

Article

Impacts of Mixing Mode on Photocatalytic Reduction of Hexavalent Chromium over Titanium Dioxide Nanomaterial under Various Environmental Conditions

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Abstract: This study explores the effects of initial Cr(VI) concentration, wavelength, hole-scavenger (absence and presence of salicylic acid), and oxygen conditions (aeration by air, nitrogen gas, and mechanical stir only) on photocatalytic reduction of hexavalent chromium over titanium dioxide photocatalyst and the chromic species distribution after photocatalysis. The experimental results show the existence of strong interactions between these factors. The factor of hole-scavenger was more important than the UV light wavelength condition for a reduction of 3 mg Cr(VI) L⁻¹, whereas both factors became important when Cr(VI) concentration increased to 20 mgL⁻¹. The higher the UV wavelength was, the less the amount of chromium retained on the TiO₂ surface. The influence of oxygen-containing conditions in the solution on the reduction of 3 mgL⁻¹ Cr(VI) was unobvious, whereas its influence became remarkable for the reduction of 20 mgL⁻¹ Cr(VI) in the presence of SA. The interaction between oxygen-containing factor and other environmental factors, such as Cr(VI) concentration and scavenger presence (SA in this study), is a key factor about the degree of oxygen effect on Cr(VI) photo-reduction and the chromic species distribution. Simple stirring obtained better photocatalytic efficiency than aeration by air or nitrogen gas.

Keywords: chromium; titanium dioxide; salicylic acid; hole-scavenger; wavelength; oxygen



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1. Introduction

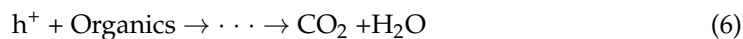
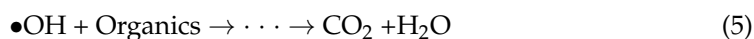
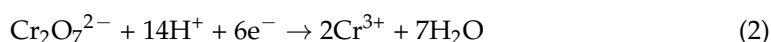
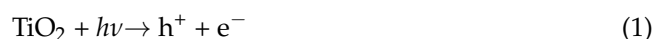
It is a well-known fact that Cr(VI) is one of the toxic pollutants introduced into the environment by discharges from industrial processes, such as leather tanning, the steel industry, electroplating, and the making of dyes. The concentration in waste streams discharged from industry can be as high as 5000 mgL⁻¹ [1]. Precipitation, adsorption, ion exchange, and membrane separation are common methods currently used for the disposal or recovery of metal ions in wastewater.

Chromium exists in two stable oxidation states—Cr(VI) and Cr(III)—in the natural environment. The former is toxic to most organisms, carcinogenic to animals, and can cause irritation and corrosion of skin in human beings. It is mobile in nature due to the weak sorption onto inorganic surfaces. On the other hand, the latter is usually adsorbed or precipitated by a variety of inorganic and organic substrates. The toxicity of Cr(VI) is one hundred times higher than that of Cr(III) [2,3]. Therefore, the reduction of Cr(VI) to Cr(III) has become a key procedure for treating Cr(VI) containing wastewater.

Titanium dioxide (TiO₂) is one of the promising photocatalysts for the removal of organic pollutants as well as inorganic ions [4–6] because it is non-toxic, inexpensive, highly photoactive, and easily synthesized and handled [7]. The redox potentials of valence and conduction bands for anatase TiO₂ are 3.0 and −0.2 V, respectively, which indicate

that TiO₂ is a good material for the oxidation of organic compounds [8,9]. TiO₂ is also a good material for the reduction of inorganic compounds. The photo-reduction over TiO₂ photocatalyst is a new technology for the removal or recovery of dissolved metal ions in wastewater. Past studies have shown its application potentials for metal ions removal or recovery, such as Mn(II) [10], Ag(I) [11], Au(III) [12], Pb(II) [13], Hg(II) [14], Ni(II), Fe(II), Fe(III) [3], Pt(IV) [15], Cr(VI) [16–18], Cu(II) [19], Se(IV) [20], Se(VI) [21,22], Cd(II) [23]. Ultraviolet lights can offer a sufficient energy to overcome the band gap of TiO₂ and thereby to form the electron-hole pairs (e⁻-h⁺) [24]. The nanostructures of TiO₂ have been studied extensively for their photocatalytic, optical, and electronic properties, as well as their application in photovoltaics [7,25–27].

The photo-reduction of Cr(VI) to Cr(III) can be achieved via a photocatalytic process with a simplified mechanism as follows [28]:



Illumination of titania with UV light exits the transition of valence band electrons to the conduction band (reaction (1)). As a result, electron-hole pairs are formed which migrate to the surface of the photocatalyst and initiate photocatalytic reactions. The electrons are able to reduce Cr(VI) to Cr(III) (reaction (2)), and the holes may lead to generation of O₂ in the absence of any organics (reaction (3)). However, the photo-reduction of Cr(VI) alone is quite slow due to a slow four-electron process for oxidation of water to oxygen [25,29]. Alternatively, in the presence of the degradable organics, the holes can produce •OH radicals (reaction (4)), which can further degrade the organics to CO₂ and H₂O (reaction (5)). Of course, the holes can also directly oxidize the organic molecules (reaction (6)). That is to say, in the presence of salicylic acid (COOH⁻), the photo-generated holes are able to be rapidly scavenged from the TiO₂ particles, suppressing the electron-hole recombination on TiO₂ and accelerating the reduction of Cr(VI) by the photo-generated electrons [30]. In this study, we attempted to formation of the oxidation products of COOH⁻ in the photocatalytic conversion of Cr(III) using chrome, an aqueous solution of COOH⁻, which was added as a hole scavenger.

The photo-born electrons are capable of reducing Cr(VI) as long as they are separated from holes. Therefore, enhancing the charge separation becomes an important strategy for promoting the photo-reduction of Cr(VI) over TiO₂ catalyst. Charge separation can be enhanced by improving the structure of photocatalyst and by introducing the scavengers of holes in the solution. It has been reported that the presence of organic species as sacrificial electrons donor (i.e., holes scavenger) can accelerate the photo-reduction of Cr(VI) [18,29,31,32]. However, it has not yet been identified that whether the concentration of hexavalent chromium influences the rate of the photo-reduction of Cr(VI) in the presence of organic compounds. In theory, if the reduction is paired with photo-oxidation of some organic compounds, the reduction of Cr(VI) should be promoted remarkably. In practice, an unexpected deactivation of the photo-reduction reaction was encountered in past studies. These contrary results might come from the formation of complex compounds between chromium and intermediate of the oxidized organic compounds.

