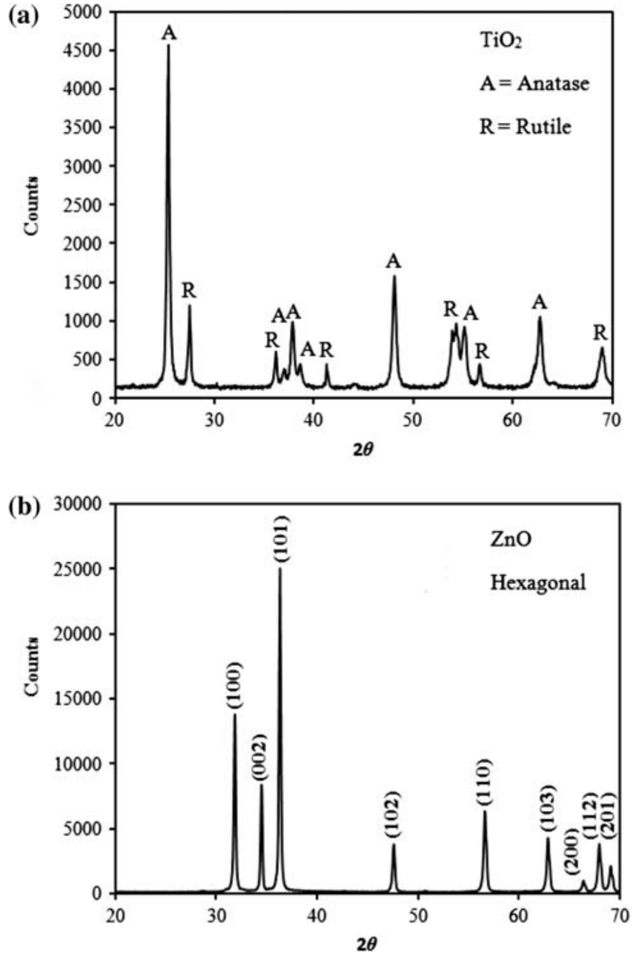

Fig. 2. XRD patterns of (a) TiO_2 and (b) ZnO.

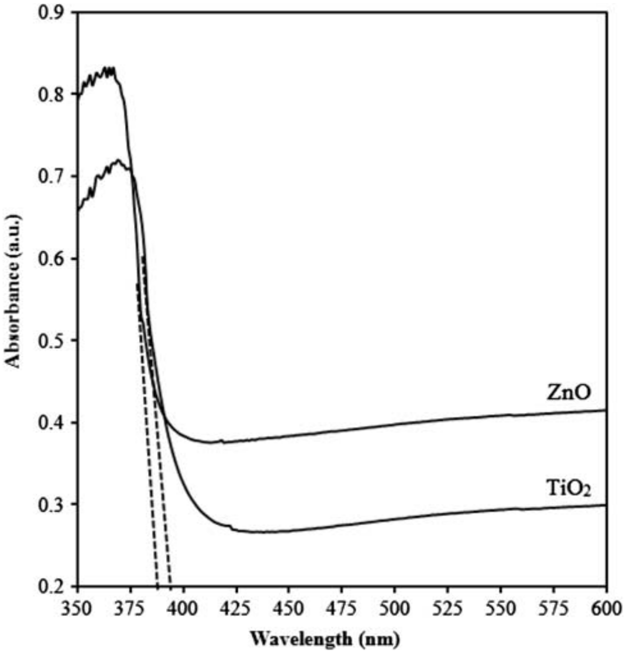

Fig. 3. UV–Vis absorption spectra of TiO_2 and ZnO.

3.2. Mechanisms for phenol and resorcinol degradation

Photocatalytic degradation reactions of organic pollutants usually take more than one elementary step to complete. An intermediate is the reaction product of each of these steps which eventually forms the final product in the last step. Identification of these reaction intermediates would provide a further insight into the mechanism involved in the photocatalytic degradation process and will help to get a total picture of the degradation pathway. On this facet, the reaction solutions were analyzed by HPLC using reference samples of various intermediates to identify individual peaks in the HPLC chromatogram.

Fig. 4 shows typical time-dependent HPLC chromatogram and proposed pathway for photocatalytic degradation of phenol with ZnO. The prominent peak was noticed at retention time (RT) 5.3 min which decreased gradually and finally disappeared demonstrating that phenol had been degraded. In

