

## Photocatalytic degradation of aniline in water using CuO nanoparticles

Samira Norzaee, Babak Djahed, Razieh Khaksefidi and Ferdos Kord Mostafapour

### ABSTRACT

The removal of aniline as a carcinogen from aqueous environments is highly significant. In the present study, the feasibility of photocatalytic degradation of aniline by CuO nanoparticles was evaluated. A batch reactor with an internal UV lamp was used and the effects of the parameters of pH (3–11), dosage of catalyst (0.01–0.1 g/L), initial concentration of aniline (50–250 mg/L), and duration of reaction (15–90 min) were investigated. The remaining concentration of aniline was determined by spectrophotometer at the wavelength of 198 nm. The Langmuir–Hinshelwood model was used for examining the kinetics of the reaction. The results showed that the degradation of aniline is maximum at pH 7. Also, the removal efficiency of 90.16% after 90 minutes of reaction in the case of initial concentration of 50 mg/L was obtained. The aniline degradation was elevated from 40 to 82% by increasing CuO nanoparticles' dosage from 0.01 to 0.1 g/L. In addition, the obtained data properly fit with the Langmuir–Hinshelwood kinetic model and showed that the  $K_{app}$  decreased from 0.029 to 0.016  $\text{min}^{-1}$  by increasing of the initial concentration of aniline. Considering the obtained results, the UV/CuO process can be an effective method for removing aniline from aqueous solution.

**Key words** | aniline, CuO nanoparticles, degradation, photocatalyst, ultraviolet radiation

#### Samira Norzaee

**Babak Djahed** (corresponding author)  
Department of Environmental Health Engineering,  
Iranshahr University of Medical Sciences,  
Iranshahr,  
Iran  
E-mail: [babak.djahed@gmail.com](mailto:babak.djahed@gmail.com)

#### Razieh Khaksefidi

Department of Environmental Health Engineering,  
Faculty of Health,  
Zahedan University of Medical Sciences,  
Zahedan,  
Iran

#### Ferdos Kord Mostafapour

Health Promotion Research Center, Faculty of  
Health,  
Zahedan University of Medical Sciences,  
Zahedan,  
Iran

### INTRODUCTION

The aromatic compounds are among the important chemical materials found in industrial wastewaters which can enter surficial and underground waters directly or indirectly (Casero *et al.* 1997). These compounds are highly toxic, carcinogenic, and mutagenic, and their existence in water is fatal to aquatic life even at very low concentrations (Saidman *et al.* 2006). One of the poisonous aromatic compounds is aniline, which is used as raw material or intermediates in certain industries such as the manufacture of plastic materials, dyes, pesticides, and pharmaceutical products. This compound can directly infiltrate the environment through industrial wastewaters or indirectly through degradation of organic compounds (Gómez *et al.* 2009).

Aniline (Figure 1) is a simple aromatic amine compound which is composed of a benzene ring attached to an amino

ring (Anotai *et al.* 2010; Matsumura *et al.* 2013). This organic compound is soluble in water soluble at 3.5%. This level of solubility makes it a potential pollution for water resources. Also, it is carcinogenic and mutagenic and it can cause numerous diseases, such as cyanosis, anemia, decreased appetite, weight loss as well as nervous, renal, hepatic, and bone marrow disorders (Tang *et al.* 2010; Anotai *et al.* 2012; Wu *et al.* 2012). Therefore, this dangerous compound should be treated and removed from wastewaters before infiltration into the environment (Dvořák *et al.* 2014; Zabihi-Mobarakeh & Nezamzadeh-Ejhieh 2014).

In previous studies, aniline had been treated by certain methods such as advanced oxidation process (Chen & Huang 2015), absorption (An *et al.* 2009), biological process (Delnavaz *et al.* 2010), reverse osmosis (Gómez *et al.* 2009),

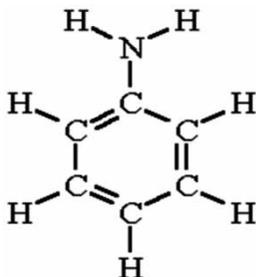
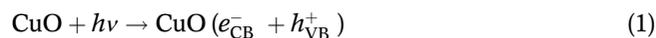


Figure 1 | Structural formula of aniline.