Oxygen molecule is also a possible capturer of electrons in the solution, it can compete with Cr(VI) in the photo-born electrons in a photo-reduction of Cr(VI) process. The existence of oxygen was considered as unfavorable to the reduction of Cr(VI) in a photo-reduction process [31]. Therefore, aeration with nitrogen gas instead of air was used in

some of past studies to prevent the photo-reduction of Cr(VI) process from the interference of oxygen in the solution [33]. Some researchers proposed that the reduction potential of Cr(VI) (0.98 eV) in an acidic condition is nearly equal to that of the oxygen molecule (1.09 eV), and thereby, the interference of oxygen can be neglected [3,31]. However, parts of researchers believe that the effect of aerating nitrogen gas on photo-reduction activity over TiO₂ catalyst is limited because oxygen is still possibly produced from the oxidization of water in the solution in a photocatalytic process [3,34]. On the contrary, Kyung et al. [35] proposed that the presence of dissolved oxygen increased the photo-reduction activity of Cr(VI) despite the competition of electrons. This might be ascribed to the presence of in situ photo-generated H₂O₂ from O₂, which acts as an active reductant of Cr(VI). According to the past studies [3,33], many conflicting opinions about the effect of oxygen on the photo-reduction of Cr(VI) were drawn, indicating the role of oxygen in a photocatalytic process is not clear yet. Some unknown factors might synergistically or reciprocally affect the role of oxygen in a photo-reduction process. It is necessary to pay more attention to the interaction between the presence of oxygen and the other key factors on the photocatalytic activity over TiO₂ catalyst.

However, it is yet unknown how the environmental factors in a photo-reduction process, such as the wavelength of light, the presence of oxygen and/or scavenger, the concentration of metals, and the formation of intermediates of oxidized organics, influence the reduction of Cr(VI) over TiO₂ catalyst coupled with photocatalytic oxidation of organic pollutants, and what the ranges of these factors being suitable for coupled photocatalytic degradation of inorganic and organic pollutants are. In the present work, therefore, the photocatalytic reduction of Cr(VI) was systematically investigated over anatase-type TiO₂ catalysts in the absence and presence of organic species (salicylic acid) and dissolved oxygen under different wavelength and initial Cr(VI) conditions. The chromium species distributions (in solution and on TiO₂ surfaces) after photo-reduction reaction are also estimated by mass balance method to track the fate of the chromium in a photocatalytic process. The photo-reduction efficiencies of Cr(VI) and the deactivation possibly originated from the formation of intermediates of oxidized salicylic acid are also compared and discussed in this paper. In this study, three ways were used to remove chromium metal ions from water. We study the influence of using salicylic acid as a hole scavenger on the photocatalytic reduction of Cr(VI) as well. Adding salicylic acid (SA) as a hole scavenger in the experiment of Cr(VI) reduction could increase the reduction rate and the efficiency.

2. Materials and Methods

2.1. Materials

Commercial titanium dioxide (P25, Degussa Co. Sigma-Aldrich, Taiwan, China) was used as the photocatalyst in the study. The crystalline composition was 80% of anatase and 20% of rutile. Its physical and chemical features are listed in Table 1. The wavelengths of UV light used in the study were 365 nm, 254 nm, and 185 nm. Potassium dichromate (K₂Cr₂O₇) and salicylic acid (SA, C₇H₆O₃) were used as the Cr(VI) source and hole-scavengers, respectively, without further purification in the study (both 99.5%, YAKURI).

Table 1. Physical and chemical features of commercial P25-TiO₂.

Features	TiO ₂ (Degussa P25)
Content of titanium oxide	99%
Average primary particle size	21 nm
Tapped density	approx. 130 gL ⁻¹
Crystal structure	Anatase:Rutile = 4:1
Specific surface area	47.5 ± 3.7 m ² g ⁻¹
Loss of weight in burning	≤2.0%
pH value of aqueous suspended matter	3.5~4.5
Appearance	White powder

2.2. Analytical Methods

All chemicals and reagents used for experiments and analyses were of analytical grades. Stock solution of 1000 mgL^{-1} Cr(VI) was prepared from $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized water. The solution was diluted to the working concentration in the range of $3\text{--}20 \text{ mg Cr(VI) L}^{-1}$. The initial pH of the working solution was adjusted by H_2SO_4 or NaOH solution. The concentration of total chromium was measured by inductively coupled plasma optical emission spectrometer (JY2000-2, ICP, France). The Cr(VI) concentration was analyzed by the diphenylcarbazide photometric method, using a UV-VIS spectrophotometer (UV-1601, Shimadzu, Kyoto, Japan) at 540 nm, which can effectively diminish the interference from the absorption of salicylic acid (SA) and its degradation intermediates [28,36]. All samples were analyzed in duplicate or more and the average values were reported in the paper. The size and morphology of nanomaterial were observed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7401F, Tokyo, Japan). The functional groups and elemental compositions of P25 were identified by Fourier transform infrared spectroscopy (FTIR) analysis (Model Spectrum One & RX1, Perkin Elmer, Waltham, MA, USA) and X-ray energy dispersive spectrometer (EDS; TOPCON ABT-32), respectively. The pH of the point of zero charge of P25 was measured using a zeta potential meter (Model Nano-ZS, Malvern Instrument Co., Malvern, UK).

2.3. Experimental Procedures

In order to investigate the effects of SA and oxygen presence as well as UV light intensity on the photocatalytic activity of TiO_2 , the photocatalytic reduction of Cr(VI) was carried out in the TiO_2 suspension under UV irradiation. Three different UV light wavelengths (365 nm, 254 nm, and 185 nm) were used to conduct the photoreduction reaction of Cr(VI) in the absence and presence of SA (hole-scavenger) under the conditions and six hours of reaction time. The reaction suspensions were prepared by adding 0.5 g of the catalyst to 1000 mL of aqueous Cr(VI) solution with an initial Cr(VI) concentration of 3 or 20 mgL^{-1} . Prior to the photoreaction, the suspension had its pH manually adjusted to ca. 3 by diluted NaOH or H_2SO_4 solution and was magnetically stirred in the dark for 30 min to establish an adsorption/desorption equilibrium condition. The aqueous suspension containing Cr(VI) and the photocatalyst was then irradiated by UV with constant stirring for six hours. At given time intervals, analytical samples were taken from the suspension and immediately centrifuged at 4000 rpm for 15 min, followed by filtering through a $0.45 \mu\text{m}$ filter. All the photocatalytic experiments were conducted in an environment with temperature controlled at ca. $25 \text{ }^\circ\text{C}$.

2.4. Slurry Reactor

All slurry reactors were performed using a Pyrex cylindrical reactor were carried out by magnetically stirring. The UV light was emitted from eight 13-watt integrally filtered low-pressure mercury UV tubes (Philips corporation, Taipei, Taiwan, China). The wavelengths of UV light used in the study were 365 nm, 254 nm, and 185 nm. Each tube was positioned vertically at a distance of 5–6 cm from each side of the exposed catalytic section of the Pyrex cylindrical reactor.