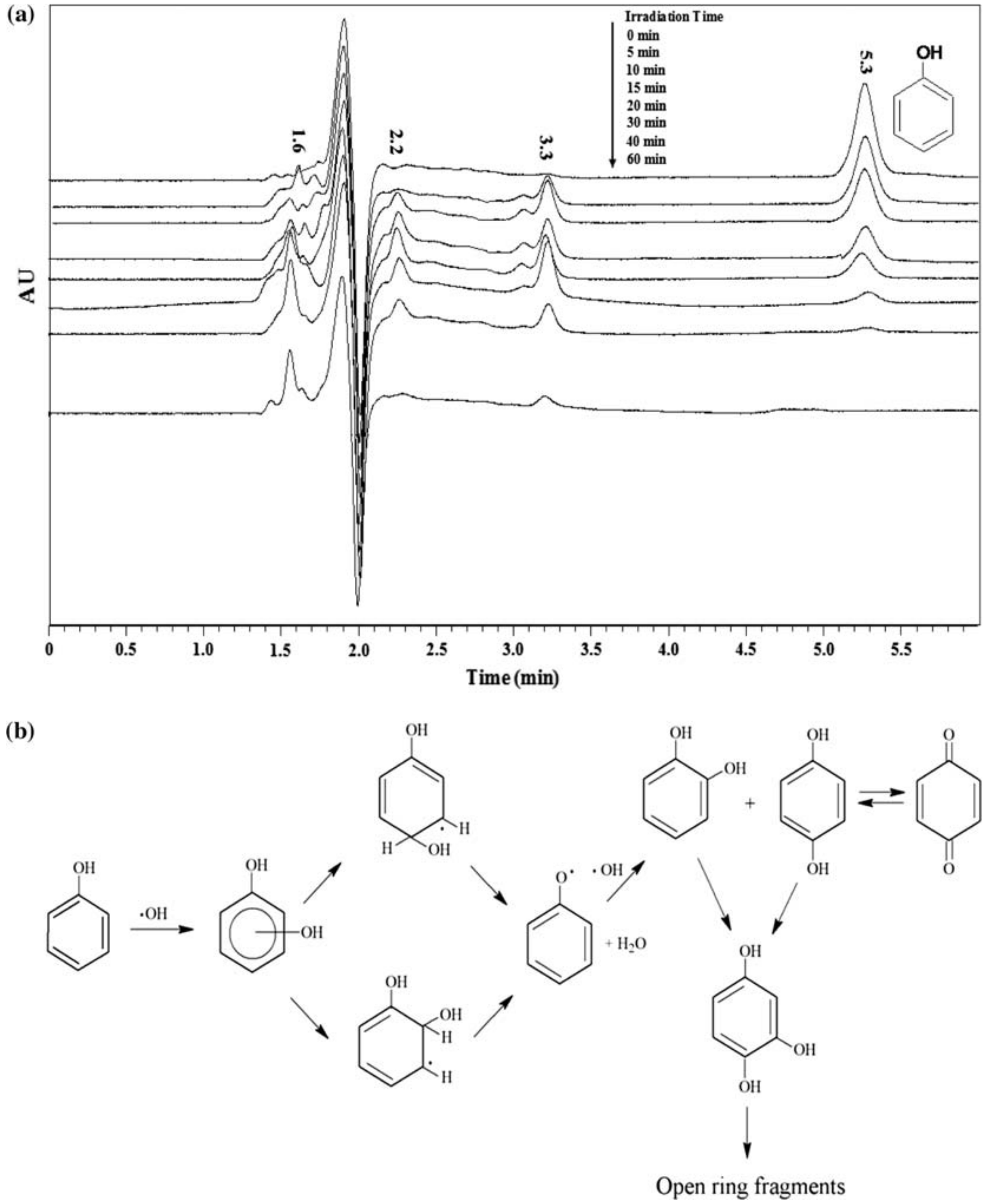

Fig. 4. Photocatalytic degradation of phenol via ZnO. (a) Time-dependent HPLC chromatogram; (b) proposed pathway during the photocatalytic reaction.

the degradation of phenol, the hydroxyhydroquinone RT 1.6 min, catechol RT 2.2 min, benzoquinone RT 3.3 min were the main intermediates identified. Photocatalysis is predominantly a •OH radical oxidation reaction involving sequential hydroxylation of the organic pollutant [11,25]. The process of degrading phenol can be seen in Fig. 4(b), where •OH radicals formed mainly attacked in the *para* and *ortho* positions and generated catechol and benzoquinone as primary intermediates. However, the *meta* position was less favoured by the electrophilic nature of •OH radicals, thus it was not surprising that no resorcinol was observed as the phenol intermediate in this study. Under the reaction of •OH radicals, these single aromatic intermediates were subsequently converted to

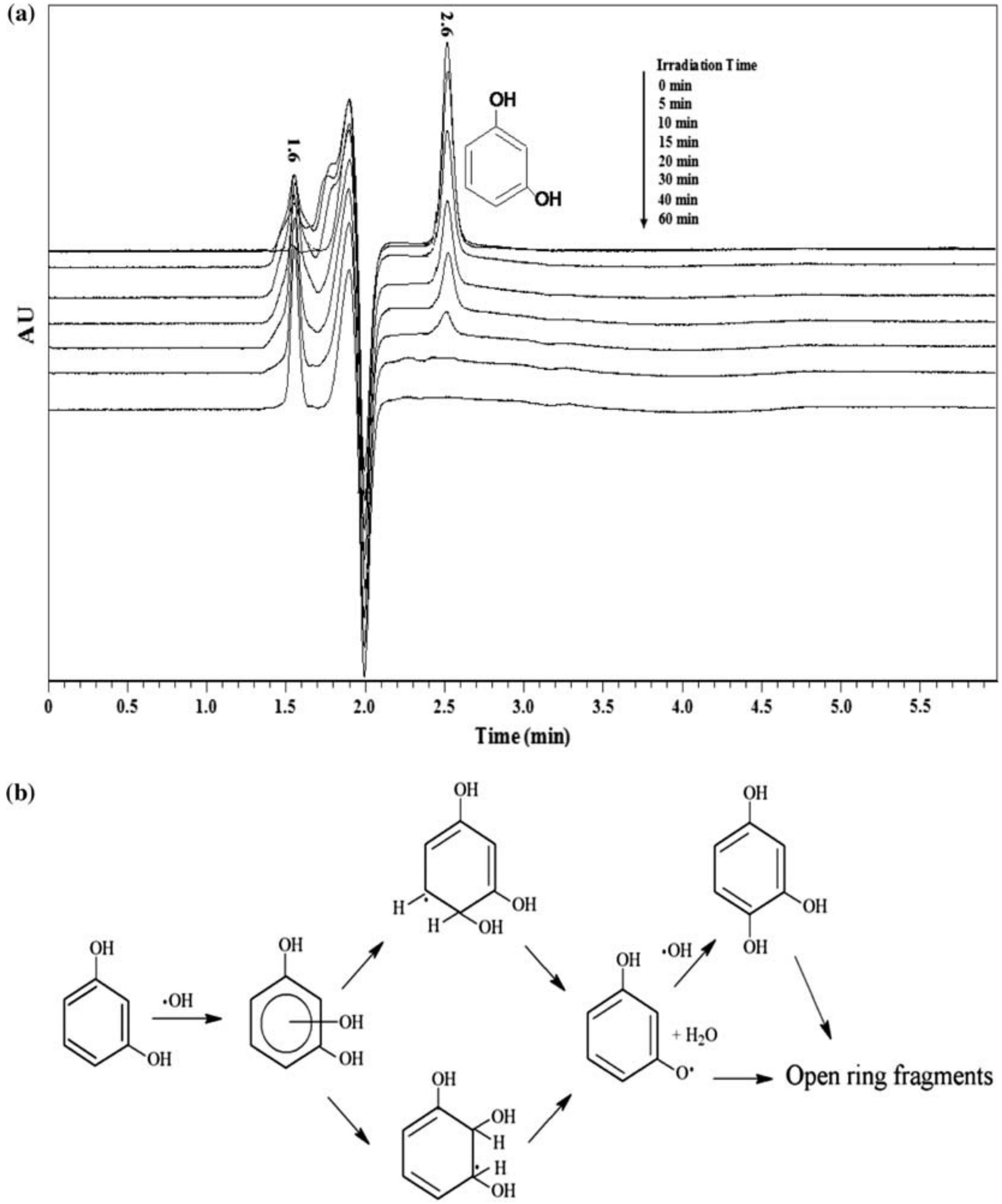

Fig. 5. Photocatalytic degradation of resorcinol via ZnO. (a) Time-dependent HPLC chromatogram; (b) proposed pathway during the photocatalytic reaction.

hydroxyhydroquinone by further hydroxylation followed by ring fragmentation.

The HPLC chromatogram and proposed pathway for photocatalytic degradation of resorcinol with ZnO are shown in Fig. 5. Resorcinol showed peak at RT equal to 2.6 min which reduced and finally disappeared during the reaction, revealing that the resorcinol was completely degraded after 60 min irradiation. Using the standard chemical, the main intermediate detected during resorcinol degradation was only hydroxyhydroquinone RT 1.6 min. The degradation pathway proposed in Fig. 5(b) was consistent with the results of other research groups using ZnO nanoparticles as catalysts [26,27]. For example, Patil et al. [27] reported that •OH radicals were also preferred to attack electron rich *ortho* or *para* carbon atoms of resorcinol. In their investigation, trihydroxycyclohexadienyl radicals were formed and underwent further oxidation to yield trihydroxybenzene.

