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Effect of organic matter on cyanide removal by illuminated titanium dioxide or zinc oxide nanoparticles

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Abstract

Effect of different type of organic compounds (humic acid, oxalate, ethylenediaminetetraacetic acid, nitrilotriacetic acid, phenol) on the photocatalytic removal of cyanide with TiO_2 or ZnO was studied in this work with variation of the solution pH, contact time, initial cyanide concentration and type of organic compounds. Photocatalytic oxidation efficiency of cyanide with TiO_2 was greatly affected by the solution pH. It increased as the solution pH decreased. Also maximum removal of cyanide by ZnO was observed near at neutral pH because of the reduced photocatalytic activity of ZnO at exceedingly low and high pH values originated from either acidic/photochemical corrosion of the catalyst and/or surface passivation with $Zn(OH)_2$. Removal efficiency of cyanide greatly decreased in the presence of humic acid, ethylenediaminetetraacetic acid, nitrilotriacetic acid compared to that without presence of organic compound because of the competitive oxidation as well as surface blocking by relatively large organic compounds. The oxidation pattern of cyanide was better described by first-order kinetic model. Finally photocatalytic reaction with TiO_2 or ZnO can be effectively applied to treat synthetic wastewater contaminated with cyanide.

Keywords: Photocatalysis, Nanoparticle, Titanium dioxide, Zinc oxide, Organic compound, Cyanide

Background

Cyanide (CN) is a highly toxic component, which is generated from several industrial activities such as gas production, pharmaceutical, mining, electroplating processes and coal gasification [1,2]. It is known that wastewater generated from electroplating industry contains high concentration of cyanide [3]. Cyanides emissions are increasing at a fast rate and cause a serious concern since they are toxic to living organisms even at very low concentrations [1,4]. Physicochemical methods such as chlorination, electrolytic oxidation, ozonation, etc. and biological methods have been applied to remove cyanides. The generally accepted physicochemical technique for the treatment for the industrial waste containing cyanide compounds is alkaline chlorination [5-10]. The first reaction product generated from chlorination is cyanogen chloride (CNCl), a

highly toxic gas having limited solubility. The toxicity of CNCl may exceed that of equal concentrations of cyanide. At an alkaline pH, CNCl hydrolyzed into the cyanate ion (CNO^-), which has only limited toxicity [1,2].

To conquer these problems, advanced oxidation processes (AOP) have been studied and are recommended as talented techniques. Overall, AOPs use hydroxyl free radical ($HO^{\cdot}$) as a strong oxidant to destroy inorganic compounds that cannot be oxidized by conventional oxidants such as oxygen, ozone and chlorine. The hydroxyl radical can be generated in aqueous solutions using UV/O_3, UV/H_2O_2, $Fe(II)/H_2O_2$ and UV/TiO_2 [11,12]. Among these methods, photocatalytic reaction using UV/TiO_2 can treat inorganic compounds and heavy metals at the same time through oxidation and adsorption process. Consequently, this method can be used as pre- or post-treatment methods to extra wastewater treatment methods because it is suitable to fit and inexpensive process in the application of wastewater treatment. TiO_2 has been widely used as the form of suspension or as a thin film in water treatment [6,8,13]. Also ZnO has much

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Table 1 Physicochemical properties of TiO₂ and ZnO

Properties	TiO$_2$	ZnO
Specific surface area (BET) (m^2/g)	50 ± 15	90
Average primary particle size (nm)	21	20
Ignition loss 2 hours at 1000°C, based on material dried for 2 hours at 105°C (wt.%)	≤ 2	≤ 2

attention because electron in valence band of ZnO can be excited at room temperature under low excitation energy. The greatest advantage of ZnO is that it absorbs over a larger fraction of the solar spectrum than that of TiO$_2$ [11]. The surfaces of ZnO support strong chemisorption of oxygen and are sensitive to ultraviolet (UV) light [14,15]. The most important properties of ZnO are non-toxic in itself, providing attractive photocatalytic efficiency [16]. Photocatalytic reaction using ZnO/UV can simultaneously treat organic compounds and metallic elements in addition to change non-biodegradable to biodegradable organic compounds [17,18]. ZnO is used as an effective, inexpensive and nontoxic photocatalyst for the degradation of synthetic dyes, oxidation cyanide and reduction of Cr(VI) [17,19,20].

