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Photochemical removal of hexavalent chromium through iodide oxidation under 254 nm irradiation

Jiman Yeo, Dong-hyo Kim, Alok D. Bokare, Wonyong Choi *

School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea

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ABSTRACT

The efficient photoreductive removal of chromate [Cr(VI)] in aqueous solution was successfully demonstrated using potassium iodide (KI) excited by 254 nm irradiation. The photoexcited iodides react with Cr(VI) (as an electron acceptor) with transforming Cr(VI) to Cr(III) and I^- to I_3^- at the same time. The hexavalent chromium of 200 μM was mostly removed within an hour of 254 nm irradiation in the presence of 1 mM KI at pH 3. However, the removal process was only active at acidic condition and not at neutral and alkaline pH. The photo-reduction process was more efficient with higher concentration of iodides and was little affected by the presence of O_2. The photoreaction between iodides and O_2 leads to the generation of H_2O_2, which was completely inhibited by the presence of Cr(VI) because the photoexcited iodides react preferentially with Cr(VI). The presence of arsenite (As(III)) as an electron donor significantly enhanced the removal efficiency of Cr(VI) because As(III) reduce triiodides back to iodides with enabling the photocatalytic cycle of iodides under 254 nm radiation. The proposed UV_{254}/KI process can be successfully applied in the treatment of highly contaminated wastewaters with Cr(VI) and As(III), which is highly desirable because both toxic species (Cr(VI), As(III)) are transformed into less toxic forms (Cr(III), As(V)).

1. Introduction

Chromium compounds are widely used in various industrial processes like metal electroplating, leather tanning, wood preservation, dye manufacturing, metallurgy and preparation of chromium chemicals [1,2]. Thus, a large quantity of aqueous chromium wastes is produced every year, which seriously pollutes the environment without proper disposal and treatment. The average chromium concentration in industrial wastewater is estimated to be 0.1–200 mg/L [3]. Although chromium can exist in different oxidation states (from −II to +VI) [4], only two stable oxidation states, Cr(VI) (or chromate) and Cr(III), occur in the natural environment [5]. Cr(VI) is highly water soluble, extremely toxic and potential carcinogen [6–8], whereas Cr(III) is much less toxic and can be readily precipitated in the form of $Cr(OH)_3$ [9] or mixed Fe(III)–Cr(III) (oxy)hydroxides [10,11] under neutral and alkaline conditions. Therefore, the removal of Cr(VI) from aqueous solutions is an essential pollution abatement process that should be applied to all industrial chromium effluents prior to their discharge into natural water bodies.

Various treatment methods for the removal of chromium (VI) have been studied, such as biosorption [12,13], ion exchange [14–16], adsorption [17,18], photocatalysis [19–21], ionizing radiation [22,23], chemical reduction and precipitation [24,25]. Among them, the reduction of Cr(VI) to Cr(III) and the subsequent Cr(III) precipitation has been successfully achieved using various reducing agents such as ferrous compounds, hydrogen peroxide, sulfur compounds, hydrazines, hydroxylamines and formaldehyde [26–33]. In this study, we investigated the photoreduction of Cr(VI) in the presence of potassium iodide (KI) and 254 nm irradiation as a new removal process of chromate. Iodides are photochemically active under 254 nm irradiation [34,35].

$$I^- + H_2O + h\nu(254\,\text{nm}) \rightarrow (I^- H_2O)^* \quad (1)$$

$$(I^- H_2O)^* \rightarrow (I^{\cdot}, e^-)H_2O \quad (2)$$

$$(I^{\cdot}, e^-) + H_2O \rightarrow I^{\cdot} + e^-_{aq} \quad (3)$$

$$(I^{\cdot}, e^-) + O_2 \rightarrow I^{\cdot} + O_2^{\cdot-} \quad (4)$$

Light absorption by iodide (Eq. (1)) in water generates a caged complex containing an iodine atom and an electron ($I^{\cdot}$, e^-) through a charge transfer (Eq. (2)). The caged complex may dissociate into an aqueous electron and an iodine atom (Eq. (3)). The presence of an electron acceptor like dioxygen facilitates the dissociation of the caged complex (Eq. (4)) [36]. We propose that the presence of chromate, Cr(VI), as a strong electron acceptor ($E^0(HCrO_4^-/Cr^{3+}) = 1.35\ V_{NHE}$)[37] should enhance the dissociation of the iodide caged complex with accompanying the reduction of Cr(VI) to Cr(III) (Eq. (5)) and the oxidation of I^- to I_3^- (Eq. (6)).