3. Results

3.1. Titanium Dioxide Basic Characteristics

Commercial Degussa P25 was used as the photocatalyst in the study. Its physical and chemical features have been listed in Table 1. The diameter of the P25 is about 15–30 nm and aggregation behavior can be seen by FE-SEM, as shown in Figure 1a. The elemental composition was detected by X-ray energy dispersive spectrometer and is shown in Figure 1b. The FTIR spectra in Figure 1c show the major functional groups including --OH stretching at $\sim 3400 \text{ cm}^{-1}$, --OH bending at $\sim 1630 \text{ cm}^{-1}$, Ti-O stretching and O-Ti-O bending at $\sim 500\text{--}660 \text{ cm}^{-1}$ [32,37]. The zeta potential data in Figure 1d show that the iso-electric point occurs at pH 6.7.

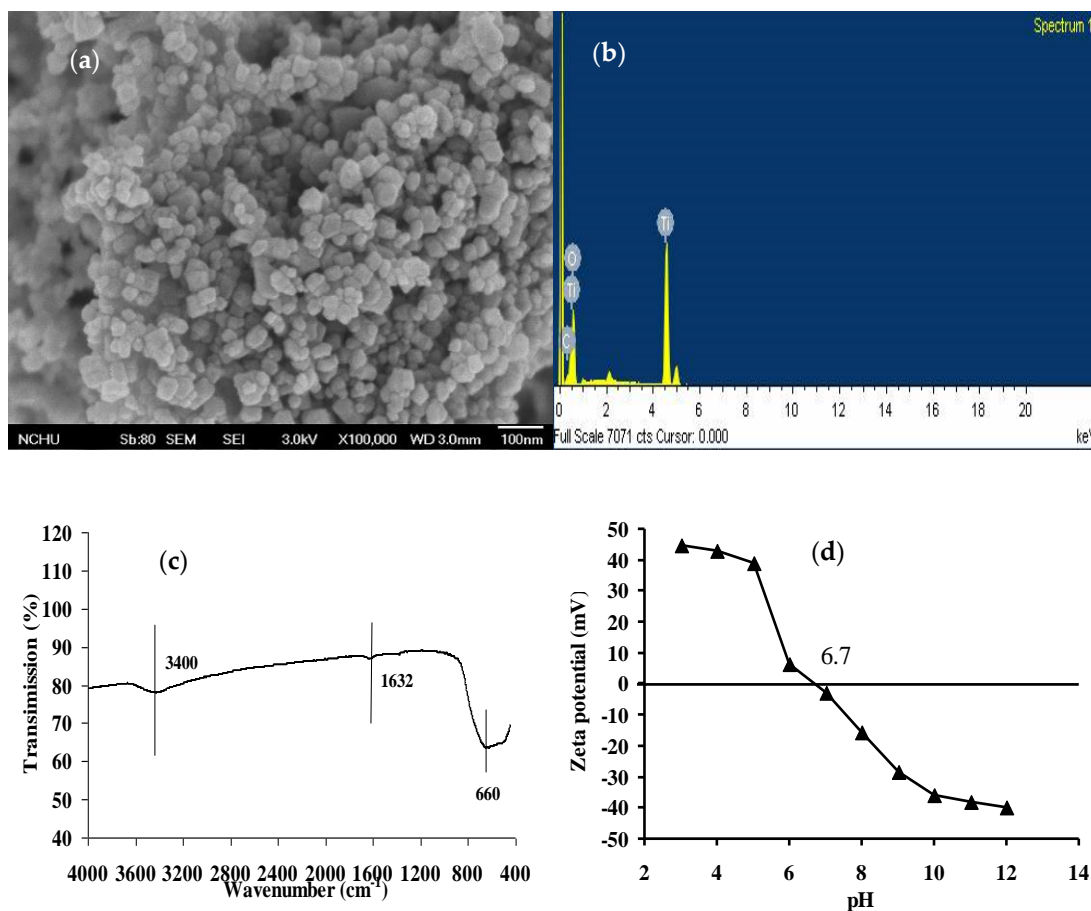


Figure 1. (a) FE-SEM image; (b) EDS spectra; (c) FTIR spectra; (d) zeta potential of commercial TiO₂ of Degussa P25 used in the study.

3.2. Control Experiment

Control experiments were conducted to confirm and pre-exclude the influence of uncontrolled factors on the results of main experiments. The first background experiment was conducted to understand the degree of chromium reduction by UV irradiation alone. Without any photocatalyst in the reactors, 3 mgL⁻¹ and 20 mgL⁻¹ of initial Cr(VI) concentrations were irradiated by 365 nm UV light for three hours under pH3 and 25 °C conditions. The experimental result showed that the total chromium concentration was equal to the hexavalent chromium concentration. No trivalent chromium formation was found (data not shown). It indicates that hexavalent chromium cannot be reduced to trivalent type by UV irradiation without any photocatalyst.

Second, the solution with 3 mgL⁻¹ or 20 mgL⁻¹ of Cr(VI) and 0.5 gL⁻¹ of P25 in the reactor was agitated in a dark room for three hours under pH3 and 25 °C conditions. The experimental result showed that the total chromium concentration was also equal to the hexavalent chromium concentration. No trivalent chromium formation was found (data not shown). This indicates that hexavalent chromium cannot be reduced to trivalent type only by contact with TiO₂ without UV light illumination. However, decreases of hexavalent chromium concentration were found. The decrease rates for the cases of 3 mgL⁻¹ and 20 mgL⁻¹ were 8.5% and 2.1%, respectively, revealing that P25-TiO₂ possibly had a low ability for adsorption of negative dichromate ion. This is in agreement with the zeta potential profile presented in Figure 1d, which shows positive potential in pH3. A past study also obtained a similar result [18]. They used pure TiO₂ to photocatalyze aqueous Cr(VI) under the common conditions of Cr(VI) concentration 10 mgL⁻¹, pH7, TiO₂ dose 2 gL⁻¹, and two hours of contact time. A near 22% decrease rate of Cr(VI) was found in

the absence of UV light illumination. On the other hand, less than 7% loss of Cr(VI) was found under UV irradiation but in the absence of TiO₂.

3.3. Interaction of Wavelength and Hole-Scavenger on Photo-Reduction Efficiency of Cr(VI)

The experimental results are shown in Figure 2. In the absence of SA, the reduction rate of 3 mg Cr(VI) L⁻¹ initial concentration under 365 nm light illumination was significantly less than those under 254 nm and 185 nm illuminations. Additionally, the reduction rate under 254 nm illumination was almost the same with that under 185 nm illumination. Within 20 min, 3 mgL⁻¹ Cr(VI) could be completely removed for 254 and 185 nm cases as well as within 30 min for 365 nm case, as shown in Figure 2a. This result concludes that 254 nm light is more suitable than 365 nm for the purpose of photo-reduction of lower-level Cr(VI) by TiO₂ in the absence of SA.