As wastewater generated from electroplating industry generally contains high concentration of cyanide, synthetic wastewater containing cyanide concentration ranging from 50 to 200 mg/L was used in this work [3]. The present study investigated the effect of different type of organic compounds (humic acid (HA), oxalate, ethylenediaminetetraacetic acid (EDTA), nitrolotriacetic acid (NTA), phenol) on the photocatalytic removal of cyanide by illuminated titanium dioxide or zinc oxide nanoparticles with variation of solution pH, contact time and initial cyanide concentration. In addition, kinetic parameters were obtained by application of zero, first and second-order equations.

Material and methods
P-25 TiO$_2$ (an 80/20 mixture of anatase and rutile) was obtained from Degussa Corp. It has approximately spherical and non porous shape with greater than 99.5%

purity. The specific surface area of the TiO$_2$ particles was 50±15 m^2/g according to Evonik-Industrial Co. Average particle size of the TiO$_2$ particles was 21 nm. Also ZnO with greater than 99% purity was obtained from Nano Pars Lima Company in Iran. It has approximately spherical and non porous shape. Average particle size of the ZnO particles was 20 nm. Physicochemical properties of TiO$_2$ and ZnO were summarized in Table 1. Also organic compounds with greater than 99% purity were obtained from Merck Company in Germany. All chemicals were analytical grade and solutions were prepared with deionized water (18 MΩ-cm) from a Hydro-Service reverse osmosis/ion exchange apparatus.

Experimental set-up
The experimental set-up for photocatalytic reactor used in this work is schematically shown in Figure 1. A 125 W medium-pressure UV-lamp emitting maximum wavelength at 247.3 nm and light intensity equal to 1020 μw/cm^2 measured by a Spectroline model DRC-100× digital radiometer combining with a DIX-365 radiation sensor (Shokofan Tosee company in Iran). The reactor consists of two compartments: the outer one can contain 2 L solution and the inner one house a UV lamp. The outer part of the reactor is a 10 L water-bath maintained at 25°C for all experiments. All photocatalytic experiments were performed with 1,000 mL solution. During experiments, the test solution in the reactor was constantly stirred.

Stock solution (1,000 mg/L) of cyanide was prepared by dissolving NaCN into deionized water. After the solution temperature decreased to room temperature, deionized water was added to the specified scale of the volumetric flask. Experimental solutions of the desired concentrations were prepared by successive dilutions. Photocatalytic experiments were performed with variation of the solution pH (3, 7, 11), contact time (15–120 min) and initial cyanide concentration (50, 100, 200 mg/L) in the presence of different type of organic compounds (each 100 mg/L). HA, oxalate, EDTA, NTA and phenol were used as organic matter. TiO$_2$ and ZnO dosage equal to
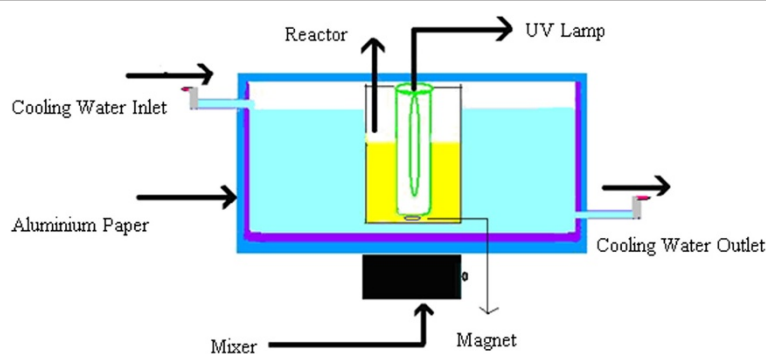
Figure 1 A schematic diagram of the experimental set-up for photocatalysis.

1 g/L was used for all experiments because this dosage was identified as an optimum dosage from our previous paper [2,17]. The initial solution pH was adjusted by adding 0.1 M NaOH and HCl. All experiments were performed under ambient conditions for 2 h. TiO_2 or ZnO suspensions were equilibrated in the dark for 30 min for control test in order to evaluate the contribution of cyanide removal through adsorption process. After the equilibration period, the UV-lamp was turned on and a portion of suspension was periodically taken from the reactor. All the samples were covered by aluminum foil to avoid ambient light. All experiments were accomplished at constant temperature (25 ± 2°C). The sample suspensions were centrifuged at 4,000 rpm for 60 and 10 min to remove TiO_2 or ZnO nanoparticles, respectively, and then analyzed residual cyanide concentration in supernatant. The remaining concentration of cyanide was analyzed by 4500-CN D. Titrimetric Method according to Standard Methods for the Examination of Water and Wastewater [21]. Indicator solution and titrant were p-dimethylaminobenzalrhodanine and silver nitrate ($AgNO_3$), respectively. Then residual cyanide concentration was calculated using following equation:

$$\frac{mg\ CN^-}{L} = \frac{(A\text{-}B) \times 1000}{mL\ orginal\ sample} \times \frac{250}{mL\ portion\ used} \quad (1)$$

where A and B is volume (mL) of standard $AgNO_3$ of sample and of blank, respectively.

All experiments were repeated three times and the average values with error percents were reported.

Results and discussion
Removal of cyanide at different solution pH
Effect of solution pH on the removal of 100 mg/L cyanide by UV/ TiO_2 and UV/ZnO was investigated at constant catalyst dosage (1 g/L) by varying the initial solution pH (3, 7, 11) at different time interval. Figure 2 shows the removal of cyanide (a) by UV/ TiO_2 and (b) by UV/ZnO at different solution pH. At initial condition, the removed fraction of cyanide through adsorption process ranged from 28.9% to 45.7% in UV/TiO_2 system and ranged from 23.4% to 38.7% in UV/ZnO system depending on the solution pH. Cyanide adsorption onto TiO_2 was greatly dependent on the solution pH compared to ZnO. Figure 2(a) shows the effect of solution pH on the removal of cyanide with UV/TiO_2. Photocatalytic removal of cyanide increased as the solution pH decreased. The greatest photocatalytic removal of cyanide was observed at pH 3 over the entire reaction time. This result may be explained from combined effects of several factors such as adsorption behavior of cyanide onto metal (hydr-)oxide as well as favorable conditions for photocatalytic reaction at low pH. At high solution pH, increased negative charges on the surface of TiO_2 causes difficult
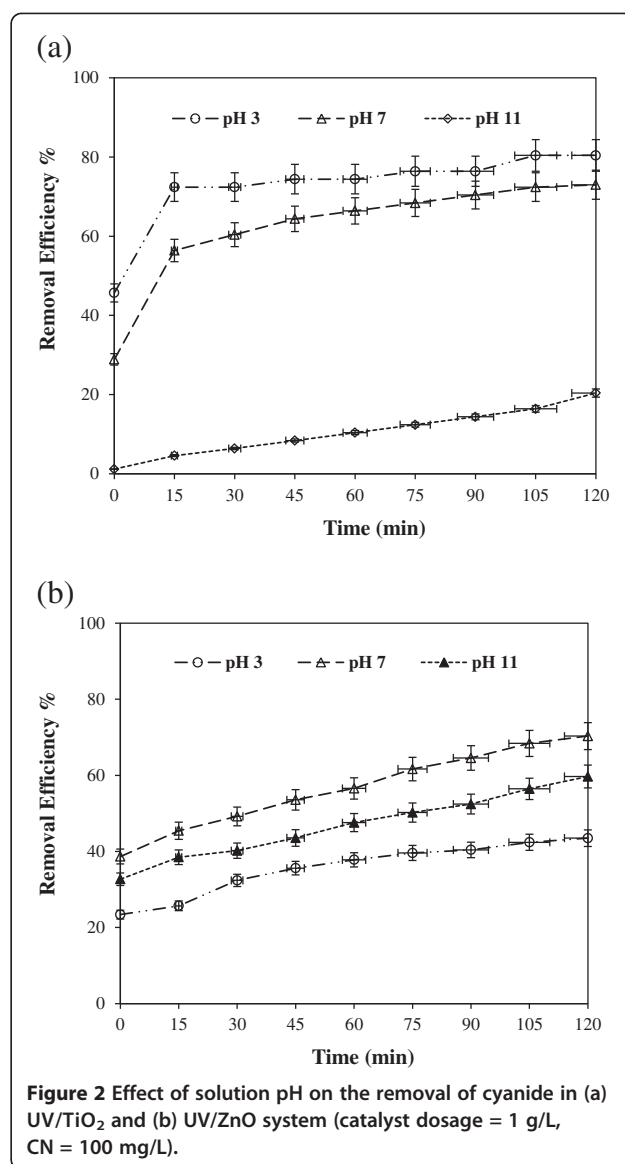
Figure 2 Effect of solution pH on the removal of cyanide in (a) UV/TiO₂ and (b) UV/ZnO system (catalyst dosage = 1 g/L, CN = 100 mg/L).

approach of cyanide ions to the surface of TiO_2. Similar observations have also been reported previously [22]. Other reasons are an anodic shift of the potential of positive holes and change of the speciation of dissolved CO_2. As the solution pH increased above neutral pH, bicarbonate is presents as a predominant species. It is a known radical scavenge and causes depression of photocatalytic activity [23].