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* Corresponding author. Tel.: +82 54 279 2283; fax: +82 54 279 8299.
E-mail address: wchoi@postech.edu (W. Choi).

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$$3(I^{\cdot}, e^-) + Cr(VI) \rightarrow 3I^{\cdot} + Cr(III) \quad (5)$$

$$I^- + I^{\cdot} \rightarrow I_2^- \quad (6.a)$$
$$I_2^- + I_2^- \rightarrow I_3^- + I^- \quad (6.b)$$
$$I^{\cdot} + I^{\cdot} \rightarrow I_2 \quad (6.c)$$
$$I_2 + I^- \rightarrow I_3^- \quad (6.d)$$

In this work, we demonstrate the successful use of potassium iodide and 254 nm irradiation for the reduction of aqueous Cr(VI) to Cr(III) as a new photochemical remediation method. The effect of O_2, concentration of KI, and presence of arsenite [As(III)] on the photoreduction efficiency are also discussed in detail.

2. Experimental details

$Na_2Cr_2O_7 \cdot 2H_2O$ (Aldrich) was used as the source of Cr(VI). $NaAsO_2$ (As(III), Aldrich) and $Na_2HAsO_4 \cdot 7H_2O$ (As(V), Kanto) were used as the source of arsenic. KI (99.5%, Samchun Chemical) was used as the iodide source. I_2 (Shinyo), KIO_3 (Yanagishima), $Na_2B_4O_7 \cdot 10H_2O$ (Junsei) were of reagent grade and used as received. N_2 (Linde) and O_2 (Sinan) gases were used as a sparging gas when the effect of dissolved oxygen was investigated. Ultrapure deionized water (18 MΩ cm) was used in all experiments and prepared by a Barnstead purification system.

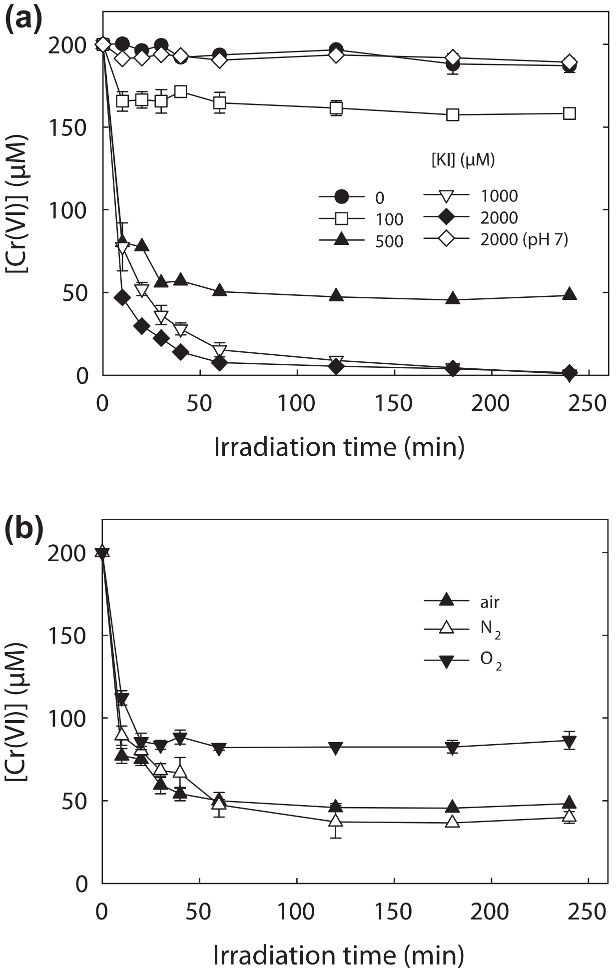

Fig. 1. Time profiles of Cr(VI) removal in the UV_{254}/KI system (a) with different iodide concentrations, and (b) under different dissolved gas conditions (air, N_2, and O_2). The experimental conditions were: air-equilibrated, $pH_i = 3.0$, $[Cr(VI)]_0 = 200\ \mu M$, $[KI]_0 = 500\ \mu M$ (for (b)).