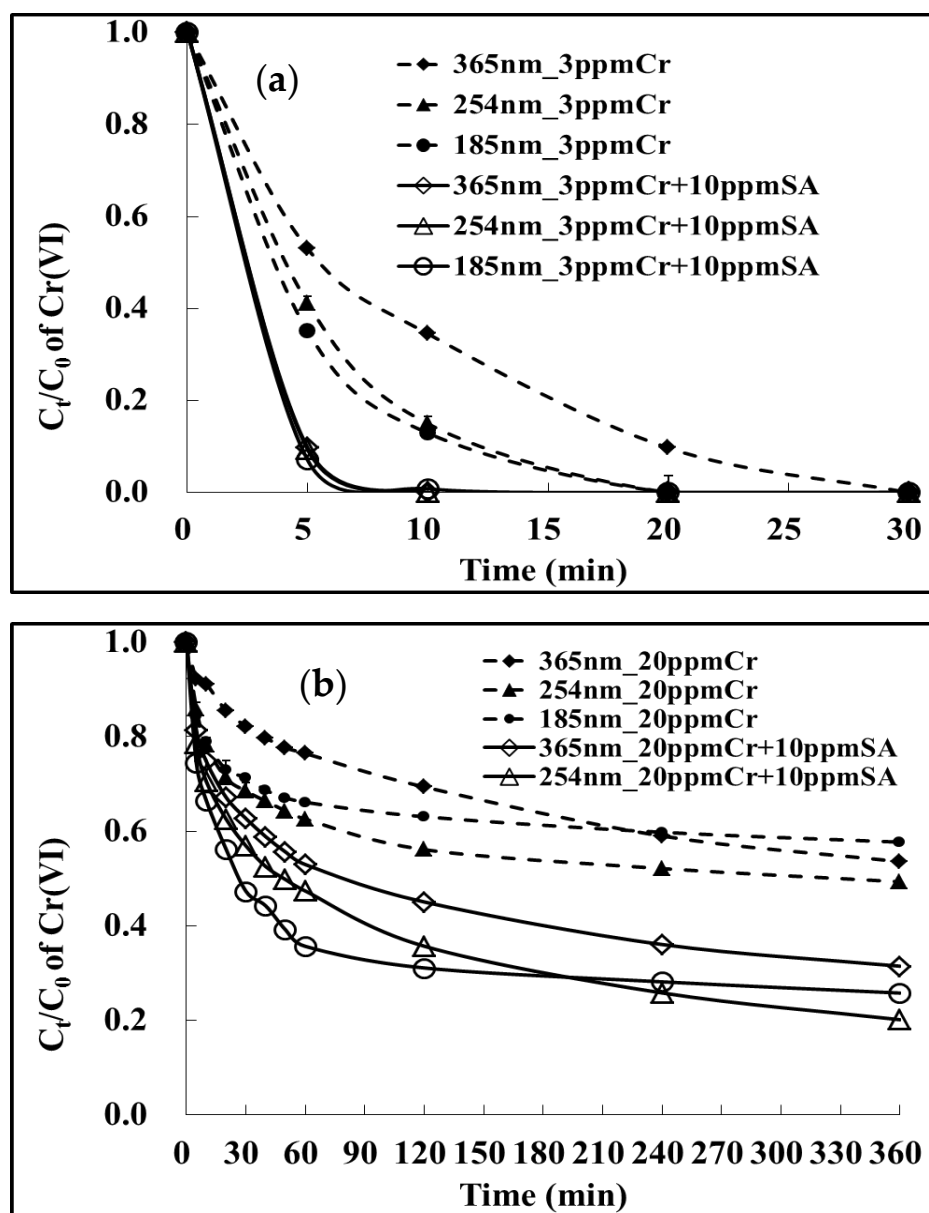


Figure 2. Effects of the wavelength factor on residuals of Cr(VI) after photo-reduction by TiO₂ (a) Cr(VI) 3 mgL⁻¹ (b) Cr(VI) 20 mgL⁻¹.

On the other hand, in the presence of SA, the reduction rates for these three cases were almost the same and 3 mgL⁻¹ Cr(VI) could be completely removed within six minutes,

revealing that the effect of wavelength on reduction efficiency became tiny. These results indicate that the introduction of SA as a hole-scavenger in the photo-reduction reaction can indeed speed up the reduction rate of Cr(VI) and then shorten the reaction time. The energy of 365 nm UV light is enough to photo-reduce low concentration of Cr(VI) by TiO₂ in the presence of SA and the effect of the hole-scavenger presence on photo-reduction of Cr(VI) is more significant than that of light wavelength, revealing that the addition of hole-scavenger can not only promote the photo-reduction efficiency of Cr(VI), but can also reduce the energy requirement for photo-reduction of Cr(VI). Similar results can be found in the past studies [28,30,36].

In order to understand the effect of the initial Cr(VI) concentration on the photo-reduction rate, 20 mgL⁻¹ of higher Cr(VI) concentration was used and the same experiments were repeated again. The results are shown in Figure 2b. In the absence of SA, only ca. 40% of Cr(VI) was photo-reduced after six hours illumination. As with the case of 3 mgL⁻¹ Cr(VI), the reduction rate for 365 nm was lower than those for 254 nm and 185 nm.

On the contrary, the photo-reduction efficiency was promoted in the presence of SA. About 80% of Cr(VI) was photo-reduced after six hours illumination. The reduction rates for 185 nm and 254 nm illuminations were higher than those for 365 nm case. By comparing Figure 2a,b, in the presence of SA the illumination of 365 nm UV light has enough energy to adequately reduce 3 mgL⁻¹ Cr(VI) but higher energy by the illumination of 185 nm or 254 nm UV light is necessary if the Cr(VI) concentration is increased to 20 mgL⁻¹. Unlike the 3 mgL⁻¹ Cr(VI) case, UV light wavelength and hole-scavenger are important factors when the initial Cr(VI) concentration is as high as 20 mgL⁻¹.

Unexpectedly, the absence of SA illuminating by highest energy UV light (185 nm) did not obtain a better photo-reduction efficiency, revealing that the energy state plays an important role. This might be because the high energy from 185 nm light excites more electrons and electron-hole pairs, thereby increasing the possibility of collision and recombination for electrons and hole. Moreover, illumination by elevated energy produces more •OH and •O₂⁻ radicals, which might further re-oxidize trivalent chromium to hexavalent chromium, resulting in the decrease in photo-reduction efficiency for hexavalent chromium. The experimental result reported by Ku and Jung [17] also showed the defect of elevated irradiation energy. This phenomenon disappeared when SA (hole-scavenger) was present in the solution. This might indicate that SA presence effectively reduces the opportunity of electrons-holes recombination.

3.4. Effect of Wavelength on Distribution of Chromium Species

In order to further understand the transformation of chromium species after photo-reduction, we assume that most of the chromium after photo-reduction reaction exists in only two stable oxidation states, i.e., Cr(VI) and Cr(III). Other oxidation states can be neglected due to the relatively unstable state and small quantity. Furthermore, based on the concept of law of mass conservation, the amount of total chromium within the reactor before and after photocatalytic reduction reaction is assumed to be unchanging and equal to the initial hexavalent chromium mass. Thirdly, we assume the Cr(III) in the solution, formed after photo-reduction reaction, only exists by ionic state due to the difficulty of the formation of chromium hydroxide in the solution at pH3; i.e., the formation of chromic hydroxide is assumed to be negligible [38]. Additionally, chromic hydroxide can only present on the surface of the TiO₂ particles [33]. This hypothesis is reasonable because our recent research found by X-ray photoelectron spectroscopy (XPS) the existence of both hexavalent and trivalent chromium ions on the surface of TiO₂ particles after photocatalytic reaction (data not shown). Past studies also found the existence of both chromium oxidation states on the surface of carbon nanotubes [39,40]. Therefore, in the study, we suppose that both hexavalent and trivalent chromium ions are possibly retained on TiO₂ surfaces. Based on the above assumptions, we define that the theoretical total chromium quantity ($C_{\text{total_theory}}$) is equal to the total chromium quantity adding into the reactor at the beginning of the experiment. Furthermore, the detected total chromium

quantity ($Cr_{total_detected}$) is defined as the total chromium quantity analyzed by ICP after being filtered by 0.45 μm filter to remove any particles or photocatalyst after the photo-reduction. Then, the following balance equations can be obtained:

$$Cr_{solid} = Cr_{total_theory} - Cr_{total_detected} \quad (7)$$

$$Cr(III)_{aqua} = Cr_{total_detected} - Cr(VI)_{aqua} \quad (8)$$

The Cr_{solid} in Equation (1) is the quantity of chromium retained on TiO_2 surface. The states of chromium on TiO_2 surface are very complicated. It could possibly be the deposited chromium hydroxide, adsorbed hexavalent, and trivalent chromium ions or their complex compounds formed via photo-reduction reaction. Theoretically, it could also possibly be the zero-valent chromium if the photo energy is high enough. It is difficult to distinguish all the species of them. The $Cr(VI)_{aqua}$ is the quantity of hexavalent chromium in solution after photo-reduction, analyzed by the diphenylcarbazide photometric method, as described previously. $Cr(III)_{aqua}$ is the quantity of trivalent chromium ion in solution after photo-reduction, which was obtained from Equation (2). Although the toxicity and mobility of Cr(III) are lower than those of Cr(VI), high concentrations of Cr(III) can cause adverse effects because of its high capability to combine with various organic compounds, which might inhibit various enzymes of living organisms [41]. In addition, the soluble complexes of Cr(III) could possibly be re-oxidized to Cr(VI) either by naturally occurring oxidants [42] or by chlorine or other strong oxidizing disinfectants during drinking water treatment [43]. Therefore, removal of both Cr(III) and Cr(VI) is vital to a successful Cr treatment or remediation technology.

According to the above assumptions and definitions, the quantities of hexavalent and trivalent chromium in the solution and the quantity of chromic hydroxide deposition on the surface of TiO_2 after photo-reduction reaction are further compared in Figure 3. Figure 3a shows the photocatalytic result of 3 mgL^{-1} of Cr(VI) in the absence of SA, indicating that 93.1–100% of total chromium was retained on the surface of TiO_2 and only a small amount of trivalent chromium (0–6.9%) existed in the solution. It is clear that the effect of wavelength on the distribution of chromium species was insignificant. On the other hand, more trivalent chromium ions were released into the solution in the presence of SA (Figure 3b) than in the absence case (Figure 3a) and the influence of wavelength on the distribution of chromium species became significant in the presence of SA. A total of 24.3% of trivalent chromium species was found in the solution for 365 nm light, whereas only 1.5% was found for 185 nm case, indicating the lower the energy of UV illumination, the more the amount of trivalent chromium ions remained in the solution and the less the amount of chromium retained on TiO_2 surface. During photocatalytic experiments, we found the mineralization rate of SA was increased from 56.4% to 79.7% while decreasing the wavelength from 365 nm to 185 nm. At the same time, the percentage of intermediate products resulted from the photo-oxidation of SA—for example, quinine, hydroquinone, or other polyhydroxy derivative, etc.—was decreased from 36.4% to 20.3%. We believe that the release of trivalent chromium into the solution was highly related to the amount of intermediate because of the formation of complex compounds between Cr(III) ion and intermediate. Part of chromium might be bonded with the intermediate in the form of complex compounds, resulting in a decrease in the amount of chromic hydroxide solids deposited on TiO_2 surface. Moreover, part of the adsorption sites on TiO_2 surface might also be occupied by the intermediate and its complex compounds, resulting in being unfavorable to the adsorption of chromium ions on TiO_2 surface. These can probably explain why lower energy of UV illumination resulted in a higher amount of Cr(III) in the solution and lower amount of chromium on TiO_2 surface in the presence of SA.

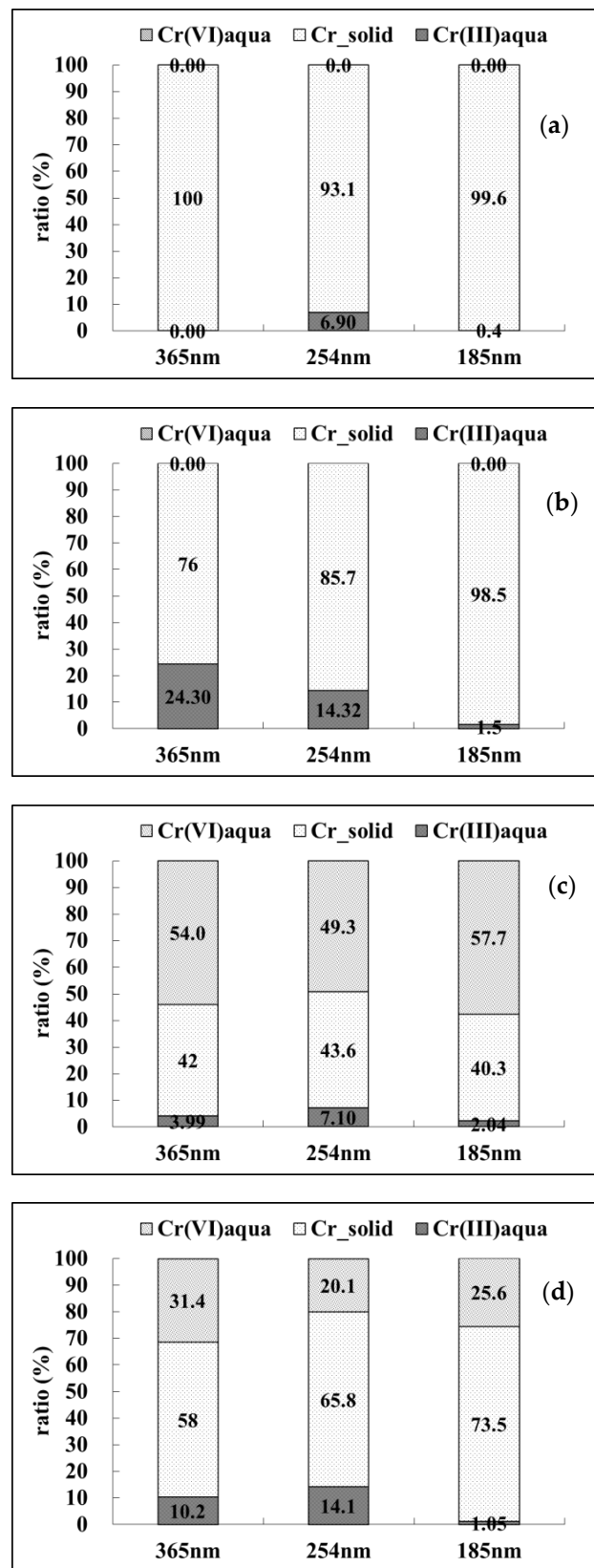


Figure 3. Effects of the wavelength factor on chromium species distribution after photo-reduction by TiO₂ (a) Cr 3 mgL⁻¹ alone, (b) 3 mgL⁻¹ of Cr(VI) coupled with 10 mgL⁻¹ of SA, (c) Cr 20 mgL⁻¹ alone, and (d) 20 mgL⁻¹ of Cr(VI) coupled with 10 mgL⁻¹ of SA.

Figure 3c,d show the distribution of chromium species in the absence and presence of SA, respectively, for the case of 20 mgL^{-1} of Cr(VI). It is easy to discern that the presence of SA remarkably increases the photo-reduction efficiency. The residual of hexavalent chromium in solution was significantly decreased from 49.3–57.7% to 20.1–31.4%. The 254 nm illumination had the lowest residual Cr(VI) in solution for both SA absence and presence cases. Moreover, the distribution of $\text{Cr(III)}_{\text{aqua}}$ for the 20 mgL^{-1} of Cr(VI) case was similar to that for the 3 mgL^{-1} case. The presence of SA also significantly increased the ratio of $\text{Cr(III)}_{\text{aqua}}$, except for the case of 185 nm condition.

3.5. Interaction of Oxygen and Hole-Scavenger on Photo-Reduction Efficiency of Cr(VI)

In order to understand the effect of oxygen on the photo-reduction of Cr(VI), we conducted the photocatalytic experiments using three sorts of oxygen-containing conditions during the period of photolysis, including (1) continuously purging by nitrogen gas (N_2), (2) continuously aerating by air (AIR) and (3) continuously stirring (STIR) without aeration. Continuous aeration by nitrogen gas, called the “ N_2 ” condition, was used to remove the dissolved oxygen in the solution. We assumed no oxygen in the solution at this condition. Continuous aeration by air, called the “AIR” condition, was used to fully supply the dissolved oxygen in the solution. We assumed that the oxygen concentration in the solution was maintained at the saturation level at this condition. Stirring only, called the “STIR” condition, represented the condition of neither oxygen removal nor oxygen supply in the solution. We assumed that the oxygen dissolved in the solution was limited at this condition. The variation of oxygen concentration in the solution related to the photocatalytic reaction in which oxygen molecular was involved. The experiments were conducted under the conditions of 365 nm UV light illumination and 1.5 L min^{-1} of gas flow rate (if applicable). Other experimental conditions were the same as previous sections. The experimental results are shown in Figure 4.

Figure 4a shows the result of 3 mgL^{-1} Cr(VI) and indicates that the oxygen-containing conditions did not remarkably influence the photo-reduction degree, regardless of the absence or presence of SA. Figure 4b shows the result of 20 mgL^{-1} Cr(VI) and indicates a significantly different result from the case of 3 mgL^{-1} Cr(VI). In the absence of SA, N_2 run had a highest reduction rate at the first three hours, but became the lowest one at the end of the experiment. In the presence of SA, the reduction degree, regardless of the absence or presence of SA. Figure 4b shows the result of 20 mgL^{-1} Cr(VI) and indicates a significantly different result from the case of 3 mgL^{-1} Cr(VI). In the abs of N_2 run was obviously lower than those of AIR and STIR runs throughout the experiment. The STIR run had the highest reduction efficiency throughout the experiment except for the point at 60 min. It is noticeable that the reduction of AIR condition was almost the same with that of the STIR condition at the beginning of 60 min in the experiment. However, an abruptness occurred after 60 min of the experiment. The photo-reduction reaction almost ceased after 60 min of the experiment at the AIR run. It seemed to be a possible phenomenon of deactivation.

In our study, we found that the role of oxygen in photo-reduction of Cr(VI) is dependent on the concentration of Cr(VI) participating in the reaction. The influence of oxygen on the reduction reaction was unobvious when the initial Cr(VI) concentration was low (3 mgL^{-1} in this study) due to a lower requirement on photo-born electrons; thereby, the influence of oxygen molecule competing electrons with Cr(VI) became trivial. However, the reduction reaction became sensitive to the oxygen condition in the solution when the initial Cr(VI) concentration was high (20 mgL^{-1} in this study), especially in the presence of SA. The reduction activity of N_2 was conspicuously lower than those of AIR and STIR. Aerating nitrogen gas would decrease dissolved oxygen concentration in solution and thereby decrease the amounts of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ producing from the exciting of oxygen molecule in solution. Both $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ are important in a photocatalytic process. That is why a lower reduction activity was found in the N_2 run. It seems that the supply of oxygen in solution benefited the chromium reduction. However, a noticeable result occurred in our

experiment. The reduction activity was only improved at the beginning of 60 min in the experiment for AIR run. The reduction reaction suddenly stopped after 60 min (Figure 4b). Theoretically, the reduction degree should be remarkably promoted at AIR run because oxygen was fully supplied. However, an unexpected result occurred in our experiment. An unknown factor deteriorated the proceeding photocatalytic reduction reaction halfway for the AIR run. We speculate that the speed-up formation of chromic particulates on the surfaces of TiO_2 prevents the catalysts from UV light irradiation and then makes the catalysts deactivated.