While highest adsorption of cyanide onto ZnO was observed at pH 7 because ZnO was easily dissoluble in both strong acidic and basic solutions [24]. The effect of pH on the photocatalytic performance can be thus explained in terms of electrostatic interaction between the surface of catalyst and cyanide. Unfortunately, the mere electrostatic argument is unable to exhaustively account for the different photocatalytic efficiency at

different solution pH. Other concomitant effect should be considered. It is generally known that ZnO can undergo photocorrosion through self oxidation as expressed in (Eq. 2) [16,18]:

$$ZnO + 2h^+ \rightarrow Zn^{2+} + 1/2\ O_2 \qquad (2)$$

In particular, ZnO powder dissolves well at lower solution pH (Eq. 3) [17,19]:

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \qquad (3)$$

In addition, ZnO can undergo dissolution in a strong alkaline environment as expressed in Eq. 4:

$$ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4{}^{2-} \qquad (4)$$
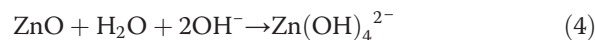
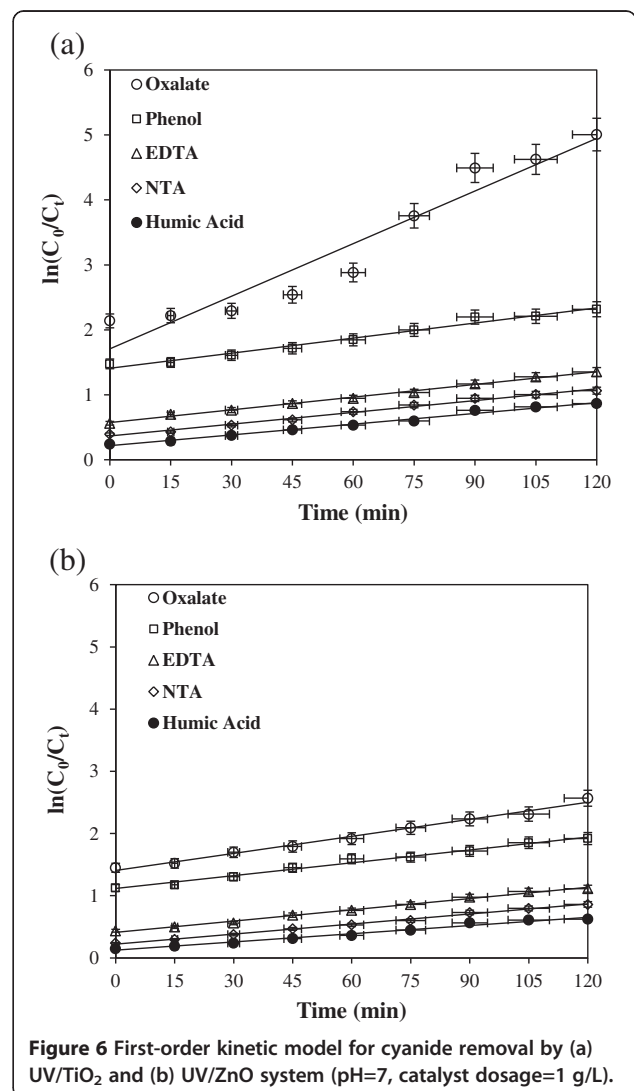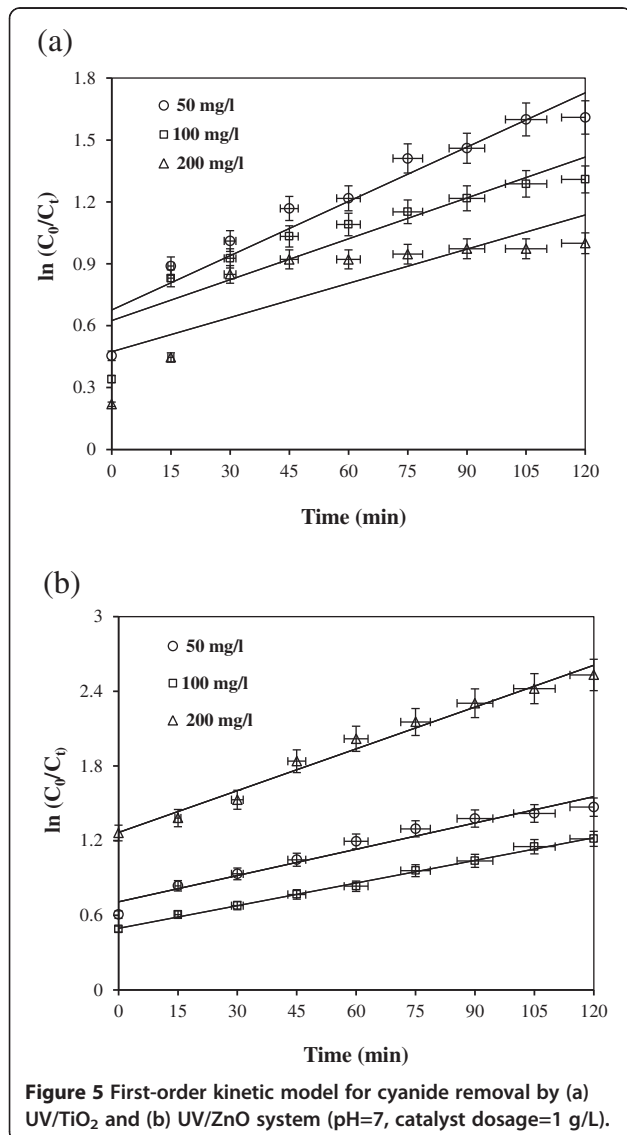### Removal of cyanide at different concentrations cyanide

Removal of cyanide by UV/TiO_2 and UV/ZnO was investigated with variation of initial cyanide concentration (50, 100, 200 mg/L) at initial pH 7 and at constant TiO_2 and ZnO dosage (1 g/L). Figures 3(a) and 3(b) shows that, for all concentrations, a rapid increase of the cyanide removal was observed up to 30 min and then the slope was gradually reduced. Cyanide removal by UV alone was observed for all concentrations, suggesting photolysis of cyanide. A

Figure 3 Effect of initial cyanide concentration on the removal of cyanide in (a) UV/TiO_2 and (b) UV/ZnO system (pH=7, catalyst dosage=1 g/L).

Figure 4 Effect of different organic compounds on the removal of cyanide in (a) UV/TiO_2 and (b) UV/ZnO system (pH=7, catalyst dosage=1 g/L, CN =100 mg/L, organic compound = 100 mg/L).
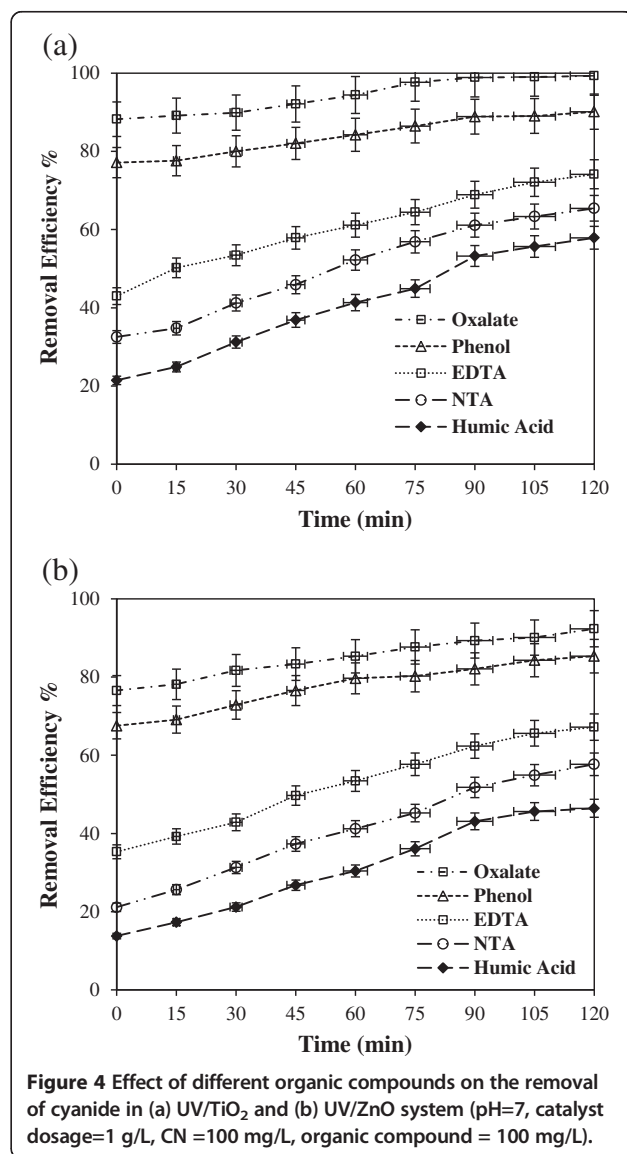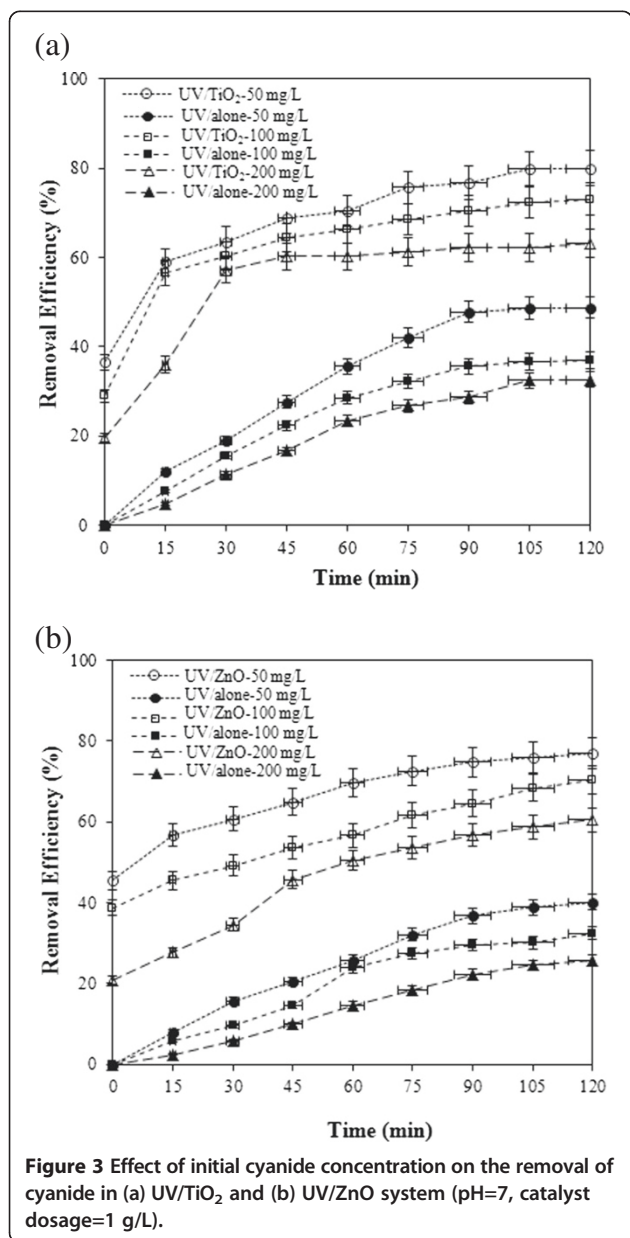
fraction of cyanide photolysis increased as the cyanide concentration decreased. Percent cyanide removal after 120 min by UV alone in the presence of 50, 100 and 200 mg/L cyanide was 48.7, 37.0 and 32.7%, respectively. Although cyanide removal was possible through photolysis, it was not effective, suggesting necessary of photocatalysts.
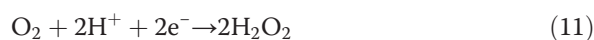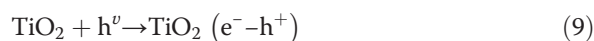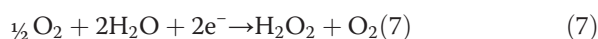
In the presence of photocatalysts, it can be seen that percent cyanide removal decreased as the initial cyanide concentration increased. The presumed reason is that when the initial cyanide concentration increased, more cyanide molecules can be removed on the surface of TiO_2 or ZnO. The large amount of removed cyanide might have an inhibitive effect on the further photocatalytic reaction of cyanide because of the decreased adsorption sites on the TiO_2 or ZnO as well as the limited oxidants on the surface of TiO_2 or ZnO [25,26].

The mechanism of cyanide removal is based on the absorption, by the semiconductor particles, of light of energy greater than the band gap energy of the semiconductor, which produces electron hole pairs (e^- h^+). These photogenerated charges can be very reactive depending on the energy of the conduction and valence band edges of the semiconductor and can migrate to the particle surface and react with suitable redox species in solution. From the reaction of cyanide ion with positive hole, CN^- is oxidized to OCN^-, while oxygen is photoreduced to hydrogen peroxide by photogenerated electrons in the conduction band of photocatalysts [20]. This reaction show in equation (5, 6, 7, 8, 9, 10 and 11) [26,27]:

$$ZnO + h^v \rightarrow ZnO \left(e^- - h^+\right) \tag{5}$$

$$ZnO \left(e^- - h^+\right) \rightarrow ZnO \tag{6}$$

Figure 5 First-order kinetic model for cyanide removal by (a) UV/TiO$_2$ and (b) UV/ZnO system (pH=7, catalyst dosage=1 g/L).

Figure 6 First-order kinetic model for cyanide removal by (a) UV/TiO$_2$ and (b) UV/ZnO system (pH=7, catalyst dosage=1 g/L).

Table 2 Kinetic parameters for the photocatalytic removal of cyanide by UV/TiO$_2$ and UV/ZnO at different initial cyanide concentration (catalyst dosage = 1g/L, pH=7)

UV/TiO$_2$ CN (mg/L)	Zero-order		First-order		Second-order	
	k$_0$ (mol L^{-1} min^{-1})	R^2	k$_1$ (min^{-1})	R^2	k$_2$ (L mol^{-1} min^{-1})	R^2
50	0.490	0.798	0.008	0.919	0.001	0.978
100	0.276	0.688	0.006	0.815	0.002	0.918
200	0.586	0.623	0.005	0.67	0.001	0.718
UV/ZnO CN (mg/L)	Zero-order		First-order		Second-order	
	k$_0$ (mol L^{-1} min^{-1})	R^2	k$_1$ (min^{-1})	R^2	k$_2$ (L mol^{-1} min^{-1})	R^2
50	0.122	0.903	0.007	0.959	0.002	0.988
100	0.677	0.927	0.006	0.996	0.002	0.985
200	0.26	0.987	0.011	0.983	0.001	0.983

$$\tfrac{1}{2}O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + O_2(7) \quad (7)$$

$$CN^- + 2OH^- + 2h^+ \rightarrow OCN^- + H_2O \quad (8)$$

$$TiO_2 + h^v \rightarrow TiO_2\,(e^- - h^+) \quad (9)$$

$$CN^- + 2OH^- + 2h^+ \rightarrow OCN^- + H_2O \quad (10)$$

$$O_2 + 2H^+ + 2e^- \rightarrow 2H_2O_2 \quad (11)$$

Effect of type of organic compound
Effect of organic compound on the removal efficiency of cyanide by UV/TiO$_2$ and UV/ZnO was investigated in the presence of four different organic compounds. Figures 4 (a) and 4(b) show that percent removal of cyanide at initial reaction is oxalate > phenol ~ EDTA ~ NTA~ HA. The removed amount of cyanide at initial reaction time in the presence of oxalate and phenol was greater than that in the absence of any organic additives shown in Figure 4(a) and 4(b).

The removed amount of cyanide in the presence of oxalate and phenol gradually increased and was greater than that in the absence of any organic additives over the entire reaction time. Removal efficiency of 100 mg/L cyanide without presence of organic compound increased from 28.9% at 15 min to 73% at 120 min in UV/TiO$_2$ system and increased from 38.67% at 15 min to 70.32% at 120 min in UV/ZnO system. The removal efficiency of cyanide in the presence of oxalate increased from 88.2% at 15 min to 99.3% at 120 min in UV/TiO$_2$ system and increased from 76.6% at 15 min to 92.3% at 120 min in UV/ZnO system, showing greatly different removal efficiency over the entire reaction time.

