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Effect of different type of organic compounds on the photocatalytic reduction of Cr(VI) in presence of ZnO nanoparticles

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ABSTRACT

Effect of different type of organic compounds (humic acid, oxalate, ethylenediaminetetraacetic acid, nitrilotriacetic acid, phenol) on the photocatalytic reduction of Cr(VI) with illuminated ZnO was studied in this work with variation of solution pH, contact time, initial Cr(VI) concentration, and type of organic compounds. Maximum removal of Cr(VI) was observed at near 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 Cr(VI) increased in the presence of oxalate compared to that without presence of organic compound because of positive holes in the valence band of ZnO were scavenged by oxalate. However, it was decreased in the presence of the other organic compounds due to the blocking effects of electron transfer between ZnO surface and Cr(VI). The reduction pattern of Cr(VI) was better described by first-order kinetic model. Finally photocatalytic reaction with illuminated ZnO can be effectively applied to treat wastewater contaminated with Cr(VI).

Keywords: Photocatalysis; Nanoparticle; ZnO; Organic Compound; Cr(VI)

1. Introduction

One of the major environmental pollutants is heavy metals originated from several industrial activities [1]. Most of the heavy metals participate in biological reactions in living cells. And their metabolic functions can impair bodily organs. Therefore, the presence of metallic elements in the aquatic environment is a great concern because of their toxic properties and other adverse effects on receiving water [2]. Chromium is widely used in several industrial purposes such as metal processing, industrial plating, textiles, and leather treatments. The fate of chromium within the environment is closely related to its chemistry. Chromium found in most industrial wastewater is both Cr(VI) and Cr(III). Compared with the Cr(III), Cr(VI) is very toxic, carcinogenic, and mutagenic for human and environment as well as has greater mobility [3–5]. Therefore, Cr(VI) reduction to Cr(III) is highly required in order to reduce toxicity and to retard mobility of Cr(VI). The widely used

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physicochemical treatment of industrial wastewater containing organics and metallic elements are ion exchange, reverse osmosis, direct precipitation, and adsorption with activated carbon [4–6]. These methods require greater exposed liquid surface area and long detention periods. Besides, most of these methods need high capital cost and recurring expenses such as chemicals. These are much burden in the management of small-scale industrial facility [6,7].

To conquer these problems, advanced oxidation processes (AOP) have been used as talented techniques. Overall AOPs, generating hydroxyl radical (·OH) have been widely used to destroy organic compounds that cannot be oxidized by conventional oxidants such as oxygen, ozone, and chlorine [2,8,9]. The hydroxyl radical can be generated in aqueous solutions using O_3/UV, H_2O_2/UV, Fe(II)/H_2O_2, TiO_2/UV, and ZnO/UV [10,11]. Among several photocatalysts, ZnO has much attention because ZnO can be excited at room temperature under low excitation energy. The greatest advantage of ZnO is that it absorbs larger fraction of the solar spectrum compared to TiO_2 [10]. The surfaces of ZnO support strong chemisorption of oxygen and are sensitive to ultraviolet (UV) light [12,13]. The most important properties of ZnO are nontoxic in itself, providing an attractive photocatalytic efficiency [8]. Photocatalytic reaction using ZnO/UV can simultaneously treat organic compounds and metallic elements in addition to change nonbiodegradable to biodegradable organic compounds [14,15]. ZnO is used as effective, inexpensive, and nontoxic semiconductor photocatalysts for the degradation of synthetic dyes and reduction of Cr(VI) [14,16].

Photocatalytic reduction of Cr(VI) by electrons in the conduction band of the ZnO could be influenced by the scavenged amounts of positive holes by organic compounds. This scavenging effect can be affected by the type of organic compounds because both natural organic compounds such as fulvic and humic acids having polycarboxylic groups and Cr(VI) wastes are likely present in natural water or wastewater systems. A research regarding the enhancement of Cr(VI) reduction in the presence of oxalate was reported previously [15]. However, a limited information is available for the removal efficiency and removal kinetics of Cr(VI) with illuminated ZnO in the presence of organic compounds having different functional groups.

