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Freezing-Induced Simultaneous Reduction of Chromate and Production of Molecular Iodine: Mechanism, Kinetics, and Practical Implications

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ABSTRACT: A new method for the concurrent treatment of Cr(VI)-contaminated wastewater and production of the useful I_2 chemical was developed. The method is based on the redox reaction between Cr(VI) and I⁻ that occurs when an aqueous wastewater solution containing Cr(VI) and I⁻ is frozen, producing I_2 and allowing for the effective removal of Cr. The redox reaction occurs primarily because of the accumulation of Cr(VI), I⁻, and protons in the ice grain boundaries formed during freezing (i.e., the freeze concentration effect). This effect was verified by confocal



Raman spectroscopy and the experiments varying I⁻ concentration and pH. The reduction of Cr(VI) (20 μ M) was near complete after freezing at I⁻ concentrations \geq 100 μ M, pH \leq 3.0, and temperatures \leq -10 °C. The freezing method (liquid cooling vs air cooling) had little effect on the final Cr(VI) reduction efficiency but had a significant effect on the Cr(VI) reduction rate. The freezing method was also tested with Cr(VI)-contaminated electroplating wastewater samples, and simultaneous Cr(VI) reduction and I₂ production proceeded rapidly in a frozen solution but was not observed in an aqueous solution. Additionally, other substances in electroplating wastewater did not reduce the rate and final efficiency of Cr(VI) reduction and I₂ production. Therefore, the freezing/Cr(VI)/I⁻ system can be considered a feasible approach to water-energy nexus technology for simultaneous I₂ production and Cr(VI)-contaminated wastewater treatment.

INTRODUCTION

Chromium (Cr) is a heavy metal that is widely used in industrial processes such as wood preservation, leather tanning, chrome plating, metallurgy, and pigment manufacturing. These processes produce large amounts of Cr-containing wastewater that need to be treated. Cr can be found in different forms with oxidation states ranging from -2 to +6. Among various Cr species, hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)] are dominant in water. Compared to Cr(VI), Cr(III) is far less toxic and easier to physically remove;² therefore, the reduction of Cr(VI) to Cr(III) is necessary to physically remove Cr in wastewater by precipitation, ion exchange, adsorption, and coagulation.^{3–5} In this regard, a variety of chemical and photochemical methods including zero-valent iron (Fe⁰),⁶ ferrous ion (Fe²⁺),⁷ hydrogen peroxide (H_2O_2) ,⁸ copper-doped titanium dioxide (Cu-TiO₂) with UV-A light,⁹ and polyaniline-modified tin dioxide (PANI/SnO2) with visible light¹⁰ have been employed to convert Cr(VI) to Cr(III).

Generally, chemical reactions in aqueous media (i.e., at temperatures above the freezing point) are faster than those in ice media (i.e., at temperatures below the freezing point). However, several examples demonstrating enhanced chemical reactions in ice media have been reported in the literature.

Freezing has significantly enhanced the humification of phenolic compounds by nitrite (NO_2^{-}) .¹¹ The NO_2^{-} -mediated conversion of iodate (IO_3^-) into molecular iodine (I_2) , which was negligible in aqueous solutions, has been clearly observed in frozen solutions.¹² In addition, the freezing process significantly accelerated the degradation of organic pollutants by peroxymonosulfate (HSO_5^{-}) ,¹³ periodate (IO_4^{-}) ,¹⁴ and NO₂^{-.15} These behaviors are contrary to the Arrhenius law, which shows that reaction rates decrease with the decrease of the temperature. These contrasting behaviors proceed primarily because of the freeze concentration effect. Frozen solutions contain small pockets of liquid between ice crystals, which are often referred to as ice grain boundaries. Solutes primarily exist in the ice grain boundaries within a frozen solution.^{16,17} This phenomenon increases the concentrations of solutes and the collision frequency between solutes, thereby

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enhancing chemical reactions.¹⁸ Under acidic conditions, protons also accumulate in the ice grain boundaries in frozen solutions.¹⁹ The resulting decrease in pH provides optimal conditions for proton-coupled chemical reactions.