The residual cyanide concentration after 120 min of photocatalytic reaction with illuminated TiO$_2$ in the

Table 3 Kinetic parameters for the photocatalytic removal of cyanide by UV/ TiO$_2$ and UV/ZnO with organic compounds (catalyst dosage= 1g/L, pH=7, cyanide= 100 mg/L, organic compounds= 100 mg/L)

UV/TiO$_2$ Organic Compounds	Zero-order		First-order		Second-order	
	k$_0$ (mol L^{-1} min^{-1})	R^2	k$_1$ (min^{-1})	R^2	k$_2$ (L mol^{-1} min^{-1})	R^2
Humic Acid	0.322	0.988	0.005	0.988	0.012	0.975
Oxalate	0.108	0.946	0.027	0.931	0.011	0.82
Phenol	0.12	0.976	0.007	0.978	0.011	0.961
EDTA	0.253	0.986	0.006	0.995	0.001	0.979
NTA	0.297	0.98	0.006	0.989	0.002	0.986
UV/ZnO Organic Compounds	Zero-order		First-order		Second-order	
	k$_0$ (mol L^{-1} min^{-1})	R^2	k$_1$ (min^{-1})	R^2	k$_2$ (L mol^{-1} min^{-1})	R^2
Humic Acid	0.298	0.984	0.004	0.981	0.001	0.972
Oxalate	0.131	0.985	0.006	0.987	0.002	0.94
Phenol	0.154	0.965	0.006	0.993	0.011	0.986
EDTA	0.281	0.988	0.009	0.989	0.001	0.093
NTA	0.314	0.992	0.005	0.995	0.002	0.984

presence of oxalate was below the discharge standard of cyanide in USA (1.2 ppm as a maximum value in a day) or Korea (1.0 ppm). It was difficult to explain the enhanced cyanide removal in the presence of oxalate and phenol. Removal efficiency of cyanide greatly decreased in the presence of HA, EDTA and NTA compared to that without presence of organic compound because of the competitive oxidation as well as surface blocking by relatively large organic compounds. Osathaphan et al. (2008) investigated kinetics of the photocatalytic oxidation of cyanide in aqueous TiO_2 suspensions in the presence of EDTA (0.4-40 mM) at pH 13.0 [28]. They reported a retardation of the cyanide removal rate in the presence of EDTA, indicating that EDTA successfully competed with cyanide for oxidizing species during the photocatalytic processes.

Kinetic study

In order to obtain the kinetic information, the experimental results in Figures 3(a) and 3(b) and 4(a) and 4(b) were fitted with zero, first and second-order equations. From this evaluation, the removal pattern was better described by first-order kinetic model. Because the initial concentration of cyanide employed in this study was low, the adsorption kinetics can be described adequately by a simplified first-order rate equation (Eq. 12).

$$\ln[CN^-_0/CN^-_t] = k_1 t \qquad (12)$$

where C_0 and C_t is the cyanide concentration at initial and at time t, respectively. k_1 is the first-order rate constant and t is the reaction time. Figures 5(a) and 5(b) show the plot of $\ln[C_0/C_t]$ versus of t for the removal of cyanide by UV/TiO_2 or UV/ZnO. Figures 6(a) and 6(b) show the plot of $\ln[C_0/C_t]$ versus of t for the removal of cyanide by UV/TiO_2 or UV/ZnO in the presence of organic compound. Also first-order rate constants including zero- and second-order rate constants at three different concentrations of cyanide with or without presence of organic compounds are summarized in Tables 2 and 3, respectively. As the cyanide concentration increased, the rate constant in both system decreased.

Conclusions

The major findings of this study are as follow:

Removal of cyanide by UV/TiO_2 or UV/ZnO increased through photocatalytic removal in the presence of organic compounds, especially oxalate. The cyanide removal decreased at higher pH because of the decreased potential difference between the conduction band of TiO_2 and cyanide and the anionic-type adsorption of cyanide onto the surface of TiO_2. Maximum cyanide removal was observed near at neutral pH because of the reduced photocatalytic activity of ZnO at exceedingly low and high pH values. Photocatalytic oxidation rate of cyanide was well described by the first-order kinetics. Photocatalytic reaction with UV/TiO_2 and UV/ZnO in the presence oxalate can be effectively applied to treat industrial wastewater contaminated with cyanide.

Authors' contributions
All authors read and approved the final manuscript.

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