The objectives of this investigation were to examine the effect of the carboxylic group and phenol group on the photocatalytic reduction of Cr(VI) by employing five model organic compounds such as humic acid, oxalate, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and phenol in synthetic wastewater. Although this research work performed with synthetic wastewater may be far beyond real situation, the obtained result can provide basic information to apply UV/ZnO system in real wastewater. As the selected five different model compounds have different number of functional groups such as carboxyl and phenols groups, the effect of different type of organic compounds on the photocatalytic reduction of Cr(VI) was investigated with variation of solution pH, contact time, and initial Cr(VI) concentration with synthetic wastewater. In addition, kinetic parameters were obtained by application of zero-, first- and second-order equations.

2. Materials and methods

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 according to Nano Pars Lima Company in Iran. Also organic compounds with greater than 99% purity were obtained from Merck Company in Germany. All chemicals were of analytical grade and solutions were prepared with deionized water (18 MΩcm) from a Hydro-Service reverse osmosis/ion exchange apparatus.

3. Experimental set-up

The experimental set-up for photocatalytic reactor used in this work is schematically shown in Fig. 1. A 125 W medium-pressure UV lamp emitting maximum wavelength at 247.3 nm and light intensity equal to 1,020 μw/cm^2 measured by a Spectroline model DRC-100X 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

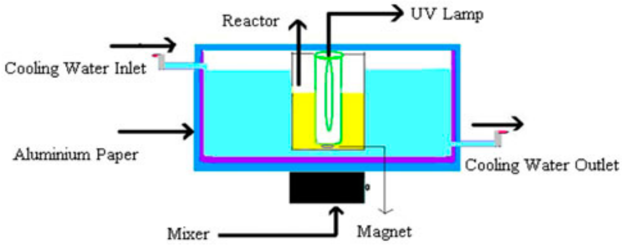

Fig. 1. A schematic diagram of the experimental set-up for photocatalysis.

1,000 mL solution. During experiments, the test solution in the reactor was constantly stirred.

Stock solution (1,000 mg/L) of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ 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 (4, 6, 8), contact time (15–120 min), and initial Cr(VI) concentration (10, 20, 30, 40, and 50 mg/L) in the presence of different type of organic compounds (each 10 mg/L). Five different organic compounds such as humic acid (HA), oxalate, EDTA, NTA, and phenol. ZnO dosage equal to 1 g/L were used for all experiments because this dosage was identified as an optimum dosage from our previous paper [14]. The initial solution pH was adjusted by adding 0.1 M NaOH and HCl. In order to maintain the solution pH during Photocatalytic experiments, a continuous pH adjustment was performed with 0.1 M HCl or NaOH. All the experiments were performed under ambient conditions for 2 h. ZnO suspensions were equilibrated in the dark for 30 min for control test in order to evaluate the contribution of Cr(VI) 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 10 min to remove ZnO nanoparticles and then analyzed the residual Cr(VI) concentration in supernatant. Cr(VI) was analyzed by 1,5-diphenylcarbazide method by a spectrophotometer (Shimadzu UV-160A) at a wavelength of 540 nm [17].

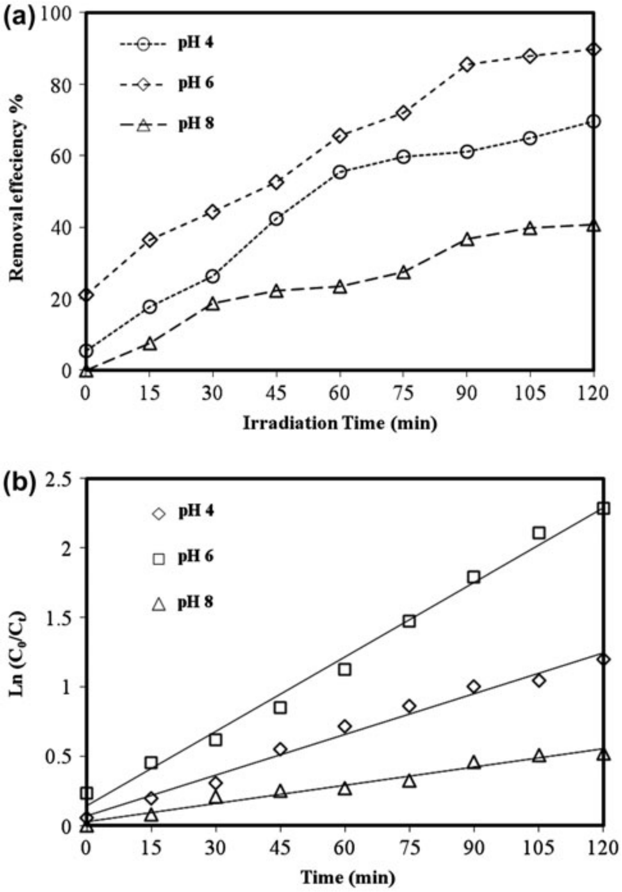

Fig. 2. Effect of solution pH on the (a) percent removal of Cr(VI) with variation of time and (b) linear plot of $\ln(C_0/C_t)$ versus time (ZnO = 1 g/L, Cr(VI) = 10 mg/L).