and electrochemical process (Ferreira *et al.* 2015). Among different methods, in aqueous environments, advanced oxidation processes are one of the most effective and efficient technologies for degradation and removal of dangerous, resistant, and non-biodegradable organic pollutants (Babaa-hamdi-Milani & Nezamzadeh-Ejhih 2016). This method is based on the generation of hydroxyl radical (OH<sup>•</sup>) which can quickly oxidize organic pollutants. Among advanced oxidation processes, photocatalysis is used as a successful method to degrade various organic pollutants (Xiao *et al.* 2015). Heterogeneous photocatalysis is a combination of a semi-conductive catalyst such as TiO<sub>2</sub>, ZnO, ZnS, Fe<sub>2</sub>O<sub>3</sub>, CdS, WO<sub>3</sub>, ZrO<sub>2</sub>, and CuO and radiation of visible or ultraviolet light (El-Kemary & El-Mehasseb 2010; Behnajady & Eskandarloo 2013). Different studies on aniline removal in aqueous environments have used photocatalytic degradation. For instance, Nitoi *et al.* (2015); Ku *et al.* (2010), and Zabihi-Mobarakeh & Nezamzadeh-Ejhih (2014) used TiO<sub>2</sub> semiconductor for removing aniline from aqueous environments. In addition, Karunakaran and Senthilvelan used ZrO<sub>2</sub> (Karunakaran & Senthilvelan 2005a) and CdS (Karunakaran & Senthilvelan 2005b), separately, for degradation of aniline.

In the present study, the feasibility of using CuO nanoparticles as catalyst in the photocatalysis process of aniline removal in aqueous solution is investigated. When CuO nanoparticles are exposed to UV radiation, the photons with equal or higher energy level than the band gap are absorbed. Consequently, the electrons are stimulated from the valence band (VB) to conduction band (CB) and an electron hole, called 'hole', is concurrently formed in the VB (Derikvandi & Nezamzadeh-Ejhih 2017). A number of electrons and holes can attain the surface of nanoparticles and cause decrease or oxidation of organic and inorganic

forms which are adsorbed on the surface of nanoparticles. Oxygen acts as a receiver and it attracts electrons, consequently, highly oxidative radicals of hydroxyl are made (Equations (1)–(4)) (Skoumal *et al.* 2006; Katsoni *et al.* 2011; Rauf *et al.* 2011):



## MATERIALS AND METHODS

### Apparatus and materials

All chemical materials required in the present study including NaOH, HCl, dimethyl sulfoxide, aniline (molar mass of 93.13 g/mol and purity of 99.5%), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), silver sulfate (Ag<sub>2</sub>SO<sub>4</sub>), mercury (II) sulfate (HgSO<sub>4</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and potassium hydrogen phthalate (KHP) were supplied by Merck Company. In addition, copper oxide nanoparticles (size >50 nm, molecular weight: 79.55 g/mol) were purchased from Sigma-Aldrich Chemical Company. Also, a UV-C lamp with definite power (30 watt) and wavelength (254 nm) was prepared by Philips Company. In addition, a UV-visible spectrophotometer (Labnics, model: LUV-100A) was used for measuring the concentration of aniline in the collected samples while another type of spectrophotometer (HACH, model: Dr5000) was used for measuring chemical oxygen demand (COD). The D5220 method is adopted to determine COD according to *Standard Methods for the Examination of Water and Wastewater*, 22nd edition (2012).

### Methodology and analysis

A batch system was used to conduct the present study. The aniline stock solution and dimethyl sulfate were prepared

daily. Then, from the stock solutions, different concentrations were prepared through dilution in deionized water.

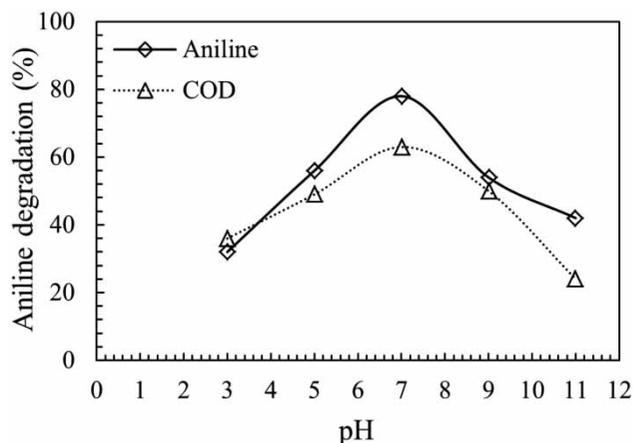
The aniline solution was inserted into a Plexiglas reactor and inside the reactor; a 30 watt UV-C lamp was installed for irradiating the aniline solution. For reflection of the UV light output and to increase its efficiency, all around the reactor was covered by aluminum sheets. For homogenization of the solution within the reactor, magnetic stirring was used. At the beginning of each experiment and after adding nanoparticles to the solution, the sample was put in the dark for 30 minutes so as to let the aniline solution and nanoparticles attain equilibrium. All experiments were repeated three times at the laboratory temperature ( $27 \pm 3$  °C). For sedimentation and separation of nanoparticles, each sample was centrifuged for 10 minutes at a speed of 3,000 rpm. To ensure complete separation of the nanoparticles, a 10 mL sample was passed through 0.2  $\mu$ m polytetrafluoroethylene syringe filters.

The effect of different parameters, including pH (3, 5, 7, 9, and 11), duration of exposure (15, 30, 60, and 90 minutes), dose of CuO nanoparticles (0.01–0.1 g/L) and different concentrations of aniline (50–250 mg/L) on the aniline removal efficiency was evaluated. For studying the effect of each parameter, in each round of experiments three parameters were constant and only one parameter varied. The concentration of aniline for each collected sample was measured at the wavelength of 198 nm. In addition, for determining the influence of UV alone on degradation of aniline, in the case of different contact times, 100 mg/L aniline was exposed to UV and the remaining concentration of aniline was measured.

## RESULTS AND DISCUSSION

### Effect of pH

One of the parameters affecting photocatalytic degradation is the pH of the solution. In order to examine the effect of pH, the aniline removal at different pH levels (3, 5, 7, 9, and 11) was determined (Figure 2). Based on Figure 2, as pH level increases from 3 to 7, the aniline removal efficiency increases significantly in the way that at pH 7, the efficiency of removal obtained was 78%. By increasing pH from 7 to



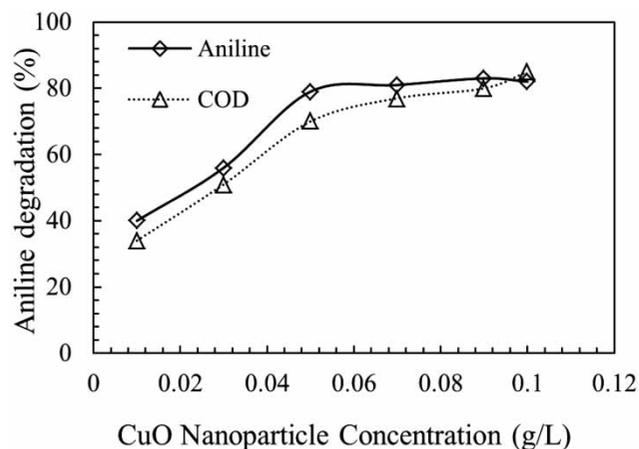
**Figure 2** | Effect of pH on UV/CuO process for aniline degradation (concentration of CuO = 0.05 g/L, aniline concentration = 100 mg/L, time = 60 min).

11, the efficiency of removal of aniline reduced so that the percentage of removal at pH 11 was about 42%. The effect of pH depends on the zero point charge of catalyst and acidity constant ( $pK_a$ ) (Jonidi-Jafari et al. 2015). Hence, in the present study the decline of efficiency for acidic and alkaline pH levels is associated with  $pK_a$  and  $pH_{ZPC}$  parameters. The value of  $pK_a$  for aniline is 4.6 (Ku et al. 2010), and the value of  $pH_{ZPC}$  for CuO nanoparticles is equal to 9.4 (Mahdavi et al. 2012). Therefore, aniline and CuO nanoparticles at pH levels of 4.6 and 9 had positive charge. At pH level higher than these values, aniline and CuO nanoparticles had negative charge. In adjacency to these pH levels, aniline and CuO nanoparticles had neutral charge. As a result, at pH levels of lower than 4 and higher than 9, or pH levels close to these values, the absorption of aniline on copper oxide nanoparticle is reduced due to the neutrality of surface charge of one of these two materials and this leads to reduced efficiency of removal. Also, the previous studies suggest that at pH level lower than 7, the increase of  $H^+$  concentration and the increase of  $OH^-$  absorption into the solution lead to reduced formation of hydroxyl radical and therefore removal efficiency is decreased (Yang & Lee 2006). Also, with acidification of the solution by HCl, a high amount of conjugated base is added. Inorganic radical ions ( $ClO^-$ ) are generated by enabling of  $Cl^-$  to react with hydroxyl radicals. These generated inorganic radical anions are less reactive than  $OH^-$ , thus they do not take part in the aniline degradation. There is serious competition between the aniline and