The reduction rate of Cr(VI) to Cr(III) increases with increasing concentrations of Cr(VI) and reductants. Additionally, the reduction of Cr(VI) is favored in acidic conditions because protons are required in the Cr(VI) reduction process $[HCr^{VI}O_4^- + 7H^+ + 3e^- \rightarrow Cr(III) + 4H_2O]$ ²⁰ In this regard, the freezing process, which can increase solute concentration and decrease pH, was recently applied to the reduction of Cr(VI). H_2O_2 ²⁰ NO_2⁻²¹ and 4-chlorophenol²² were used as reductants in the freezing-induced Cr(VI) reduction processes. All reductants previously reported showed enhanced reduction efficiency of Cr(VI) in a frozen solution. However, the oxidized forms of the reductants in the previously reported studies (i.e., H_2O , NO₃⁻, and hydroquinone/benzoquinone) are toxic or invaluable, limiting their practical applications in Cr(VI) reduction.

Although freezing-induced Cr(VI) reduction systems have previously been reported, developing an economical and ecofriendly freezing system for Cr(VI) reduction remains a challenging issue. In this study, we developed a new freezinginduced Cr(VI) reduction system using iodide (I⁻) as a reductant. This system not only reduces Cr(VI) to Cr(III) but also generates I2, which is frequently used as a catalyst or reagent in various organic synthetic processes and as an antimicrobial substance in pharmaceutical production.^{23,24} The dual function of the freezing/ $Cr(VI)/I^-$ system (i.e., the simultaneous reduction of Cr(VI) and production of I_2) provides a favorable system for wastewater treatment and resource recovery. The reduction efficiencies of Cr(VI) in frozen solutions are measured under various experimental conditions and compared with those in aqueous solutions. In addition, the reaction mechanism between Cr(VI) and I⁻ in frozen solution is discussed. Finally, the practical viability of the freezing/ $Cr(VI)/I^-$ system is verified using Cr(VI)contaminated wastewater samples taken from an electroplating factory.

EXPERIMENTAL SECTION

Chemicals. Chemicals used in this work include the following: sodium dichromate dihydrate (Na₂Cr₂O₇·2H₂O, Cr(VI), Aldrich, \geq 99.5%), potassium iodide (KI, Samchun Chemical, \geq 99.5%), acetone (C₃H₆O, Junsei, \geq 98.0%), sulfuric acid (H₂SO₄, Aldrich, \geq 96.0%), 1,5-diphenylcarbazide (C₁₃H₁₄N₄O, DPC, Aldrich, \geq 98.8%), perchloric acid (HClO₄, Aldrich, 1 M), and sodium hydroxide (NaOH, Samchun Chemical, 1 M). Ultrapure deionized water (\geq 18.2 MΩ·cm) produced by a water purification system (Barnstead Milli-Q Direct 16) was used to prepare experimental solutions. Cr(VI)-contaminated wastewater produced from a local electroplating factory in Republic of Korea {[Cr(VI)] \approx 600 mM and pH \approx 0.4} was used without pretreatment.

Experimental Procedure. Aliquots of chemical stock solutions { $[Cr(VI)] = 2 \text{ mM} \text{ and } [I^-] = 1 \text{ mM}$ } were added to deionized water in a beaker to yield the desired initial concentrations for the experimental solutions {usually [Cr-(VI)] = $20 \ \mu\text{M}$ and [I^-] = $100 \ \mu\text{M}$ }. The initial pH of the solution was adjusted using a HClO₄ or NaOH solution (usually pH = 3.0). Ten milliliters of the Cr(VI) and I⁻ solution was transferred to a 15 mL plastic conical tube

(Falcon) and sealed with a plastic cap. The plastic conical tubes containing aqueous solution of Cr(VI) and I⁻ were placed in a laboratory-made conical tube holder installed inside the temperature-controlled ethanol bath. The temperature of ethanol was adjusted to the desired temperature (usually -20or 25 °C) before putting the plastic conical tubes into the temperature-controlled ethanol bath. The start of the reaction time is considered to be when the plastic conical tubes are placed into the temperature-controlled ethanol bath. The plastic conical tubes were withdrawn from the temperaturecontrolled ethanol bath at regular time intervals and put into a lukewarm water bath at 35 °C for 1 min. The frozen samples were completely thawed within 1 min. The aqueous (or melted) samples were analyzed immediately afterward. All experiments were performed at least twice to confirm data reproducibility.

Chemical Analyses. The concentration of Cr(VI) was measured using the spectrophotometric method with a 1,5-diphenylcarbazide (DPC) reagent.²⁵ To make the DPC reagent, DPC powder (0.05 g) was added to a mixture of acetone (25 mL) and sulfuric acid (250 μ L). The DPC reagent (250 μ L) was added to the aqueous sample diluted sixfold (3 mL) and mixed vigorously for 1 min. The absorbance of the aqueous sample colored by the DPC reagent was measured at 540 nm using a UV–visible spectrophotometer (Shimadzu UV-2600) after 1 h in the dark. The Cr(VI) concentration in the solution was retrieved using the absorbance value at 540 nm and the calibration curve of sodium dichromate dihydrate.

Quantitative analysis of I⁻ was performed using an ion chromatograph (Dionex ICS-1100) equipped with a Dionex AERS 500 suppressor, a Dionex IonPac AS19 column, and a conductivity detector. The eluent was made by the potassium hydroxide (KOH) eluent generator cartridge (Dionex EGC III). The flow rate and concentration gradient of the eluent (KOH) were 1.0 mL/min and 10–45 mM, respectively. The concentration of I⁻ was determined based on the calibration curve of potassium iodide. The production of I₂ and I₃⁻ was monitored by measuring the absorbances of the aqueous sample at 460 and 353 nm, respectively. The absorbances were converted to the concentrations of I₂ and I₃⁻ using the Beer–Lambert law with the molar absorption coefficients (ε) for I₂ and I₃⁻ (ε = 746 M⁻¹ cm⁻¹ at 460 nm and 26,400 M⁻¹ cm⁻¹ at 353 nm, respectively²⁶).

Confocal Raman spectroscopy was used to monitor the spatial distributions and disappearances of Cr(VI) in the frozen solutions without melting. One droplet of the aqueous solution $\{[Cr(VI)] = 1 \text{ mM}, [I^-] = 1 \text{ mM}, \text{ and } pH = 3.0\}$ was added dropwise on a temperature-controlled microscope stage (Linkam Scientific THMS600). The temperature was decreased from 0 to -20 °C at a rate of -1.5 °C/min by liquid nitrogen. The images of the distribution of Cr(VI) concentration in the frozen solution were obtained by measuring the Raman intensity at 852 cm⁻¹ using a confocal Raman spectroscope (Renishaw inVia Qontor) with monochromatic laser (532 nm) irradiation.

RESULTS AND DISCUSSION

Reduction of Cr(VI) by I⁻ in Aqueous and Frozen Solutions. The reduction of Cr(VI) by I⁻ in frozen solutions at -20 °C was measured and compared with that in aqueous solutions at 25 °C under the conditions of [Cr(VI)] = $20 \ \mu M$, [I⁻] = $100 \ \mu M$, and pH = 3.0 (Figure 1a). The concentration of Cr(VI) rapidly decreased after freezing and was almost zero



Figure 1. (a) Time profiles of Cr(VI) concentration, (b) absorbance changes, and (c) time profiles of I⁻, I₂, and I₃⁻ concentrations in aqueous and frozen solutions containing Cr(VI) and I⁻. Experimental conditions: $[Cr(VI)] = 20 \ \mu M$, $[I^-] = 100 \ \mu M$, pH = 3.0, and reaction temperature = 25 °C for aqueous phase reaction or -20 °C for frozen phase reaction.

(less than 0.5 μ M) after 20 min in the frozen solution. However, the reduction of Cr(VI) was negligible in the aqueous solution. In the absence of I⁻ in a frozen solution, Cr(VI) was reduced by only a small amount (less than 2.0 μ M after 2 h of reaction) through the proton-mediated pathway [4HCr^{VI}O₄⁻ + 16H⁺ \rightarrow 4Cr(III) + 3O₂ + 10H₂O].²⁷ The control experiments in the absence of freezing or I⁻ indicate that I⁻ and freezing synergistically accelerate the reduction of Cr(VI). Therefore, Cr(VI) reduction is significantly enhanced in the presence of I⁻ after freezing because I⁻ can act as a reductant for Cr(VI) in frozen solutions.