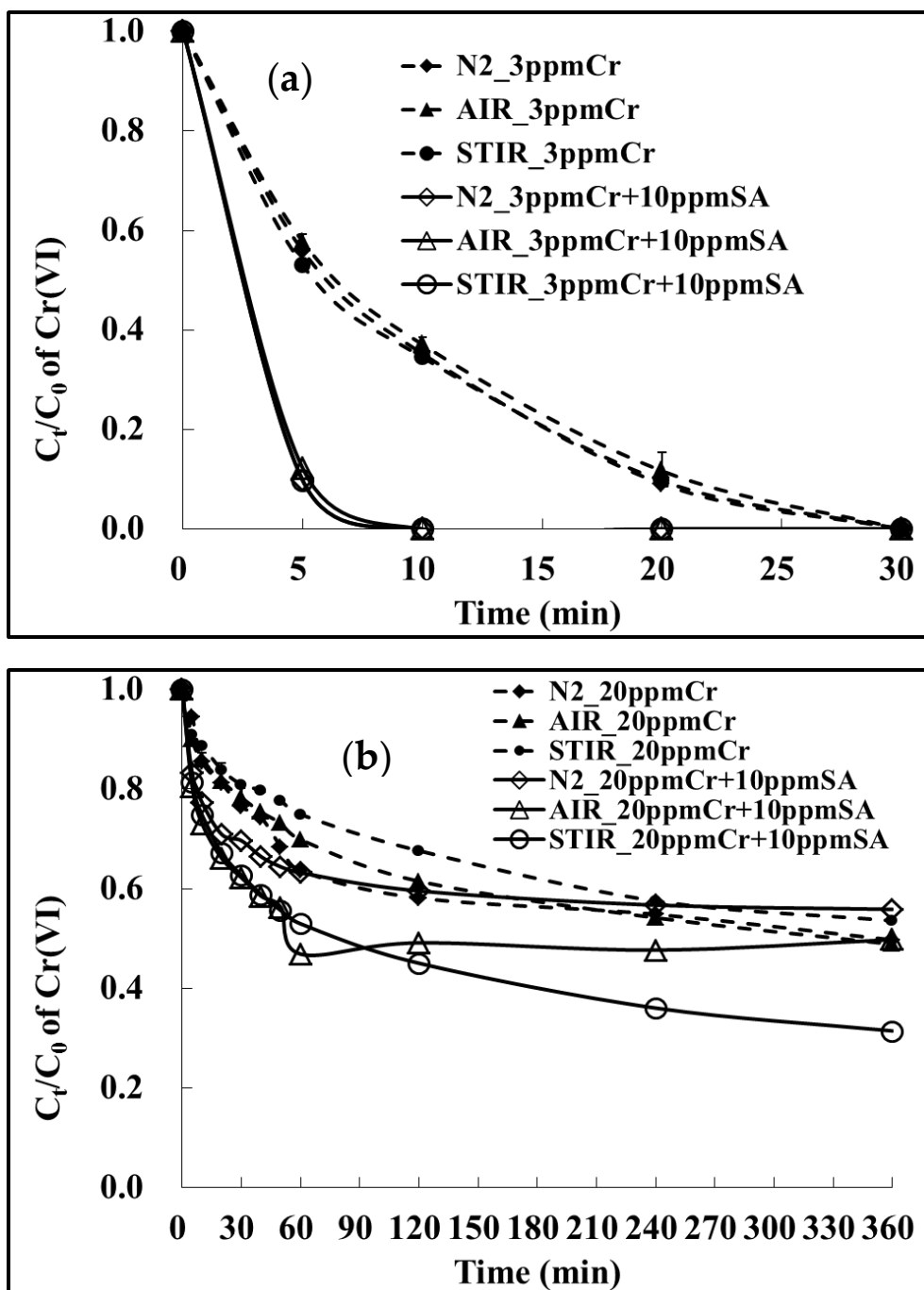


Figure 4. Effects of oxygen on residuals of Cr(VI) after photo-reduction by TiO_2 (a) Cr 3 mgL^{-1} and (b) Cr 20 mgL^{-1} .

Past studies frequently showed conflicting results about the effect of oxygen on the photo-reduction of Cr(VI) [31,33–35], indicating that oxygen presence is a complex factor influencing this reaction. The interaction between oxygen presence and other environmental conditions, such as Cr(VI) concentration and scavenger presence (SA in this study) has been demonstrated to be a key factor about the degree of oxygen effect on Cr(VI) photo-reduction.

3.6. Effect of Oxygen on Distribution of Chromium Species

According to previous assumptions and definitions, the quantities of hexavalent and trivalent chromium in the solution and the quantity of chromium hydroxide depositing on the surface of TiO₂ after photo-reduction reaction were further compared in Figure 5. The experiments were conducted under the conditions of 365 nm UV light illumination and 1.5 L min⁻¹ of gas flow rate (if applicable). It can be seen from Figure 5a,b that almost all the chromium in solution were eventually transferred to the surface of TiO₂ after photocatalysis for 3 mgL⁻¹ of Cr(VI) case, except for the STIR run in the presence of SA, which had 24.3% of Cr(III) in solution. During our photocatalytic experiments, we found that the mineralization rates of SA in binary system were 36.1%, 43.6%, and 56.4% for N₂, AIR, and STIR tests, respectively. At the same time, the percentages of intermediate products resulted from the photo-oxidation of SA were 43.7%, 51.3%, and 36.4% for N₂, AIR, and STIR tests, respectively. Both mineralization and intermediate percentages data showed that STIR run had the largest photo-oxidation activity. However, the ratio of trivalent chromium in solution was markedly high (24.3%) in the STIR test. We believe it might be ascribed to the extent of photo-reduction due to the fact that Cr(III) can form complexes with inorganic and organic ligands present in the environment, leading to a higher solubility.

Figure 5c,d show the results of 20 mgL⁻¹ of Cr(VI) concentration. In the absence of SA, 48.9% of total chromium was retained on the surface of catalysts for N₂ run, whereas in the presence of SA only 42.9% of chromium was retained on catalysts' surfaces for N₂ run. The residual of hexavalent chromium in the solution in the presence of SA (55.9%) was also higher than that in the absence of SA (49.7%), revealing that the photo-reduction efficiency was not improved by the introduction of the scavenger (SA) for the N₂ run. The distribution of chromium species for AIR run was similar to N₂ run.