anions with regard to  $\text{OH}^\cdot$  (Arabpour & Nezamzadeh-Ejehieh 2015). In addition, the increase of pH level from 7 to 10 is followed by increased formation of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . These ions consume  $\text{OH}^\cdot$  radicals and reduce their concentrations. As a result, for high pH the reason for reduced efficiency is the existence of a proper context for formation of carbonate ions. This ion can effectively capture  $\text{OH}^\cdot$  ions and, therefore, can reduce the rate of degradation (Yang & Lee 2006). At higher pH values, the presence of high amounts of  $\text{OH}^\cdot$  radicals causes radical-radical reactions, and then leads to the consequent deactivation of  $\text{OH}^\cdot$  radicals (Nezamzadeh-Ejehieh & Khorsandi 2010). The results reported by Anotai et al. (2012) on photocatalytic degradation of aniline are consistent with the results of the present study; they found pH 7 to be the optimum pH for removal of aniline.

### Effect of CuO nanoparticle concentration

The concentrations of 0.01, 0.03, 0.05, 0.07, 0.09, and 0.1 g/L of CuO were used for examining the effect of CuO nanoparticle concentration. As seen in Figure 3, the obtained results suggest that as the dose of CuO nanoparticles increases from 0.01 to 0.05 g/L, the efficiency increases from 40 to 79% and the percentage of COD removal increased from 34 to 70%. The increase in the level of removal efficiency is due to the fact that as the value of CuO increases, the number of active sites absorbing aniline will increase. This will lead to an increase in production of free electrons in the CB,



**Figure 3** | Effect of CuO nanoparticle concentration on aniline degradation (pH = 7, aniline concentration = 100 mg/L, time = 60 min).

higher production of hydroxyl radicals as well as increased percentage of aniline removal (Goswami et al. 2012). Based on Figure 3, with the increase in the concentration of nanoparticles from 0.05 to 0.1 g/L, the efficiency of removal increased to 82%. However, it did not significantly affect the removal efficiency. This is due to the fact that if the dose of nanoparticles goes higher than a definite concentration, the level of UV light penetration into the nanoparticles declines because of adhesion of nanoparticles. Hence, less catalyst particles can be activated, and then the production of hydroxyl radicals and the degradation efficiency of aniline consequently reduces (Gondal et al. 2011; Nezamzadeh-Ejehieh & Shirzadi 2014). These results have good concordance with the findings of Chiou et al. (2008), who stated, that as the concentration of nanoparticles increases, the number of electron holes will rise and this could increase the number of hydroxyl radicals as well as removal percentage, but as the concentration of nanoparticles rises above a definite value, it inhibits the UV penetration and removal percentage does not increase significantly.

### Effect of initial concentration of aniline and reaction time

The kinetics of photocatalytic degradation of organic compounds in aqueous solutions is generally described through the Langmuir-Hinshelwood model (Equation (5)). This model represents the effect of pollutant concentration on photocatalytic degradation rate (Cheng et al. 2007; Chiou et al. 2008). This model is fundamentally used for expressing the association of degradation rate ( $r$ ) with reactant concentration in water ( $C$ ) and time ( $t$ ) (Cheng et al. 2007; Chiou et al. 2008).

$$r = -\frac{dc}{dt} = \frac{k_r K_{ad} C}{1 + K_{ad} C} \quad (5)$$

In the above equation,  $r$  is the rate of degradation,  $C$  is the concentration of reactant,  $k_r$  is the rate constant and  $K_{ad}$  refers to absorption equilibrium constant. In the case of photocatalytic degradation, if the surface adsorption or concentration of organic compounds is low, the above

equation can be simplified such as in Equation (6) (Shaban et al. 2013):

$$\ln\left(\frac{C}{C_0}\right) = k_r K_{ad} t = K_{app} t \quad (6)$$

In Equation (6),  $C_0$  shows the initial concentration of aniline. For determining  $K_{app}$  constant,  $\ln(C/C_0)$  in contrast versus reaction time was plotted (Figure 4). In the resulting diagram, the line slope is equal with  $K_{app}$ . In Table 1,  $K_{app}$  and correlation coefficient ( $R^2$ ) of the aniline degradation kinetic model are represented for different initial concentrations.

For studying the effect of initial concentration of aniline and reaction time, the removal percentage of initial concentrations of 50, 100, 150, 200, and 250 mg/L of aniline was examined at 15, 30, 60, and 90 minutes. As shown in Figure 5, the increase of reaction time to up to 30 minutes leads to high slope of the aniline removal percentage in all studied concentrations; however, as reaction time increases, the slope of the

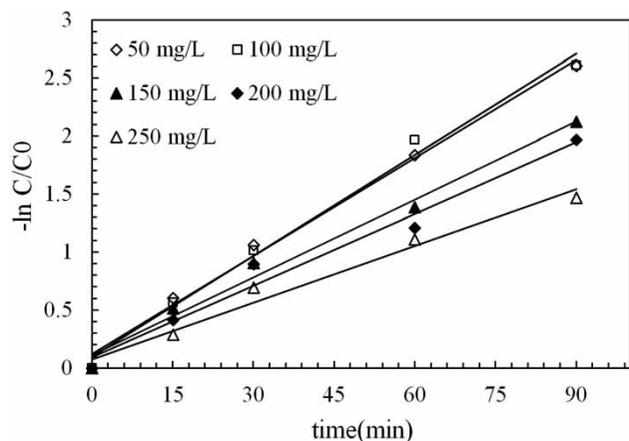


Figure 4 |  $\ln(C/C_0)$  versus reaction time.

Table 1 | Rate constant ( $K_{app}$ ) and correlation coefficient ( $R^2$ ) for different initial concentrations of aniline

$C_0$ (mg/L)	$K_{app}$ ( $\text{min}^{-1}$ )	$R^2$
50	0.029	0.9926
100	0.0282	0.9911
150	0.0224	0.9858
200	0.0206	0.9779
250	0.0163	0.9742

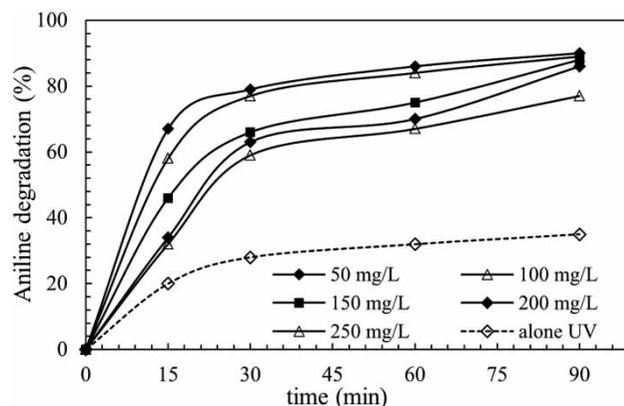


Figure 5 | Effect of initial concentration of aniline and reaction time on efficiency of aniline degradation (pH = 7, concentration of CuO = 0.05 g/L).

vector reduces. This could be due to quick degradation of pollutants by free radicals generated from excitement of electronic nanoparticles at the initial times of the process. As the time of reaction increases and despite the fact that excitement of nanoparticles and generation of free hydroxyl radicals do not decline, the degradation of aniline forms some intermediate organic compounds and a part of the generated radicals is used in the degradation of these compounds; as a result, the rate of aniline removal is reduced by increasing time. On the other hand, the increase of initial concentration of aniline from 50 to 250 mg/L was followed by decreased efficiency of aniline removal. At the reaction time of 60 minutes, the removal efficiency levels at concentrations of 50, 100, 150, 200, and 250 mg/L were 86.41, 84.23, 75.11, 70.90, and 67.16%, respectively. Likewise, Rauf et al. (2011) reported that by increasing the pollutant concentration and reaction time, the rate of pollutant removal would decline which completely supports our findings. The reduced efficiency in the case of high aniline concentrations is due to the fact that active nanoparticle sites are covered by aniline and, consequently, the generation of hydroxyl radical declines (Ahmed et al. 2011; Saggiaro et al. 2011). In addition, the results of different studies suggest that by increasing concentration, the generation of intermediate compounds increases and this state deactivates the active sites of nanoparticles; hence, due to the short lifetime of the generated hydroxyl radicals, they should instantly participate in the aniline degradation reactions (Azimi & Nezamzadeh-Ejhieh 2015). As well, these intermediate compounds compete for reaction with hydroxyl radicals and cause efficiency declines

(Gaya et al. 2009). Also in Figure 5, the level of aniline degradation through UV is compared with UV/CuO degradation scenario. As shown in Figure 5, the sole use of UV has less efficiency in comparison with the UV/CuO process. In fact, the efficiency of UV is suitable for degradation of those materials which have high molar absorption coefficients such as phenol. Hence, as can be seen in Figure 5, the combined process has a higher efficiency for aniline removal.

### Pathways of aniline removal reactions

In the photocatalytic degradation process, when semi-conductive nanoparticles are placed against photons with equal energy or higher energy than band-gap energy, some electron pairs are generated. In neutral and relatively alkaline pH, the released electrons (as shown in Equations (7)–(14)) can react with oxygen atoms which act as the final recipient of electrons. Consequently, the oxygen atom changes from  $O_2$  to  $O_2^{\cdot-}$  (Ahmed et al. 2011):



The probable mechanism of aniline degradation by hydroxyl radicals is shown in Figure 6. As seen in Equations (7)–(14) and Figure 6, the generated  $O_2^{\cdot-}$  and  $OH^\circ$  react with aniline and cause its degradation. Consequently, aniline is decomposed to intermediate compounds such as dianiline, 4-anilino phenol, and azobenzol. Then, the benzene ring of these intermediate compounds is debonded by hydroxyl radical ( $OH^\circ$ ) and certain compounds such as

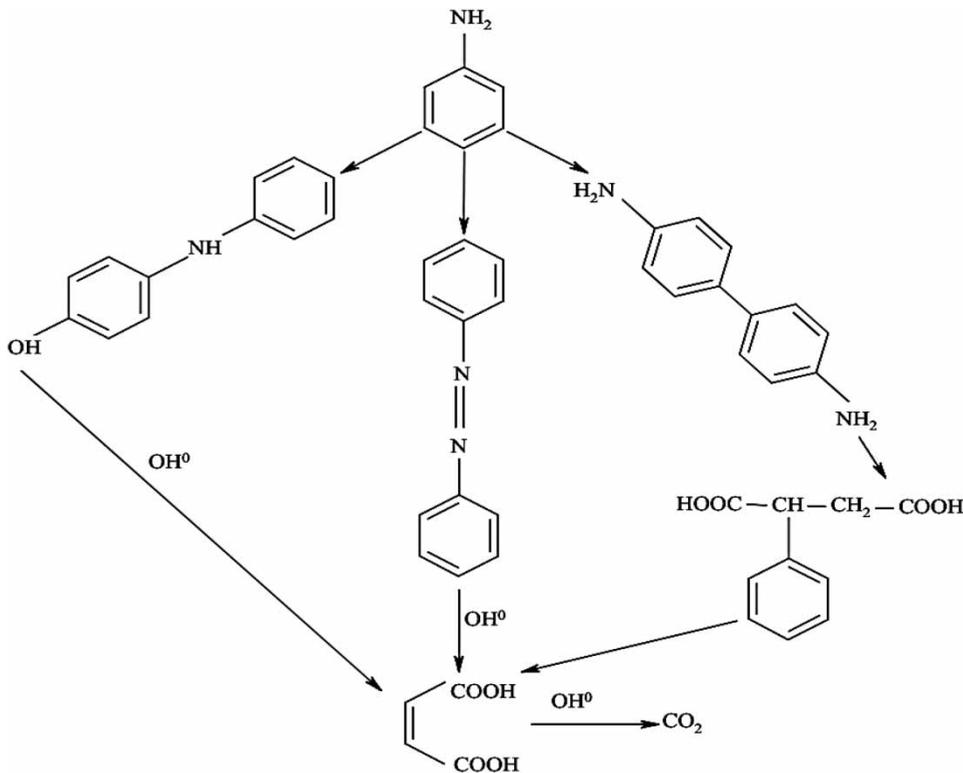


Figure 6 | Probable mechanism of aniline degradation by hydroxyl radicals (Li et al. 2003).

phenylsuccinic acid, maleic acid, and other organic compounds with low molecular weight are generated, and finally, the latter compounds are degraded into CO<sub>2</sub> and H<sub>2</sub>O (Li et al. 2003; Kumar & Mathur 2004; Jiang et al. 2016).

## CONCLUSION

In the present study, the feasibility of removing water-soluble aniline through UV/CuO process was investigated. The results of the present study show that the combination method of UV/CuO could degrade aniline in aqueous solution efficiently, such that it could even reach 89% of aniline removal at the initial concentration of 50 mg/L. As well, the obtained data from COD reduction revealed that the proposed method not only can decompose soluble aniline, but it also obviously mineralized this organic pollutant. It was also found that at neutral pH the presented method is more efficient and the kinetics of aniline removal is explained by the Langmuir-Hinshelwood model properly. Finally, the results of the present study proved that photocatalytic degradation using CuO nanoparticles could be used as an effective water treatment process for removal of aniline from polluted waters.

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