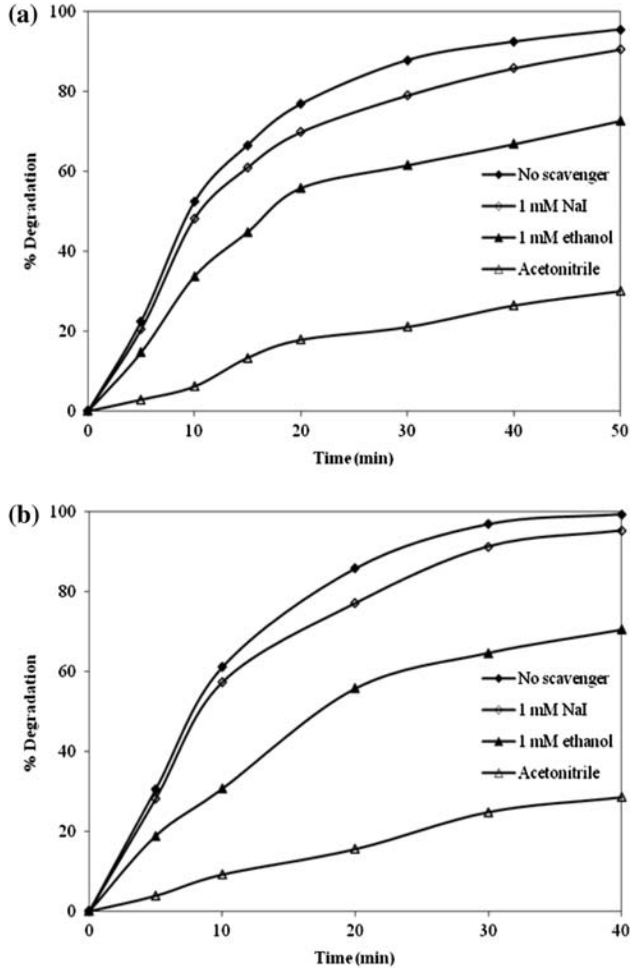

Fig. 6. Effect of radical scavengers on the photocatalytic degradation of (a) phenol (ZnO dose = 2 g/L; pH 5.2; [phenol] = 10 mg/L) and (b) resorcinol (ZnO dose = 2 g/L; pH 6.8; [resorcinol] = 10 mg/L). Scavenger concentration: ethanol 1 mM, sodium iodide 1 mM and acetonitrile as solvent.

To test whether the photocatalytic degradation of phenol and resorcinol took place via •OH radicals, experiments were carried out by adding different radical scavengers into the reaction solution. It is well-known that ethanol is a very effective trap for •OH radical and NaI is a very effective trap for h_{vb}^{+} [14,28,29]. As shown in Fig. 6(a) and (b), the degradation efficiencies of phenol and resorcinol on ZnO decreased significantly from 92.5% to 66.9% and 99.5% to 70.5%, respectively after 40 min irradiation when ethanol was added into the photocatalytic reaction solution, reflecting the participation of •OH radical in the reaction mechanism. Differently, the degradation efficiencies of phenol and resorcinol were slightly retarded from 92.5% to 85.9% and 99.5% to 95.3%, respectively in the same duration with the addition of NaI, revealing that h_{vb}^{+} played a minor role on the degradation of both single EDCs compared to the •OH radical. Furthermore, acetonitrile, an extremely stable molecule was used to replace water as a solvent in order to further distinguish the participation of •OH radical or h_{vb}^{+} in the photocatalytic reaction mechanism. A non-aqueous reaction medium ruled out the participation of •OH radical, formed by water getting trapped in the hole, in the oxidation process [28,30]. The results showed that when the reaction was performed without water (100% acetonitrile), the reaction was greatly suppressed. Hence, the photogenerated active •OH radical was the main driving for the photocatalytic degradation of phenol and resorcinol in these present experiments.

3.3. Degradation of phenol under different experimental conditions

Degradation of phenol was examined under five different experimental conditions via UV alone, UV/TiO_2, UV/ZnO, dark/TiO_2 and dark/ZnO. Fig. 7 shows the photocatalytic degradation of phenol under these experimental conditions. Initially blank experiments under UV alone revealed that in the absence of catalyst there was no noticeable change in phenol concentration after 60 min irradiation. Then photocatalytic experiments were performed using both catalysts at constant catalyst dosage 2 g/L and phenol concentration 10 mg/L. When experiments were carried out with UV/ZnO, the complete degradation of the solution was obtained after 60 min irradiation, while with UV/TiO_2, 52.9% of the initial concentration of phenol remained in the solution for the same duration. It indicated that ZnO demonstrated to be more

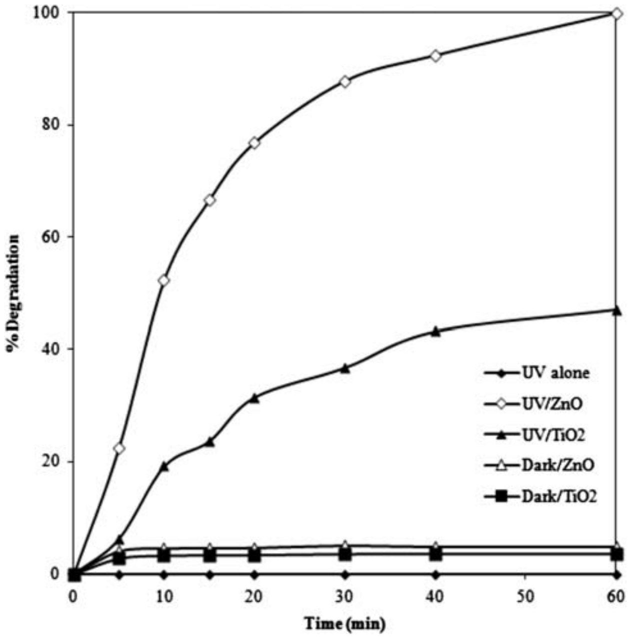

Fig. 7. Photocatalytic degradation of phenol (photocatalyst dosage = 2 g/L; pH 5.2; [phenol] = 10 mg/L).

efficient than TiO_2 for the photocatalytic degradation of phenol. Subsequently, the adsorption of phenol with both dark/ZnO and dark/TiO_2 were found to have very low removal (<5%).