To verify the role of I⁻ as a reductant, the products generated from the oxidation of I⁻ by Cr(VI) (i.e., I₂ and I₃⁻) were spectrophotometrically investigated (Figure 1b). In an aqueous solution containing Cr(VI) and I⁻, the UV-visible absorption spectra did not change, whereas two new peaks were observed when the aqueous solution was frozen for 2 h. The absorption band at 288 nm after freezing indicates the production of I₃⁻ in the frozen solution. The presence of the peak at 460 nm is primarily attributed to the formation of I₂.²⁶ The production of the oxidized forms of I⁻ (i.e., I₂ and I₃⁻)

after freezing clearly indicates that I⁻ can act as a reductant for Cr(VI) in a frozen solution. It should be noted that the peak at 353 nm observed in the frozen solution after 2 h is primarily responsible for the generation of I_3^- , which exhibits the maximum absorption wavelengths at both 288 and 353 nm,²⁶ rather than the existence of Cr(VI).

Figure 1c shows time profiles of I^- , I_2 , and $I_3^$ concentrations in the aqueous and frozen solutions containing Cr(VI) and I⁻. Consistent with the limited reduction of Cr(VI) observed in an aqueous solution, the concentration of I^- did not change and the production of I_2 and I_3^- was negligible in the aqueous solution. On the other hand, the concentration of I⁻ decreased, while concentrations of I₂ and I_3^- increased with reaction time in the frozen solution. The iodine mass balance $\{([I^-] + 2 \times [I_2] + 3 \times [I_3^-])/(initial)\}$ $[I^-]$ × 100 (%)} in the frozen solution was almost 100% throughout the reaction period, confirming that the conversions of I⁻ to I₂ (reaction 1) and I₃⁻ (reaction 2) are the primary oxidation pathways and production of other oxidized forms of I^- is negligible. Between I_2 and I_3^- , the production of I_2 was much higher than that of I_3 . This result indicates that the direct conversion of I^- to I_2 (reaction 1) is favored in a frozen solution and/or I_3^- , which is produced from the oxidation of I⁻ through reaction 2, rapidly dissociates into I⁻ and I_2 in frozen solutions (reaction 3).

$$2HCr^{VI}O_{4}^{-} + 6I^{-} + 14H^{+} \rightarrow 2Cr(III) + 3I_{2} + 8H_{2}O$$
(1)

$$2HCr^{VI}O_{4}^{-} + 9I^{-} + 14H^{+} \rightarrow 2Cr(III) + 3I_{3}^{-} + 8H_{2}O$$
(2)

$$I_3^- \to I^- + I_2 \tag{3}$$

In Situ Monitoring of I⁻-Mediated Reduction of Cr(VI) in the Ice Grain Boundaries. Because protons are involved in the I^- -mediated reduction of Cr(VI) (reactions 1 and 2), the pH of solution (i.e., the concentration of protons) significantly affects the kinetics of Cr(VI) reduction. When the acidic solution is frozen, protons are expelled from the ice crystals and situated in the ice grain boundaries. Protons continue to accumulate in the ice grain boundaries as ice crystals grow during the freezing process.¹⁹ The extremely acidic environment induced by the freeze concentration effect can facilitate I⁻-mediated reduction of Cr(VI) by providing sufficient protons for reactions 1 and 2. In addition, the accumulation of both Cr(VI) and I^- in the ice grain boundaries during freezing is likely to have a synergistic effect on the I⁻-mediated reduction of Cr(VI) by increasing the chance of collisions between Cr(VI) and I⁻ for their redox transformation [see Thermodynamic Interpretation of Redox Reaction between Cr(VI) and I^- in the Supporting Information].

The distribution of Cr(VI) concentration in the frozen solution was monitored in situ (without melting) using confocal Raman spectroscopy. When the aqueous solution of Cr(VI) was frozen, the ice crystals and ice grain boundaries were clearly distinct (Figure 2a). It has been reported that in an aqueous solution, the specific Raman peak of Cr(VI), which is identified by the Cr–O stretching mode, is observed in the range of 800–1000 cm⁻¹ and its wavenumber position depends on the Cr(VI) concentration and pH.^{28,29} Two points representing the ice crystal (black circle) and ice grain boundary (red circle) were selected (Figure 2a), and the



Figure 2. (a) Optical image of a frozen Cr(VI) solution, (b) Raman spectra measured at the ice grain boundary (red circle) and ice crystal (black circle) in (a), and (c) Cr(VI) concentration distribution image of frozen Cr(VI) solution. Experimental conditions: [Cr(VI)] = 1 mM, pH = 3.0, and freezing temperature = $0 \rightarrow -20$ °C at a rate of -1.5 °C/min.

Raman spectra at each of the points were recorded (Figure 2b). The characteristic Raman Cr(VI) peak at 852 cm⁻¹ was clearly detected in the ice grain boundary region, while no Raman peaks were observed in the ice crystal region. Furthermore, the distribution of Cr(VI) concentration in the frozen solution was investigated by measuring the Raman intensity at 852 cm⁻¹ for the area within the white square (Figure 2c). The relative Raman intensities (i.e., the relative concentrations) of Cr(VI) are displayed on a rainbow scale, where red represents the highest and black represents the lowest concentrations. The ice grain boundary regions are marked with red, orange, yellow, and green, while the ice crystal regions are blue, indigo, violet, and black. This Cr(VI) concentration distribution image of the frozen Cr(VI) solution implies that Cr(VI) significantly accumulates in ice grain boundaries by exclusion from ice crystals after freezing.

To provide convincing evidence for Cr(VI) reduction by I⁻ in the ice grain boundaries during freezing, the change in Cr(VI) concentration in the ice grain boundary region was monitored in situ by measuring the Raman spectra of Cr(VI)as a function of reaction time (Figure 3). The Raman intensity at 852 cm⁻¹, which is proportional to the Cr(VI)concentration, gradually decreased with the reaction time



Figure 3. Raman spectra measured in the ice grain boundary region of a frozen solution containing Cr(VI) and I⁻. Experimental conditions: [Cr(VI)] = 1 mM, $[I^-] = 1 \text{ mM}$, pH = 3.0, and freezing temperature = $0 \rightarrow -20$ °C at a rate of -1.5 °C/min. Reaction time is defined as the time after the temperature of the microscope stage has reached -20 °C.

(Figure 3, inset). The change from red to green in the ice grain boundary region over time in the Cr(VI) concentration distribution images shown in Figure 4 also demonstrates the



Figure 4. Cr(VI) concentration distribution images of a frozen solution containing Cr(VI) and I⁻. Experimental conditions: [Cr-(VI)] = 1 mM, [I⁻] = 1 mM, pH = 3.0, and freezing temperature = 0 \rightarrow -20 °C at a rate of -1.5 °C/min. Reaction time is defined as the time after the temperature of the microscope stage has reached -20 °C.

decreasing concentration of Cr(VI) in the ice grain boundary region with increasing reaction time. Based on the results in Figures 3 and 4, it can be concluded that the redox reaction between Cr(VI) and I⁻ occurs within the ice grain boundaries and not the ice crystals.

Verification of the Freeze Concentration Effect. To verify our hypotheses that the freeze concentration effect accelerates I⁻-mediated reduction of Cr(VI) by decreasing pH and increasing I⁻ concentration locally, the effects of pH decrease and I⁻ concentration increase and their synergistic effect on Cr(VI) reduction were investigated in an aqueous solution (Figure 5). When the only concentration of I⁻ was increased by 100-fold (i.e., to [I⁻] = 10 mM) from the



Figure 5. Effect of I⁻ concentration increase and/or pH decrease on Cr(VI) reduction. Experimental conditions: $[Cr(VI)] = 20 \ \mu M$, $[I^-] = 100 \ \mu M$ or 10 mM, pH = 3.0 or 1.3, reaction time = 2 h, and reaction temperature = 25 °C for aqueous phase reaction or -20 °C for frozen phase reaction.

reference conditions (i.e., $[I^-] = 100 \ \mu M$ and pH = 3.0), the reduction of Cr(VI) by I⁻ was not observed. Simply decreasing pH from 3.0 to 1.3 enhanced Cr(VI) reduction; however, the effect was minor. With both the decrease of pH and increase of I⁻ concentration, Cr(VI) reduction was significantly enhanced. When the concentrations of I⁻ and protons were increased by 100-fold and 50-fold, respectively, the Cr(VI) reduction efficiency in the aqueous solution was comparable to that in the frozen solution. These results confirm that the enhanced I⁻-mediated reduction of Cr(VI) in the frozen solution is ascribed to the accumulation of both solutes and protons in the ice grain boundary during freezing, not solely the concentration effect of either solutes or protons.

Cr(VI) Reduction Efficiencies in Frozen Solutions under Various Conditions. We investigated the effect of I⁻ concentration, pH, temperature, and freezing method on the reduction efficiency of Cr(VI) by I⁻ {(initial [Cr(VI)] – [Cr(VI)] after 2 h of reaction)/(initial [Cr(VI)]) × 100 (%)} in a frozen solution (Figure 6). In an aqueous solution at 25 °C, Cr(VI) reduction was essentially not observed with I⁻ concentrations of up to 100 μ M. On the other hand, the reduction efficiency of Cr(VI) increased with increasing [I⁻] at -20 °C (Figure 6a), which is attributed to I⁻ acting as the primary reductant for Cr(VI) in the frozen solutions. The experimental molar ratios of added [I⁻] to reduced [Cr(VI)] were 2.0-5.2 (2.0, 2.3, 3.3, and 5.2 at [I⁻] = 5, 10, 50, and 100 μ M, respectively), which are similar to the theoretical molar ratios according to reactions 1 and 2 (3.0-4.5). The slight difference between experimental and theoretical molar ratios can be attributed to the proton-mediated reduction of Cr(VI) in a frozen solution (at low [I⁻]) and the residual (unreacted) I⁻ after 2 h of reaction (at high [I⁻]).

The reduction efficiencies of Cr(VI) in a frozen solution were also measured in the pH range 2.0–6.0 and compared to those in an aqueous solution (Figure 6b). The reduction of Cr(VI) by I⁻ in an aqueous solution was negligible in the pH range 3.0–6.0. At pH = 2.0, the Cr(VI) reduction efficiency was less than 12%. In a frozen solution, reduction of Cr(VI) by I⁻ was observed at all pH values tested. The Cr(VI) reduction efficiency increased with decreasing pH and was nearly 100% at pH = 3.0. The inverse relationship between Cr(VI) reduction efficiency and pH is attributed to the need for protons in the I⁻-mediated Cr(VI) reduction process in frozen solutions. Most Cr(VI)-contaminated waters such as electroplating wastewater and leachates containing Cr(VI) are very acidic (pH < 2.0),^{30,31} making the freezing/Cr(VI)/I⁻ system applicable for Cr(VI) reduction without acidification.

Figure 6c shows the temperature-dependent reduction efficiency of Cr(VI) with a reaction time of 2 h. A temperature-controlled ethanol bath was used to reduce the temperature of the plastic conical tubes containing Cr(VI) and I⁻ down to -80 °C. On the other hand, the plastic conical tubes containing Cr(VI) and I⁻ were introduced into liquid nitrogen to freeze down to -196 °C. At temperatures between -10 and -196 °C, the effect of the freezing temperature on the Cr(VI) reduction efficiency was minor. Cr(VI) reduction was nearly 100% in frozen solutions at all temperatures tested. This indicates that Cr(VI) reduction by I⁻ proceeds efficiently once the aqueous solution is frozen.



Figure 6. Effect of (a) I⁻ concentration, (b) pH, (c) temperature, and (d) freezing method on the Cr(VI) reduction efficiency. Experimental conditions: $[Cr(VI)] = 20 \ \mu M$, $[I^-] = 0-100 \ \mu M$, pH = 2.0–6.0, reaction temperature = 25 to -196 °C, and reaction time = 2 h.

We also compared the Cr(VI) reduction efficiencies using two freezing systems: an ethanol bath (coolant: ethanol) and a refrigerator (coolant: air). The Cr(VI) reduction efficiencies of the two systems after a reaction time of 2 h were almost the same (Figure 6d). However, the time at which the reduction process began was different between the two freezing systems. The reduction of Cr(VI) in the ethanol bath started shortly (i.e., within 10 min) after putting the plastic conical tubes containing Cr(VI) and I⁻ into the ethanol bath. In the refrigerator, Cr(VI) reduction occurred at least 10 min after the start time. The reduction of Cr(VI) was almost complete within 20 min in the ethanol bath, while it took over 30 min to complete in the refrigerator (Figure 6d, inset). This result demonstrates that the freezing method, or more precisely the type of coolant, plays an important role in determining the start time and rate of Cr(VI) reduction by influencing the growth rate of ice crystals (i.e., the degree of the freeze concentration effect over reaction time).

Practical Viability of the Freezing/Cr(VI)/I⁻ System for the Simultaneous Cr(VI) Reduction and I₂ Production. Iodine is one of the rarest nonmetals in the lithosphere with estimated global reserves of about 15 million tons. The annual global production of iodine for industrial use is about 30,000 tons and is mainly produced in Chile and Japan.^{32,33} Among the various iodine species, I2 in particular has found a wide range of practical applications. I₂ has been frequently employed as a catalyst for organic syntheses through the Diels-Alder reaction, aldol reaction, Michael addition, and esterification. $^{34-36}$ It can be used as a chemical reagent to induce iodination and oxidation reactions.^{37–39} In addition, various pharmaceuticals such as iodine tincture, Lugol's solution, and povidone-iodine contain I₂ as an antimicrobial substance.⁴⁰ Industrial production of I₂ has primarily been carried out by two methods: the oxidation of I^- by molecular chlorine (Cl₂) and the reduction of IO₃⁻ by sulfur dioxide (SO₂).⁴¹ However, the corrosive property and low selectivity of Cl₂ and SO₂ limit the feasibility of these methods for I_2 production.^{42,43} Moreover, the Cl₂- and SO₂-mediated I₂ production systems can generate toxic compounds.⁴⁴

If the production of useful I_2 accompanied by the removal of toxic Cr(VI) is achievable, this dual-function system provides an economical and ecofriendly solution in water-energy nexus technology for simultaneous reduction of Cr(VI) and production of I2.^{45,46} To verify the viability of the freezing/ $Cr(VI)/I^{-}$ system for simultaneous Cr(VI) reduction and I_{2} production, we performed the experiments using Cr(VI)containing electroplating wastewater from a factory in Republic of Korea (Figure 7). The chemical composition of the electroplating wastewater is listed in Table S1 in the Supporting Information. When the diluted electroplating wastewater {[Cr(VI)] = 20 μ M} was used as a source of Cr(VI), simultaneous Cr(VI) reduction (Figure 7a) and I₂ production (Figure 7b) was observed in frozen solutions but not in aqueous solutions. Most importantly, both the Cr(VI) reduction and I₂ production efficiencies of the electroplating wastewater were similar to those of the artificial Cr(VI) solutions. This suggests that other substances in electroplating wastewater do not inhibit the redox reaction between Cr(VI) and I^- in the frozen state. I^- -contaminated brines ($[I^-] = a$ few mM)⁴⁷ and discharged effluents from brine treatment plants $([I^-] =$ hundreds of $\mu M)^{48}$ can be a source of I⁻. Wastewaters produced from liquid crystal display (LCD) manufacturing plants contain high concentrations of both Cr(VI) and I-



Figure 7. Simultaneous (a) reduction of Cr(VI) and (b) production of I₂ in the Cr(VI)-contaminated electroplating wastewater after I⁻ addition and freezing. Experimental conditions: $[Cr(VI)] = 20 \ \mu M$ in the diluted electroplating wastewater, $[I^-] = 100 \ \mu M$, pH = 3.0, and reaction temperature = 25 °C for aqueous phase reaction or -20 °C for frozen phase reaction.

(dozens of mM).^{42,49} The freezing/ $Cr(VI)/I^-$ system would be most economical when wastewater originally containing both Cr(VI) and I^- such as LCD wastewater is used.

Previously developed systems can either successfully reduce Cr(VI) or produce I_2 but not both. We have shown that wastewater containing Cr(VI) can produce the I_2 chemical while being treated. This dual-function system has the potential to be more economical and ecofriendly than any single-function system. The freezing/ $Cr(VI)/I^-$ system has worked efficiently with Cr(VI)-containing electroplating wastewater produced from a factory and produced results similar to the artificial solutions tested. In addition, I⁻ is almost selectively converted to I₂ by Cr(VI) in frozen solutions and the generation of other volatile iodine-containing compounds is negligible, enabling the freezing/Cr(VI)/I⁻ system to produce pure I₂ without a post-separation process. I₂ molecules produced in frozen solutions are spontaneously emitted into the atmosphere after melting, allowing for the recovery of I₂ from treated wastewater. The captured air containing I_2 can be used directly when low concentrations of I₂ are required. Nanomaterials and hydrogels capable of adsorbing I2 reversibly can be used to obtain high concentrations of I_2 .^{50–52} Therefore, the freezing/Cr(VI)/I⁻ system can be proposed to be a new water-energy nexus technology for simultaneous reduction of Cr(VI) and production of I₂.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c05322.

Thermodynamic interpretation of redox reaction between Cr(VI) and I^- and chemical composition of the electroplating wastewater (PDF)

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Notes

The authors declare no competing financial interest.

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