Nevertheless, a quite different result occurred for STIR run. In the absence of SA, there was 54.1% of total chromium remained in the solution in the hexavalent form, whereas 41.9% of total chromium was retained on catalysts' surfaces for STIR run. However, in the presence of SA, there was less hexavalent chromium remained in the solution (28.6%), but a larger amount of chromium (57.4%) was retained on catalysts' surfaces for the STIR case, revealing that the photo-reduction activity was significantly enhanced by the addition of SA at the STIR condition. The merit of the presence of SA in the photo-reduction reaction was displayed for the STIR condition, but not for the N₂ and AIR conditions, indicating that the oxygen level has a great impact on the photocatalytic reaction. Neither de-oxygenation by nitrogen gas nor oxygen supplementation by air is suitable. Only simple stirring obtains a better photocatalytic reaction.

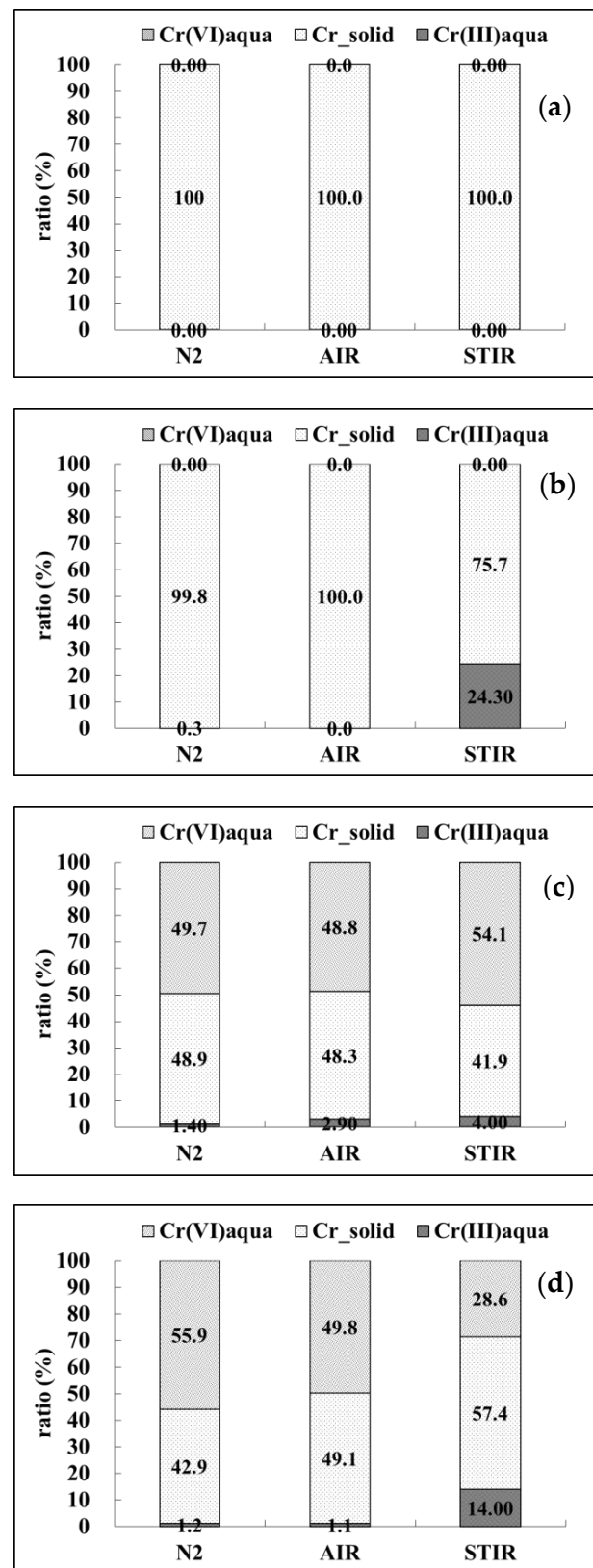


Figure 5. Effects of oxygen on chromium species distribution after photo-reduction by TiO₂ (a) Cr 3 mgL⁻¹ alone, (b) 3 mgL⁻¹ of Cr(VI) coupled with 10 mgL⁻¹ of SA, (c) Cr 20 mgL⁻¹ alone, and (d) 20 mgL⁻¹ of Cr(VI) coupled with 10 mgL⁻¹ of SA.

4. Conclusions

This study explores the effects of wavelength, hole-scavenger, and oxygen conditions on the photocatalytic reduction of hexavalent chromium over titanium dioxide photocatalyst and experimentally demonstrates the existence of interaction between these factors. Some important conclusions could be drawn, as follows:

In the absence of SA, 365 nm light had a smaller efficiency for reduction of 3 mg Cr(VI) L⁻¹ than 254 nm and 185 nm illuminations, whereas in the presence of SA, the wavelength effect became tiny, revealing that the factor of hole-scavenger presence is more important than the wavelength. However, the UV light wavelength and hole-scavenger presence became important when the Cr(VI) concentration increased to 20 mgL⁻¹.

Analysis of chromium species shows that the lower the energy of UV illumination was, the more the amount of trivalent chromium ions remained in the solution and the less the amount of chromium retained on TiO₂ surface. The release of trivalent chromium into the solution was related to the amount of intermediate from oxidizing SA due to the formation of complex compounds between Cr(III) ion and intermediate.

The influence of oxygen-containing conditions in the solution on reduction of 3 mgL⁻¹ Cr(VI) was unobvious. However, its influence became remarkable when Cr(VI) concentration increased to 20 mgL⁻¹, especially in the presence of SA. The interaction between oxygen-containing factor and other environmental factors, such as Cr(VI) concentration and scavenger presence (SA in this study) is a key factor about the degree of oxygen effect on Cr(VI) photo-reduction.

After photocatalysis of 3 mgL⁻¹ of Cr(VI), almost all the chromium in solution were eventually transferred to the surface of TiO₂, except for the STIR run in the presence of SA, which had 24.3% of Cr(III) in solution. After photocatalysis of 20 mgL⁻¹ of Cr(VI), the absence of SA oxygen-containing conditions did not significantly influence the distribution of chromium species. Nevertheless, the presence of SA STIR obtained a higher reduction efficiency and more chromium was retained on the surface of TiO₂ and less Cr(VI) remained in the solution, revealing that neither de-oxygenation by nitrogen gas nor oxygen supplementation by air is suitable. Only simple stirring obtains a better photocatalytic reaction. Using one-pot, multi-step reaction sequences with catalyst recovery in wastewater by combining magnetic catalysts with traditional gravimetrically recoverable catalyst that the Cr was absorbed on the catalyst. The experimental results demonstrated that the reduction efficiency increased with the decrease in illumination wavelength and an increase in the illumination energy but decreased with the excessive illumination energy. In addition, oxygen could compete with Cr(VI) not only for photogenerated electrons, but could also serve as an electron transfer mediator. Therefore, the experimental results also found that the reduction efficiency was increased by purging nitrogen or air appropriately.

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