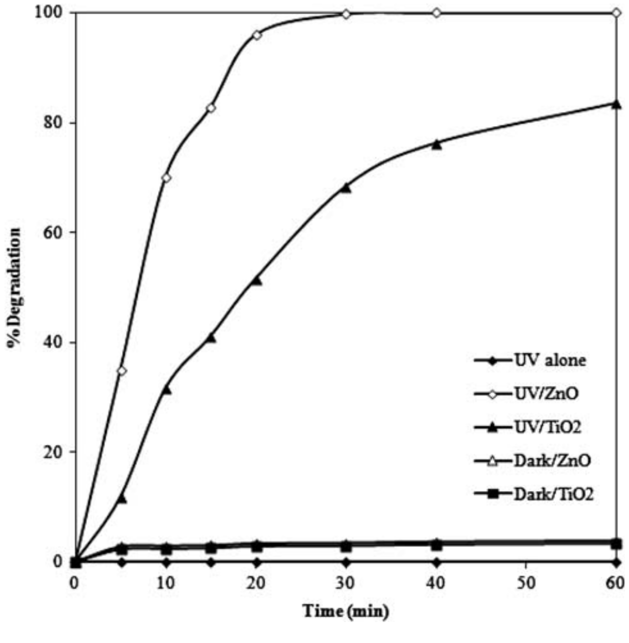

Fig. 8. Photocatalytic degradation of resorcinol (photocatalyst dosage = 2 g/L; pH 11.0; [resorcinol] = 10 mg/L).

3.4. Degradation of resorcinol under different experimental conditions

Similarly the degradation of resorcinol was investigated under different experimental conditions as that of phenol and the results are depicted in Fig. 8. In the case of UV alone, the resorcinol concentration was also remained unchanged after 60 min irradiation. Complete resorcinol degradation was observed when experiments were performed with UV/ZnO after 40 min irradiation, whereas with UV/TiO_2, only 76.2% degradation was attained for the same duration. The adsorption of resorcinol was found to be less than 4% with both dark/ZnO and dark/TiO_2. The findings also clearly exhibited that ZnO was a more efficient catalyst for the degradation of resorcinol. These results were concordant with those previously reported for the photocatalytic degradation of other aromatic and dye pollutants [10,14,31]. The higher photocatalytic activity of ZnO can be described on the basis of optical properties of TiO_2 and ZnO [32]. Therefore, subsequent experiments were conducted with ZnO for both single EDCs.

3.5. Degradation of single EDCs via ZnO

3.5.1. Effect of photocatalyst dosage

The dependencies of single phenol and resorcinol degradation on the photocatalyst dosage are presented in Fig. 9(a) and (b), respectively, at natural pH. The examined range of the photocatalyst dosage varied from 0.5 to 3.0 g/L. As can be seen in the figure, the initial slopes of the curves increased greatly by increasing the photocatalyst dosage from 0.5 to 2.5 g/L for phenol thereafter the efficiency of degradation decreased. In the case of phenol, maximum degradation was obtained with 2.5 g/L and for resorcinol maximum degradation was observed with merely 2.0 g/L dose and then increasing the dose of photocatalyst had no positive effect. The effect of photocatalyst dosage on the photocatalytic degradation of both EDCs can be explained in terms of the active sites on the ZnO available for photocatalytic degradation and the penetration of UV light [3,7,15,33]. As the dosage of photocatalyst increased, an increase in the number of photons absorbed and also the amount of pollutant molecules adsorbed on the ZnO surface enhanced the photocatalytic degradation [15]. However, when the photocatalyst was overdosed, the degradation efficiency decreased due to the interception of the UV light by the suspension. Mahalakshmi et al. [33] added that as the excess photocatalyst prevented the irradiation, •OH radical as a primary oxidant in the

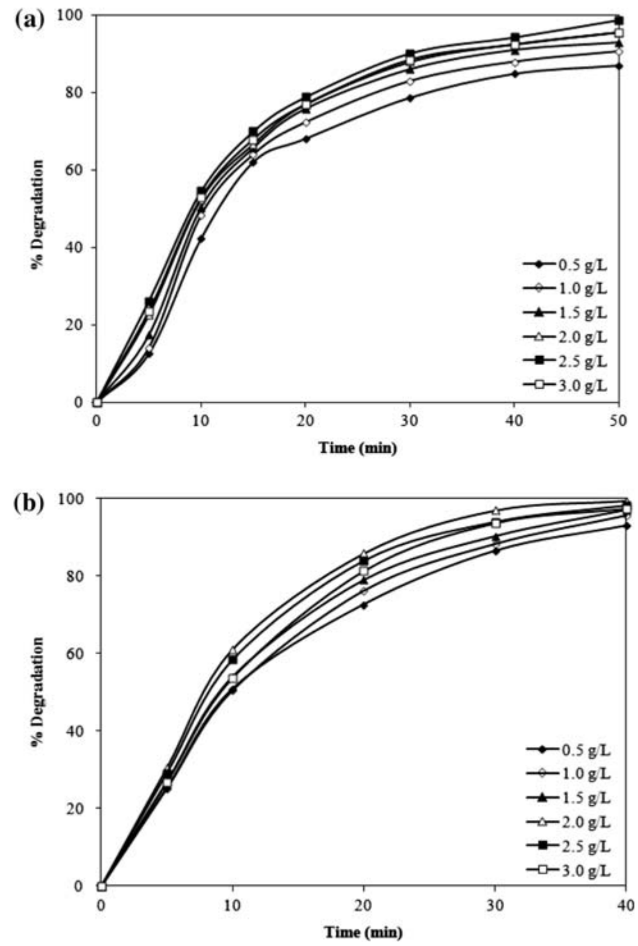

Fig. 9. Effect of ZnO dose on the photocatalytic degradation of (a) phenol (pH 5.2; [phenol] = 10 mg/L) and (b) resorcinol (pH 6.8; [resorcinol] = 10 mg/L).

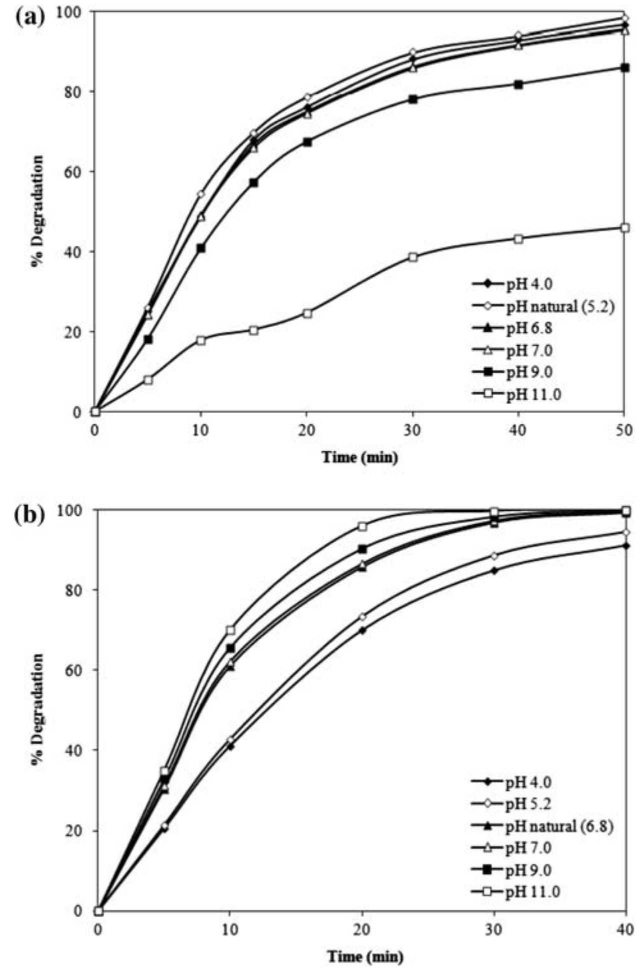

Fig. 10. Effect of pH on the photocatalytic degradation of (a) phenol (ZnO dose = 2.5 g/L; [phenol] = 10 mg/L) and (b) resorcinol (ZnO dose = 2.0 g/L; [resorcinol] = 10 mg/L).

photocatalytic system decreased and the efficiency of the degradation was reduced accordingly. Moreover, higher dosage of ZnO may increase the particle aggregation, hence a part of the photocatalyst surface became unavailable for photon absorption and degradation efficiencies of both EDCs decreased [33]. In the following experiments, the photocatalyst doses of 2.5 and 2.0 g/L were fixed for phenol and resorcinol, respectively in order to avoid the excess of photocatalyst and to ensure total absorption of efficient photons.

3.5.2. Effect of solution pH

The roles of solution pH in the photocatalytic degradation of single phenol and resorcinol were studied in the range from pH 4 to pH 11. Fig. 10(a) and (b) illustrate the degradation efficiencies of phenol and resorcinol as a function of solution pH. As can be seen, the degradation efficiency of resorcinol increased with increase in solution pH demonstrating maximum degradation at pH 11. In the case of phenol, the maximum degradation was attained at pH 5.2. The interpretation of pH effects on the efficiency of photocatalytic degradation process is associated to the acid base property of metal oxide surface and can be elucidated on the basis of zero point charge. The adsorption of water molecules at surficial metal sites is followed by the dissociation of OH^- groups, leading to coverage with chemically equivalent metal hydroxyl groups (M-OH). Due to amphoteric behaviour of most metal hydroxides, the following surface reactions are expected to occur at different pH values (Eqs. (11) and (12)) [32,34].

$$\text{M-OH} + \text{H}^+ \rightarrow \text{M-OH}_2^+ \quad \text{p}Ka_1 \tag{11}$$

$$\text{M-OH} + \text{OH}^- \rightarrow \text{M-O}^- + \text{H}_2\text{O} \quad \text{p}Ka_2 \tag{12}$$

where *Ka* is the acidity constant. The p*Ka* values for ZnO have been estimated as 7.6 for pKa_1 and 11 for pKa_2, which resulted in a pH of zero point charge ($pHzpc = 0.5(pKa_1 + pKa_2)$) of 9.3 [35]. Accordingly ZnO surface is protonated below pH 9.3 and above this pH, catalyst surface is predominantly negatively charged by adsorbed OH^- ions. The presence of large amount of OH^- ions on the ZnO surface as well as in the reaction solution favoured the formation of •OH radicals, which are considered as principal oxidizing species responsible for degradation process at neutral or high pH levels and thus the efficiency of the process is logically enhanced.

The results showed that higher degradation of phenol was found to be in acidic conditions. This behaviour was ascribed to the undissociated state of the phenol in acidic conditions which favoured its adsorption on the positive ZnO surface [36]. However, resorcinol was found to undergo degradation at faster efficiency at high pH values. The interpretation for the same could be amphoteric behaviour of the ZnO catalyst. Even though the adsorption of resorcinol was low at alkaline pH, the possible explanation for this behaviour was the presence of higher concentration of OH^- ions and/or higher fraction of hydrolyzed forms of pollutant, which can lead to the generation of more of the •OH radicals with strong oxidation power. It is important to note that the photocatalytic degradations of some phenolic EDCs is more efficient in alkaline solution [14] and others at acidic or near to neutral pH [36,37].

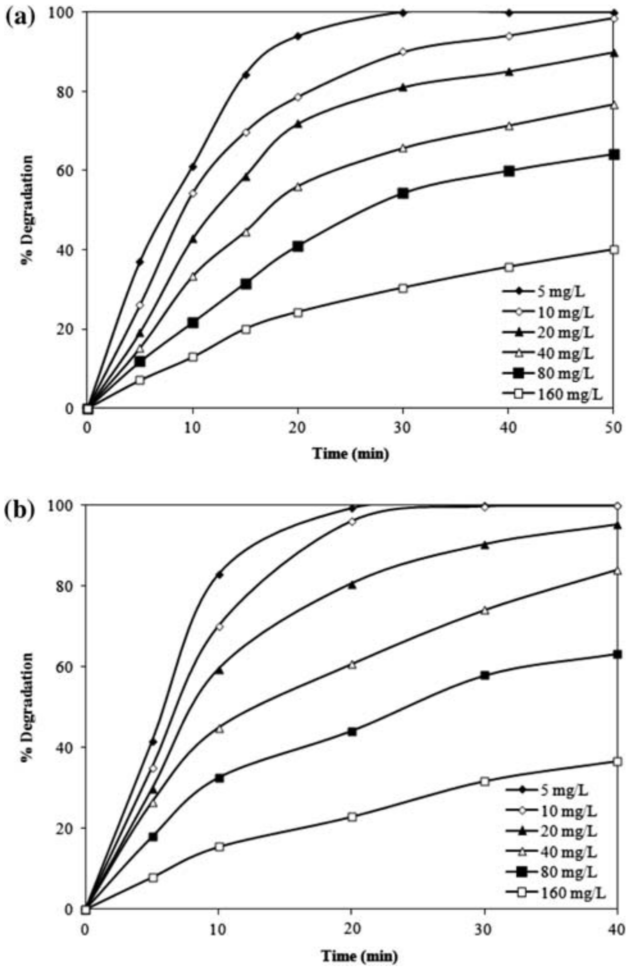

Fig. 11. Effect of initial substrate concentration on the photocatalytic degradation of (a) phenol (ZnO dose = 2.5 g/L; pH 5.2) and (b) resorcinol (ZnO dose = 2.0 g/L; pH 11.0).

3.5.3. Effect of initial substrate concentration

The influences of initial substrate concentration on the photocatalytic degradation of single phenol and resorcinol were studied under the determined experimental conditions with pH 5.2 and photocatalyst dosage 2.5 g/L for phenol and pH 11 and photocatalyst dosage 2.0 g/L for resorcinol. Fig. 11(a) and (b) shows the photocatalytic degradation of phenol and resorcinol, respectively at different initial substrate concentrations in the range of 5–160 mg/L. As can be seen, the initial substrate concentration had a pronounced effect on the amount of substrate degraded. At the same irradiation time, the degradation efficiencies of both single EDCs decreased with increasing initial substrate concentration. For example, complete phenol degradation was observed after 30 min irradiation when initial substrate concentration was 5 mg/L. However, only 30.4% of phenol was degraded in the same duration when initial substrate concentration increased up to 160 mg/L. Under the experimental conditions stated above, 100% and 31.7% of resorcinol were degraded at initial resorcinol concentration of 5 and 160 mg/L, respectively after 30 min irradiation.

The initial substrate concentration dependence of the degradation efficiencies of both single EDCs could be ascribed to three possible reasons: first, at high substrate concentrations, the generation of •OH radicals on the surface of photocatalyst are reduced [9,38]. The •OH radicals are formed by the reactions of h_{vb}^+ with adsorbed OH^- anions and water. Since most of the active sites on the surface of ZnO are covered by EDC molecules at high substrate concentrations, there are only fewer active sites available for the adsorption of OH^- anions. Second, with the increase in the substrate concentration, the UV light absorbed by the EDCs is more than that of photocatalyst. Consequently, fewer photons managed to activate the photocatalyst surface for •OH radicals generation [39]. The third possible reason is the interference of intermediates formed during the photocatalytic reaction. Zhang et al. [25] have reported that the main intermediates such as catechol, hydroquinone and hydroxyhydroquinone formed during the phenol degradation were strongly adsorbed on the surface of photocatalyst and competed with phenol molecules for the same active sites on the surface of photocatalyst, therefore hindering the degradation efficiency of phenol.

3.5.4. Reusability of photocatalyst

At the time of study of effects of various operating parameters, fresh ZnO was used for every photocatalytic degradation experiment. Reuse of ZnO was separately investigated by maintaining all other parameters constant. During this study, the catalysts resulting from the photocatalytic degradation of both single EDCs were filtrated, washed several times with deionized water and left at room temperature for 24 h. Recovered ZnO was then reused for new photodegradation cycle in the absence of any further treatment such as heating in any kind of furnace. The results are shown in Fig. 12(a) and (b). At the first cycle, complete degradation of phenol and resorcinol were achieved after 30 min irradiation. As increasing the recycling cycles, the efficiencies of both single EDCs decreased slightly, which were still higher than 96% after be used for three cycles. The results revealed the stability of ZnO as a photocatalyst.

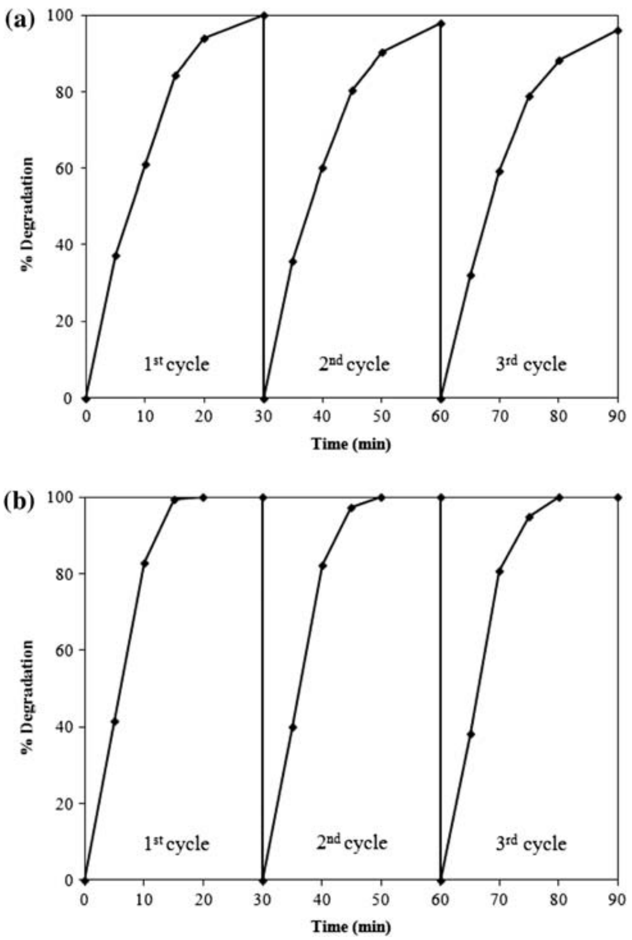

Fig. 12. Cycling runs in photocatalytic degradation of (a) phenol (ZnO dose = 2.5 g/L; pH 5.2; [phenol] = 5 mg/L) and (b) resorcinol (ZnO dose = 2.0 g/L; pH 11.0; [resorcinol] = 5 mg/L).

3.6. Kinetic analysis

The photocatalytic degradation kinetics of many aquatic organics have often been modeled with the Langmuir–Hinshelwood equation expressed as Eq. (13):

$$r = \frac{kKc}{1 + KC} \tag{13}$$

where r is the reaction rate, C is the substrate concentration, k is the reaction rate constant and K is the adsorption equilibrium constant. At low substrate concentrations, the rate r is therefore proportional to the substrate concentration with k_{obs} being the observed first order rate constant:

$$r = kKC = k_{obs}C \tag{14}$$

Further, the photocatalytic reaction equation can be expressed as an observed first order rate:

$$r = k_{obs}C = -\frac{dC}{dt} \tag{15}$$

The integral form of the pseudo-first-order rate equation is basically stated as follows:

$$\ln\left(\frac{C}{C_o}\right) = -k_{obs}t \tag{16}$$

where C_o is the equilibrium concentration of substrate after 5 min dark adsorption and C is the substrate concentration at time t. A plot of $-\ln(C/C_o)$ vs. irradiation time t generates a straight line and the slope is the k_{obs}.

Applying the fittings of pseudo-first-order model, the values of k_{obs} were listed in Table 1. On the basis of the results indicated in Table 1, the noteworthy features are as follows:

Table 1
Values of k_{obs} and R^2 for the photocatalytic degradation of phenol and resorcinol using ZnO at various experimental conditions

Operating parameter	Value	Phenol		Resorcinol	
		k_{obs} (min^{-1})	R^2	k_{obs} (min^{-1})	R^2
Photocatalyst dosage	0.5 g/L	0.0464	0.9413	0.0662	0.9991
	1.0 g/L	0.0526	0.9534	0.0748	0.9943
	1.5 g/L	0.0590	0.9636	0.0829	0.9903
	2.0 g/L	0.0655	0.9885	0.1200	0.9760
	2.5 g/L	0.0793	0.9839	0.0968	0.9939
	3.0 g/L	0.0653	0.9837	0.0895	0.9947
Solution pH	4.0	0.0695	0.9970	0.0613	0.9965
	5.2	0.0793	0.9839	0.0711	0.9921
	6.8	0.0647	0.9950	0.1200	0.9760
	7.0	0.0635	0.9948	0.1258	0.9680
	9.0	0.0443	0.9456	0.1534	0.9440
	11.0	0.0139	0.9577	0.1838	0.9536
Initial substrate concentration	5 mg/L	0.1278	0.9591	0.2345	0.9417
	10 mg/L	0.0793	0.9839	0.1838	0.9536
	20 mg/L	0.0499	0.9639	0.0777	0.9956
	40 mg/L	0.0323	0.9547	0.0463	0.9888
	80 mg/L	0.0228	0.9700	0.0273	0.9596
	160 mg/L	0.0113	0.9542	0.0122	0.9742

(1) Applying the regression analysis, the pseudo-first order kinetic model also revealed by many authors [36,40,41] emerged to be in accordance with the experimental results on the photocatalytic degradation of phenol and resorcinol as the correlation coefficients of higher than 0.94 for all the photocatalytic experiments.

(2) It was found that the variations of k_{obs} values listed in Table 1 with the operating parameters (photocatalyst dosage, solution pH and initial substrate concentration) were in parallel with results demonstrated in Figs. 9–11. For example, the k_{obs} values increased from 0.0464 to 0.0793 min^{-1} when photocatalyst dosage increased up to 2.5 g/L for phenol degradation, whereas they increased from 0.0662 to 0.1200 min^{-1} when photocatalyst dosage increased up to 2.0 g/L for resorcinol degradation. Consistently, the degradation efficiency of phenol increased with increase in photocatalyst dosage exhibiting maximum degradation at 2.5 g/L. In the case of resorcinol the maximum degradation efficiency was obtained at 2.0 g/L photocatalyst dosage.

3.7. Comparison of photocatalytic degradation of single EDCs via different photocatalysts

The effects of different operating parameters through photocatalyst dosage, solution pH and initial substrate concentration on the degradation of single

Table 2
Comparison between ZnO and TiO_2 for the photocatalytic degradation of phenol and resorcinol under optimized conditions after 20 min irradiation

Photocatalyst	Phenol				Resorcinol			
	Degradation (%)	TOC (%)	EE/O (kW h/m^3 ·order)	Cost (RM/ (m^3·order)	Degradation (%)	TOC (%)	EE/O (kW h/ m^3·order)	Cost (RM/ (m^3·order)
ZnO	93.9	46.5	11.76	2.56	99.4	50.1	6.43	1.40
TiO_2	61.5	17.3	34.47	7.51	66.2	18.9	30.33	6.61

phenol and resorcinol were also examined using TiO_2 as photocatalyst. The optimal photocatalyst dosage was observed to be 4.5 and 4.0 g/L for phenol and resorcinol, respectively. The efficiency of degradation of each EDC also decreased with increase in initial substrate concentration. The degradation of phenol and resorcinol had maximum efficiency at pH 5.2 and pH 11.0, respectively with TiO_2 (results not shown).

The comparative evaluation of TiO_2 and ZnO for the degradation, mineralization and cost estimation of single EDCs is illustrated in Table 2. The results obviously showed that ZnO was a better photocatalyst in both single EDCs. After 20 min irradiation, the resorcinol was almost completely degraded and more than 50% of the carbon content was mineralized with ZnO, whereas with TiO_2, only 66.2% degradation and 18.9% mineralization efficiencies were observed. In the case of phenol photocatalyzed by ZnO, the degradation and mineralization efficiencies were found to be 93.9% and 46.5%, respectively. As in the case of TiO_2, only 61.5% of phenol was degraded in the same duration accompanied with a low mineralization of 17.3%. The reason for greater activity of ZnO can be owing to the absorption of more light quanta. In addition, the band gap of ZnO was larger than TiO_2, and this makes the photogenerated electron-hole pair of ZnO to have a stronger redox potential, which leads to an increase of the photocatalytic efficiency. The specific surface area of ZnO (5.9 m^2/g) was far less than that of TiO_2 (47.3 m^2/g). The higher photocatalytic efficiency of ZnO implied that surface area was not the determining factor for the degradation of phenol and resorcinol. The results reported in Table 2 also revealed that the degradation was found to be faster as compared to the mineralization proving the formation of smaller organic intermediates probably corresponding to aliphatic acids that were not detected by HPLC and contributing to the carbon content remaining in solution [37,42,43]. Thus, it seems that to achieve complete mineralization of these EDCs, longer irradiation time is needed.

The evaluation of the treatment cost is an important aspect that needs greater attention. Although there are a number of important parameters affecting the decision of using one wastewater treatment technology, the economical concerns are often paramount. Since the photocatalytic degradation of organic pollutant is an electrical energy intensive and electrical energy can represent a major fraction of the operating costs, simple figures of-merit based on electrical energy consumption can be very useful and informative [44]. The UV dose when related to an AOP is a measure of the total lamp electrical energy applied to a fixed volume of water. Considering first order degradation kinetics, the UV dose was calculated to be 14.29 kW h/m^3 for each of the processes using Eq. (17).

$$\text{UV dose} = \frac{\text{lamp power (kW)} \times \text{time (h)}}{\text{treated volume (m}^3\text{)}} \tag{17}$$

On the other hand, electrical energy per order (E_{EO}) is a powerful scale-up parameter and is defined as electrical energy in kilowatt hours (kW h) required to reduce the concentration of pollutant by one order of magnitude (or 90%) in 1 m^3 of contaminated water. The relationship between UV dose and E_{EO} is shown in Eq. (18).

$$\text{UV dose} = E_{EO} \log\left[\frac{C_o}{C}\right] \tag{18}$$

The E_{EO} values calculated from the above equation are given in Table 2.

Finally, it is useful to relate the E_{EO} values observed in this study to treatment costs. The cost of 1 kW h of electricity in Malaysia is RM 0.218 (Ringgit Malaysia)

$$\text{Electrical cost}\left[\frac{\text{RM}}{\text{m}^3 \times \text{oder}}\right] = E_{EO} \times \text{power cost}\left[\frac{\text{RM}}{\text{kW h}}\right] \tag{19}$$

The estimated operating costs (electrical costs) for the photocatalytic degradation of phenol and resorcinol using both catalysts are given in Table 2, which implies that the photocatalysis process in presence of ZnO can be extremely helpful in reducing the energetic cost of real wastewater treatment.

Table 3
Values of k_{obs} and R^2 for the photocatalytic degradation of binary phenol and resorcinol solutions

C_o (mg/L)		Phenol		Resorcinol	
Phenol	Resorcinol	k_{obs} (min^{-1})	R^2	k_{obs} (min^{-1})	R^2
5	0	0.0934	0.9804	–	–
0	5	–	–	0.1402	0.9673
5	5	0.0598	0.9667	0.0766	0.9487
5	10	0.0367	0.9771	0.0513	0.9473
5	20	0.0188	0.9509	0.026	0.9566
10	5	0.0322	0.9490	0.0621	0.9689
20	5	0.0188	0.9537	0.0416	0.9768

3.8. Degradation of binary EDCs via ZnO

The photocatalytic degradation of binary phenol and resorcinol solutions was investigated under UV/ZnO. The range of C_o used in the investigated binary solutions is shown in Table 3. Initial solution pH was adjusted to 7.0 so as to create a standard for comparison. In binary solutions, the photocatalytic degradation of each EDC also followed the pseudo first-order kinetics [45–48]. For this reason, for each EDC in solutions the k_{obs} values were calculated similarly as in the earlier experiments (Section 4.5). The obtained k_{obs} values are listed in Table 3. It was observed that photocatalytic degradation of phenol and resorcinol in binary solutions was slower than the corresponding ones in single solutions under comparable conditions. In addition, the difference between the k_{obs} values of phenol and resorcinol in binary solutions became lesser compared to that in single solution, even though resorcinol still degraded faster than phenol. That was not only the retarded but also the competitive effect between phenol and resorcinol for their attachment on the surface sites of ZnO or for their attack by the •OH free radicals. A previous study that investigated the degradation of a three components mixture of 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) has reported lack of surface saturation coverage by 4-CP when equimolar mixture of 2,4-DCP and 2,4,5-TCP presented in the solution [49]. These DCP and TCP competed effectively with 4-CP for the active sites on the photocatalyst surface, leading to a significant decrease in the concentration of active 4-CP on the surface.

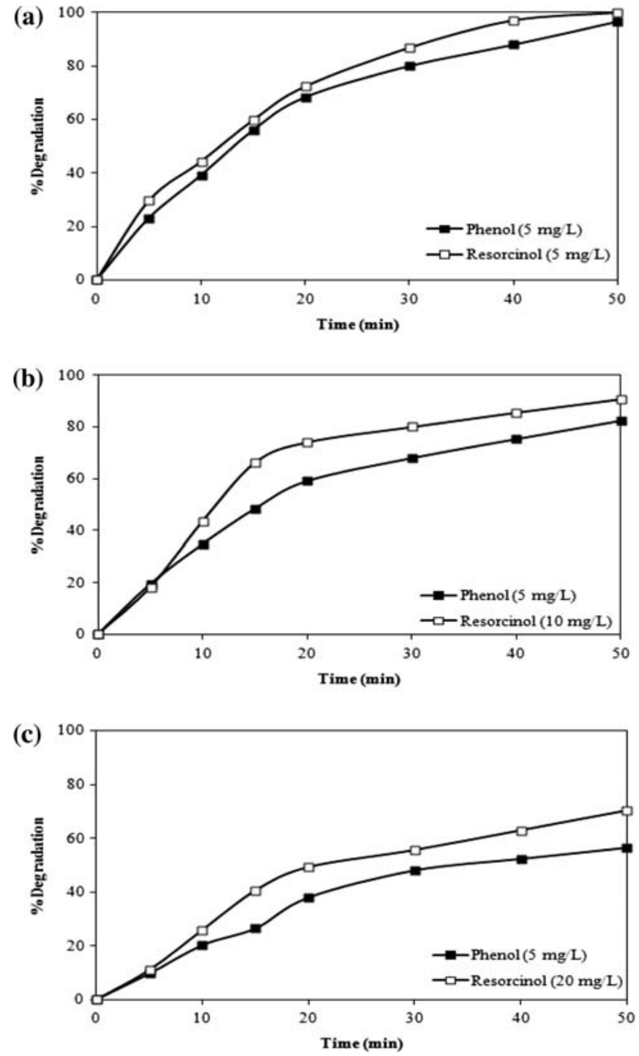

Fig. 13. Effects of initial substrate concentration on the photocatalytic degradation of phenol and resorcinol in binary solutions (ZnO dose = 2.0 g/L; pH 7.0).

Fig. 13 shows the degradation curves of 5 mg/L phenol when the concentration of resorcinol varied from 5 to 20 mg/L at pH 7.0. As can be seen, the degradation efficiency of resorcinol by the addition of phenol decreased with an increase in the initial concentration of resorcinol. Under comparable conditions, photocatalytic degradation of binary phenol and resorcinol solutions resulted in an appreciable degradation of resorcinol, whereas, degradation of phenol was comparatively much lower. The attack by the •OH radicals has been reported to be favoured in positions of *ortho* and *para* related to an OH substituent on the benzene ring already present. For this reason, resorcinol which has three positions with double activation located at 2-, 4- and 6-positions were favoured for electrophilic substitution. The 4- and 6-positions were coordinated at the *ortho*- and *para*-positions (*o*-, *p*-) and 2-position at the *ortho*- and *ortho*- (*o*-, *o*-) with respect to both hydroxyl groups of the resorcinol molecule [50]. Due to stronger activation of the resorcinol molecule, substitution reactions can take place faster than phenol (which has three unsubstituted positions activated only once). Thus, the extent of decreased degradation was more significant for resorcinol.

4. Conclusions

TiO_2 and ZnO can efficiently catalyze the degradation of phenol and resorcinol in the presence of light. Both EDCs were found to degrade more efficiently in the presence of UV/ZnO as compared to UV/TiO_2. The main reason for greater activity of ZnO can be owing to the absorption of more light quanta. The degradation of both EDCs was further confirmed by the formation of intermediates using HPLC data. It was observed that phenol and resorcinol degradation largely inhibited in the presence of •OH radical scavengers suggested that the process mainly involved •OH radical. In addition, reusability of the ZnO photocatalyst showed no significant reduction in the photocatalytic performance of both single EDCs degradation. The effects of the photocatalyst dosage, solution pH and initial substrate concentration have also investigated. The results demonstrated that the degradation efficiency increased with increase in photocatalyst dosage up to an optimum loading. Further increase in photocatalyst dosage had no positive effect. The optimal solution pH for photocatalytic degradation of single phenol and resorcinol was obtained at 5.2 and 11.0, respectively. In addition, the photocatalysis worked best at low substrate concentration as the degradation efficiencies decreased with increasing the initial substrate concentration for both single EDCs.

Photocatalytic degradation of binary phenol and resorcinol solutions was investigated under UV/ZnO. It was observed to be slower than the corresponding ones in single solutions under comparable conditions. This was the retarded effect. The difference between the observed rate constants of phenol and resorcinol in binary solutions became lesser compared to the cases in single solutions, even though resorcinol still degraded faster than phenol. Thus, the existence of competitive effect was vindicated.

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