4. Results and discussion

4.1. Removal of Cr(VI) at different solution pH

Effect of solution pH on the removal of 10 mg/L Cr(VI) by ZnO/UV was investigated at constant ZnO dosage (1 g/L) by varying the initial solution pH (4, 6, 8) at different time interval. Fig. 2(a) shows the removal trends of Cr(VI) by ZnO/UV at different solution pH. In this research, the blank test with the UV illumination was not carried out because photochemical reaction of Cr(VI) under UV light irradiation was negligible from the previous research [18]. At the initial condition before illumination by UV lamp, the removed fraction of Cr(VI) was ranged from 5.4–20.9% depending on the solution pH. The adsorbed fraction of Cr(VI) in this work was lower than that reported by Siboni et al. [14]. This different adsorption fraction could be explained by the different type of ZnO. Siboni et al. (2011) used synthesized ZnO while commercial ZnO was used in this work. Agglomeration and nonreproducibility of commercial nanoparticles is regarded as another reason for the low adsorption fraction observed in this work. The initial removal before UV illumination can be explained by the adsorption of Cr(VI) onto ZnO. Generally Cr(VI) adsorption onto metal-oxide adsorbent is more favorable at low pH because more positive charges are developed on the surface of adsorbent as well as Cr (VI) present as $HCrO_4^-$ below neutral pH. However highest adsorption of Cr(VI) onto ZnO was observed at pH 6 because ZnO was easily dissoluble in both strong acidic and basic solutions [19]. This trend was different from general Cr(VI) adsorption trend, an anionic-type adsorption behavior, observed by metal oxides such as iron-oxide [20].

Under illumination by UV lamp, the Cr(VI) solution gradually lost its original yellow color. As the reaction proceeded, the original white ZnO turned into pale green because Cr(VI) solution having orange color was changed to green color of Cr(III). The removal of Cr(VI) obviously increased in the UV/ZnO system, possibly due to plausible reduction of the Cr (VI) to Cr(III) by the electrons in the conduction band of the ZnO, as well as adsorption of the Cr(VI) onto the ZnO surface. Even though redox potential of Cr (VI) increased and adsorption is favorable as the solution pH decreased, maximum removal of Cr(VI) through photocatalytic reaction was observed at near neutral pH because ZnO was easily dissoluble in both strong acidic and basic solutions [18,19,21]. The effect of pH on the photocatalytic performance can be thus explained in terms of electrostatic interaction between the surface of catalyst and heavy metal ions. Such interaction can affect the encounter probability of the nascent hydroxyl radical with the Cr(VI) [15,19]. 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. (1) [8,15]:

$$\mathrm{ZnO} + 2\mathrm{h}^+ \rightarrow \mathrm{Zn}^{2+} + 1/2\ \mathrm{O}_2 \qquad (1)$$

In particular, ZnO powder dissolves well at lower solution pH (Eq. (2)) [8,14,16]:

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

In addition, ZnO can undergo dissolution in a strong alkaline environment as expressed in Eq. (3):

$$\mathrm{ZnO} + \mathrm{H_2O} + 2\mathrm{OH}^- \rightarrow \mathrm{Zn(OH)}_4^{2-} \qquad (3)$$

Moreover, possible formation of the photocatalytic inert $Zn(OH)_2$ surface layers upon UV irradiation which has been reported and expressed in Eq. (4) [14,16]:

$$2\mathrm{ZnO} + 4\mathrm{H_2O} + 4\mathrm{h}^+ \rightarrow 2\mathrm{Zn(OH)}_2 + \mathrm{O}_2 + 4\mathrm{H}^+ \qquad (4)$$

Therefore, the reduction of photocatalytic activity of ZnO at exceedingly low and high pH values can originate from either acidic/photochemical corrosion of the catalyst (Eqs. (1) and (3)) and/or surface passivation with $Zn(OH)_2$ (Eq. (4)). In addition reactions (2) and (3) can interfere the formation of hydroxyl radicals by decreasing the availability of holes for water or surface OH group [14,16].

In order to obtain the kinetic information, the experimental results in Fig. 2 were fitted with zero-, first- and second-order equations. Kinetic parameters and linear correlation coefficients are summarized in Table 1. From this evaluation, the reduction pattern was better described by first-order kinetic equation (Eq. (5)).

$$\ln[C_0/C_t] = k_1 t \qquad (5)$$

where C_0 and C_t is the Cr(VI) concentration at initial and at time t, respectively. k_1 is the rate constant and t is the reaction time. Fig. 2(b) shows the plot of $\ln[C_0/C_t]$ vs. t for the reduction of Cr(VI) by ZnO/UV.

4.2. Removal of Cr(VI) at different concentration of Cr(VI)

Removal of Cr(VI) by ZnO/UV was investigated with variation of initial Cr(VI) concentration (10, 20, 30, 40, and 50 mg/L) at initial pH 6 and at constant ZnO dosage (1 g/L). Fig. 3 shows that, for all concentrations, a rapid increase of the removal of Cr(VI) was observed up to 30 min and then the slope was gradually reduced. It can be seen that percent removal of Cr (VI) decreased as the initial Cr(VI) concentration increased. The presumed reason is that when the initial Cr(VI) concentration increased, more Cr(VI) molecules can be removed on the surface of ZnO.

Table 1
Kinetic parameters for the photocatalytic removal of Cr(VI) by ZnO nanoparticle in aqueous solution at different initial pH (ZnO = 1 g/L, initial Cr(VI) concentration = 10 mg/L)

pH	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
4	0.0542	0.944	0.0098	0.9843	0.004	0.9103
6	0.0582	0.9607	0.0179	0.9909	0.0072	0.9041
8	0.0334	0.9548	0.0044	0.9691	0.0006	0.9706

Table 2
Kinetic parameters for the photocatalytic removal of Cr(VI) by ZnO nanoparticle in aqueous solution at different initial Cr(VI) concentration (ZnO = 1 g/L, pH = 6)

Cr(VI) (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
10	0.0582	0.9607	0.0179	0.9909	0.0072	0.9041
20	0.1511	0.966	0.0173	0.9459	0.0008	0.8961
30	0.1179	0.9175	0.0063	0.9625	0.0003	0.9873
40	0.0847	0.9354	0.0056	0.9898	0.0002	0.9952
50	0.0591	0.9746	0.0051	0.9919	0.0001	0.9931

Table 3
Kinetic parameters for the photocatalytic removal of Cr(VI) by ZnO nanoparticle in aqueous solution with organic compounds (ZnO = 1 g/L, pH = 6, Cr (VI)= 10 mg/L, organic compounds = 10 mg/L)

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	0.0417	0.9764	0.007	0.9547	0.0056	0.0512
Oxalate	0.0492	0.0619	0.0138	0.9707	0.0045	0.9398
Phenol	0.0418	0.9805	0.0093	0.9603	0.0022	0.9189
EDTA	0.0369	0.9889	0.005	0.9772	0.0008	0.9525
NTA	0.0365	0.99	0.005	0.9838	0.0007	0.9656

The large amount of removed Cr(VI) might have an inhibitive effect on the further photocatalytic reaction of Cr(VI) because of the decreased adsorption sites on the ZnO as well as the limited oxidants on the surface of ZnO [2,9,11,14,22–24].

4.3. Effect of different type of organic compound on removal efficiency

Effect of organic compound on the removal efficiency of Cr(VI) by ZnO/UV was investigated in the presence of five different organic compounds. Fig. 4 shows that percent removal of Cr(VI) at initial reaction time is oxalate > phenol ~ humic acid ~ EDTA ~ NTA. The removed amount of Cr(VI) at initial reaction time in the presence of oxalate and phenol was greater than that in the absence of any organic additives as shown in Fig. 2(a). The removed amount of Cr(VI) in the presence of oxalate gradually increased and was greater than that in the absence of any organic additives over the entire reaction time. Removal percentages of Cr(VI) without presence of organic compound increased from 36.45% at 15 min to 89.82% at 120 min. On the other hand, removal percentages of Cr(VI) in the presence of oxalate increased from 48.52% at 15 min to 99.51% at 120 min, showing much enhanced removal efficiency over the entire reaction time. The plausible reason for this trend is easy electron utilization by positive hole in the valence band of ZnO during photocatalytic reaction. When organic compound was added into the reactor, the possibility of electron capture by Cr(VI) could be promoted because positive holes were scavenged by organic additives, increasing photocatalytic reduction rate of Cr(VI) [10,25]. Scavenging effects by organic additives can be affected by several factors such as type of organic compound and concentration of organic compound. From the photocatalytic reduction of Cr(VI) by TiO_2 in the presence of four organic compounds having different number of carboxyl group, Lee et al. (2007) reported a good comparison of initial removal rates of Cr(VI) with initial density of adsorbed carboxyl groups and suggests that adsorption density of carboxyl group on the surface of TiO_2 is determined as an important parameter in the Cr(VI) reduction [26]. However, removal trend of Cr(VI) observed in this work was not coincide with the result reported by Lee et al. (2007). The great removal

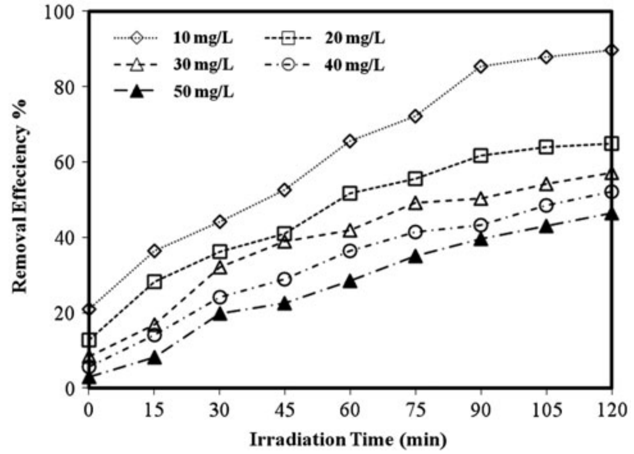

Fig. 3. Effect of initial Cr(VI) concentration on the removal of Cr(VI) by UV/ZnO (pH = 6, catalyst dosage = 1 g/L).

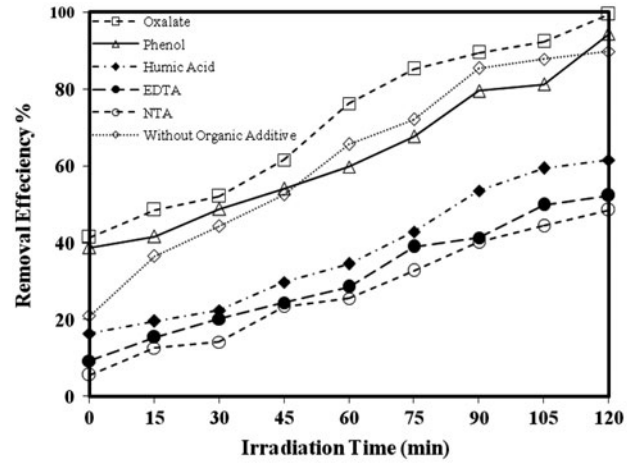

Fig. 4. Effect of different organic compounds on Cr(VI) removal by UV/ZnO (pH = 6, catalyst dosage = 1 g/L, Cr (VI)=10 mg/L, organic compound = 10 mg/L).

efficiency of Cr(VI) in the presence of oxalate in this work might be explained by the combined effects of the above reasons. Mendive et al. (2005) reported that oxalate is easily oxidized to carbon dioxide without or little accumulation of intermediates compared to other organic additives [27]. But removal efficiency of Cr(VI) in the presence of humic acid, EDTA, and NTA was much lower than that by controlled results as shown in Fig. 2(a). A plausible reason for this trend may be regarded as an interference effect of the adsorbed organic molecules having greater molecular sizes and adsorption efficiency than oxalate on the approaching of Cr(VI) to the surface of ZnO. Yang and Davis (1999) reported that the adsorbed amount of EDTA increased with a decrease in pH, reaching approximately to 100% below pH 4 from the EDTA adsorption onto TiO_2 [28]. Moreover it was reported the adsorbed reaction intermediates due to the incomplete mineralization of EDTA during photocatalytic reaction with illuminated TiO_2 [29]. When reduction reagent was absent in solution, H_2O could work as electron donor in the photocatalytic reduction of Cr(VI) to Cr(III), and H_2O_2 can be detected in solution [30]. In order to reduce Cr(VI) to Cr(III) completely, a large dosage of reduction reagent (oxalate, i.e.) has to be used [31]. Oxalate is easily oxidized to carbon dioxide, and to minimize the problem of possible accumulation of intermediate product [32]. The possible oxidation reactions of $C_2O_4^{2-}$ under UV illumination condition are (Eqs. (6)–(9)).

$$O_2 \rightarrow O_2^{\cdot-} \rightarrow HO_2^{\cdot} \rightarrow H_2O_2 \rightarrow {}^{\cdot}OH \tag{6}$$

$$C_2O_4^2 + {}^{\cdot}OH \rightarrow CO^{\cdot}{}_2 + CO_2^- + OH^- \tag{7}$$

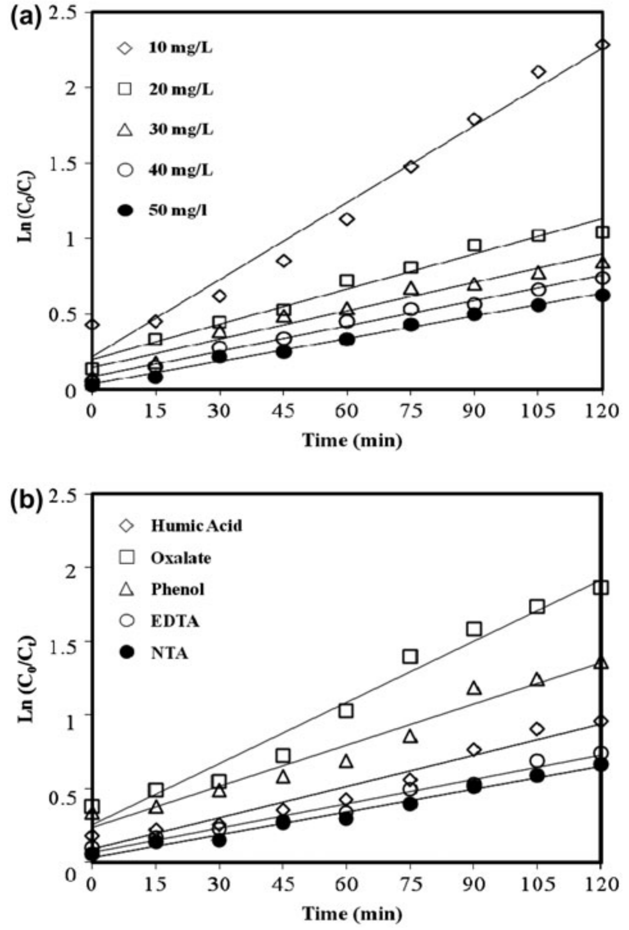

Fig. 5. First-order kinetic model for Cr(VI) removal by UV/ZnO without organic compound (a) and with organic compound (b) (pH = 6, catalyst dosage = 1 g/L).

$$CO_2^{\cdot -} + OH \rightarrow CO_2 + OH^- \qquad (8)$$

The net oxidation equation of $C_2O_4^{2-}$ to CO_2 is (Eq. (9)).

$$C_2O_4^{2-} + 1/2O_2 + H_2O \rightarrow 2CO_2 + 2OH^- \qquad (9)$$

In order to obtain the kinetic information, the experimental results in Figs. 3 and 4 were fitted with zero-, first- and second-order equations. From this evaluation, the reduction pattern was better described by first-order kinetic model. Since the initial concentration of Cr(VI) employed in this study was low, the adsorption kinetics can be described adequately by a simplified first-order rate equation (Eq. (5)). Fig. 5(a) and (b) show the plot of $\ln[C_0/C_t]$ versus t for the reduction of Cr(VI) by ZnO/UV. First-order rate constants including zero- and second-order rate constants at three different concentrations of Cr(VI) without organic compound and with organic compound are summarized in Tables 2 and 3, respectively. As the concentrations of both Cr(VI) increased, the rate constant in both system decreased.

5. Conclusions

The major findings of this study are as follows:

Removal of Cr(VI) by UV/ZnO through photocatalytic reduction in the presence of oxalate was greater than that in the absence of any organic additives. Maximum removal of Cr(VI) was observed at near 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 $Zn(OH)_2$. Considering these trends, it is possible to suggest that photocatalytic reaction using UV/ZnO, as a pre-treatment process, can be applied to treat wastewater containing Cr(VI) with the adjustment of solution pH and just by addition of oxalate as an efficient organic additive. Then conventional technique such as precipitation can be used to remove Cr(III) species from aqueous solution.

Acknowledgments

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