The initial Cr(VI) concentration employed in this work was 200 μM. The pH of the solutions was adjusted with 1 N $HClO_4$ or 1 N NaOH solution to a desired value. The photoreduction experiments were carried out in a 4-mL quartz cell reactor without stirring. Photoirradiation at $\lambda = 254$ nm employed a 15-W germicidal lamp (GLD15MQ, Sankyo, Japan) as the light source. The distance between the lamp and the photo-reactor was 11 cm. The incident light flux was measured by iodide/iodate actinometry [35]. The standard actinometer solution consisted of 0.6 M KI, 0.1 M KIO_3, and 0.01 M borate buffer (pH 9.25). The irradiation of the actinometer solution resulted in the formation of triiodide, which was quantified by measuring its absorbance at 352 nm ($\varepsilon = 26{,}400\ M^{-1}\ cm^{-1}$). The absorbance-time curve showed a good linearity ($R^2 \sim 0.99$) with the present photoreactor setup. The incident light flux (I_i) was determined to be $3.5(\pm 0.3) \times 10^{-6}$ Einstein $L^{-1}\ s^{-1}$. For the photoreduction experiments in the absence of dissolved oxygen, the reactor was purged with nitrogen gas for 20 min prior to irradiation and continuously during irradiation. All experiments were performed in triplicates to assure reproducibility.

The residual Cr(VI) concentration after the photoirradiation was determined colorimetrically at 540 nm using diphenylcarbazide as the color reagent [38]. Identification and quantification of photogenerated arsenate, As(V), was performed using an ion chromatograph (IC, Dionex DX-120) (with a detection limit of ~5 μM) equipped with a Dionex IonPac AS 14 (4 mm × 250 mm) column and a conductivity detector [39,40]. The eluent was a mixture of 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$ solutions. The IC calibration for [As(V)] was done using standard aqueous solutions of Na_2HAsO_4 in the concentration range up to 2000 μM. The concentration of photogenerated triiodide (I_3^-) was determined by measuring the absorbance at 352 nm ($\varepsilon = 26{,}400\ M^{-1}\ cm^{-1}$) using a UV/Vis spectrophotometer (Agilent 8453) [41]. The concentration of photogenerated H_2O_2 was measured by the DPD (*N,N*-diethyl-*p*-phenylenedimine) method (with the detection limit of 0.8 μM) [42,43]. The quantification of triiodide and H_2O_2 was carried out immediately after sampling to minimize the error associated with the dark decay.

3. Results and discussion

3.1. Photoreduction of Cr(VI) with iodide

Fig. 1a shows the time profiles of Cr(VI) removal under 254 nm irradiation in the absence or presence of iodide. The direct photoreduction of Cr(VI) in the absence of iodide was negligible whereas the removal of Cr(VI) was significantly increased with increasing [KI] at pH 3. This observation clearly indicates the photoinduced electron transfer occurs between iodide and Cr(VI) in water (Eq. (5)). Since the reduction of Cr(VI) is favorable at acidic conditions (Eqs. (7) and (8)), Cr(VI) removal was negligibly slow at ⩾pH 7, even with high concentration of KI (2000 μM).

$$3e_{aq}^- + 7H^+ + HCrO_4^- \rightarrow Cr^{3+} + 4H_2O \quad (7)$$
$$6e_{aq}^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \quad (8)$$

Since the stoichiometric ratio between the oxidized iodide and the reduced Cr(VI) is 3–1 (Eq. (5)), the removal of chromate ($[Cr(VI)]_0 = 200\ \mu M$) was not complete when the concentration of iodide was below this ratio (i.e., $[KI]_0 = 100$ and 500 μM in Fig. 1a). Therefore, when the concentration of iodide was raised to 1000 μM which is above the stoichiometric requirement (600 μM), the complete removal of Cr(VI) was achieved. The photoconversion of iodide and chromate proceeds stoichiometrically. The quantum yield (Φ) of Cr(VI) photoreduction at 254 nm radiation was determined by the following equation: