



Use of spent coffee ground as a reducing agent for enhanced reduction of chromate by freezing process



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ABSTRACT

In this study, the freezing-mediated reduction of chromate (Cr(VI)) was investigated using spent coffee ground (SCG) as a reducing agent. The results obtained showed that the rate of Cr(VI) reduction using SCG was dramatically enhanced in the frozen phase (-20°C) compared with the aqueous phase (25°C), and after 3 h of reaction, the residual Cr(VI) concentration in the aqueous phase was $15.25 \pm 0.58 \mu\text{M}$, while that in the frozen phase was only $1.89 \pm 0.16 \mu\text{M}$ (initial experimental conditions: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}]_i = 0.1 \text{ g/L}$, and $\text{pH}_i = 3.0$). Additionally, based on the results obtained under different experimental conditions, the accelerated reduction of Cr(VI) using SCG in the frozen solution could be attributed to the freeze concentration phenomenon, which is associated with the accumulation of Cr(VI) and protons, as well as the phenolic compounds in SCG extracts.

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Introduction

Owing to potential human and ecosystem health hazards, there has been an increased interest in water and soil contamination by heavy metals, such as chromium, cadmium, mercury, arsenic, and lead [1]. Chromium is a major heavy metal, and it is introduced in the environment from both anthropogenic and natural sources [2]. Particularly, its major anthropogenic sources include electroplating and tannery industries [3], and in recent decades, there has been a gradual increase in its concentration in the natural environment owing to its intensive use in these industries [4].

The most common forms of chromium in the aqueous phase are the trivalent and hexavalent forms (i.e., Cr(III) and Cr(VI)), which have different effects on human and ecosystem health. Cr(III) is considered as an essential element for plants and animals, and it plays an important role in sugar and fat metabolism in humans. Contrarily, Cr(VI) (i.e., chromate), which is more soluble in water and soil, is designated as a hazardous substance owing to its carcinogenic and mutagenic properties [5–7]. Therefore, its reduction to Cr(III) or its removal from effluents is necessary to

meet effluent quality standards and reduce environmental risk before their discharge into the environment [8].

Even though conventional methods for Cr(VI) removal, including ion exchange, adsorption, and precipitation, have been employed, most of them are not cost-effective [9], e.g., the direct removal of Cr(VI), which is easily desorbed when the sorbent reaches its adsorptive capacity, by adsorption is more difficult than the direct removal of Cr(III) [10,11]. Additionally, sorbent regeneration is often required, and this increases operation and process cost. Removal of Cr(VI) by modified activated carbon and carbon-coated Mg–Al layered double oxide nanosheets has recently been attempted to improve Cr(VI) adsorption and reusability [12,13]. Although the use of carbon-based adsorbents can enhance these functions, additional costs and technical knowledge are needed to successfully synthesize these materials. Thus, chemical treatment for Cr(VI) removal is usually conducted in two steps: (1) reduction of Cr(VI) to Cr(III) using sulfur compounds (sulfur dioxide, sodium bisulfite, and sodium metabisulfite) and iron salts (ferrous sulphate) as reducing agents, and (2) precipitation using sodium hydroxide or lime [4,8]. However, large quantities of solid waste (sludge), which increase environmental burden, are generated. Consequently, the reduction of the toxic Cr(VI) to low-toxicity Cr(III) is considered as an essential step in Cr(VI) removal using cost-effective and eco-friendly technologies. The literature indicates that a higher kinetic rate of Cr(VI) reduction can be achieved under the following conditions [14–19]: (1) low pH value of the reaction

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system [14–16], (2) high concentration of reducing agents [19], and (3) use of a combined system of solid materials (i.e., biochar and nanocomposite) with organic acids [16–19]. Organic acids can enhance the reduction capacity of Cr(VI) by biochar and a nanocomposite because of the chelating effect of organic acids [18]. In addition, the capacity of Cr(VI) reduction depends on the ligand properties of organic acids and the electron-shuttling (or mediating) properties of solid materials [20].

In this aspect, bioresources have potential for application in Cr(VI) reduction. Various biomass types, including grape stalks and yohimbe bark [21], bracken fern [4], sewage sludge compost biomass [22], fungal biomass (i.e., *Neurospora crassa*) [23], marine macroalgae (i.e., *Sargassum cymosum*) [24], and amine-impregnated crab shells [25], have been extensively employed in Cr(VI) removal. Among these biomass types, waste biomass, in particular, has attracted a lot of interest as a potential material and feedstock for Cr(VI) removal in terms of the basic concept for municipal solid waste management (i.e., the 6 Rs: reduce, reuse, recycle, redesign, remanufacture, and recover) [26]. In this regard, spent coffee ground (SCG) has been considered as a suitable bioresource for Cr(VI) reduction and removal. Coffee, which is the second most consumed beverage worldwide after water, is sold in the order of an average of several billion cups daily, and reportedly, six million tons of soluble coffee are produced annually [8]. This results in the generation of large amounts of SCG, and owing to the growth of the coffee industry, a steady increase in the quantity of SCG generated annually is expected [27,28]. Therefore, a strategy should be established for the use of SCG as a resource. The use of SCG as a raw material has recently been attempted for the synthesis of value-added compounds and for environmental purification [27,29]. They include the production of chemicals by catalytic pyrolysis of SCG [27], the purification of phenol by SCG coated with Fe₃O₄ nanoparticles via the solar-Fenton process [29], and Cr(VI) reduction/removal by SCG [7,8,30,31]. According to previous literature, it has been demonstrated that SCG can be used to successfully reduce and/or remove Cr(VI) from chromium-contaminated solutions. However, the reduction efficiency is still lower than that of conventional techniques, and for such reduction to be realized, large quantities of SCG are required [7,8,30]. This implies that an additional purification process will be required to minimize the total organic carbon (TOC) level, and also ensure the separation of SCG particles, given that SCG extracts contains caffeine and several polyphenols [32].

Recently, it has been reported that redox conversions can be dramatically enhanced by freezing processes due to the freeze concentration effect [2,20,33–36]. During the freezing process, solid regions (i.e., ice crystals) and liquid regions (i.e., ice grain boundaries) co-exist, and the total volume of the solid regions gradually increases, which induces the release of solutes and protons into the liquid regions, i.e., the so-called freeze concentration phenomenon. Thus, lower quantities of reducing or oxidizing agents will be required for the remediation of pollutants within a shorter time using the freeze-mediated process compared with the same process in the aqueous phase. Further, it has been reported that the pH of the system can be significantly decreased by the freezing process, which increases the acidity of the system because protons (H⁺) can also accumulate with solutes in the ice grain boundaries [36]. Therefore, in terms of practical application, the combined system of SCG/freezing has the advantage of purifying the toxic Cr(VI) solution because the system can satisfy conditions for enhancing the Cr(VI) reduction rate via the freezing process without other treatments.

Therefore, in this study, the feasibility of the freezing-mediated reduction of Cr(VI) using SCG as a reducing agent was explored. Firstly, to investigate the efficiency of Cr(VI) reduction in both the aqueous and frozen phases, the rates of Cr(VI) reduction using SCG

and washed SCG were explored in the aqueous (25 °C) and ice (−20 °C) phases. Secondly, to verify the predominant pathway of the enhanced Cr(VI) reduction during the freezing process, the efficiencies of Cr(VI) reduction using SCG under different experimental conditions were explored. Finally, the feasibility of employing the SCG/freezing-assisted Cr(VI) reduction system in real electroplating wastewater was also investigated.

Materials and methods

Spent coffee ground and chemical preparations

SCG, which was obtained from a cafeteria at the Korea Polar Research Institute (KOPRI), was dried at 80 °C for 48 h. Thereafter, it was sieved to obtain particles with sizes in the range 63–250 μm. To determine the physico-chemical characteristics of the SCG (Table 1), proximate and ultimate analyses, as well as higher heating value (HHV) measurements were performed as previously described [37]. Washed SCG was also prepared to investigate the main reduction pathway of Cr(VI) by SCG, i.e., to investigate whether the organic component eluted from SCG was the main reducing agent for Cr(VI) reduction. To prepare washed SCG, 0.1 g of SCG was placed in a beaker containing deionized (DI) water (1 L; Milli-Q Direct 16 System, Merck-Millipore, Darmstadt, Germany) for 48 h to remove organic components of SCG, after which it was collected using a filtering equipment, and dried at 80 °C for 48 h. Additionally, to confirm the feasibility of using SCG to reduce Cr(VI) via the freezing process, Cr(VI)-contaminated wastewater from an electroplating plant in the Republic of Korea, was used.

In this study, all chemicals were used as received, i.e., without further purification. Sodium dichromate dihydrate (Na₂Cr₂O₇·2H₂O, Cr(VI), ≥99.5%), 1,5-diphenylcarbazine (C₆H₅NHNHCONHNHC₆H₅, DPC, ≥99.95%), and cresol red (C₂₁H₁₈O₅S, ≥95.0%) were purchased from Sigma-Aldrich (St. Louis, Missouri, United States). Sulfuric acid (H₂SO₄, ≥96.0%) and acetone (CH₃COCH₃, ≥99.5%) were purchased from Kanto Chemical (Tokyo, Japan). Additionally, liquid chromatograph–mass spectrometry (LC–MS) grade methanol (CH₃OH), formic acid (CH₂O₂), and acetonitrile (CH₃CN) were purchased from Supelco Co. (Bellefonte, USA).

Experimental procedure

An aliquot of the Cr(VI) stock solution and the desired amount of SCG were added to DI water to obtain the desired initial concentration (i.e., [Cr(VI)]_i = 20 μM and [SCG]_i = 0.1 g/L). The initial pH value of the artificial Cr(VI)-wastewater containing the SCG was adjusted to the desired value (usually [pH]_i = 3.0) using perchloric acid (1 M) and sodium hydroxide (1 M) solutions. To determine the rates of Cr(VI) reduction in the aqueous and frozen phases, conical

Table 1
Physico-chemical characteristics of SCG.

	SCG	
Proximate analysis (wt.%)	Water	3.71
	Volatiles	72.79
	Fixed carbon	21.20
	Ash	2.30
Ultimate analysis (wt.%) ^a	C	52.53
	H	6.20
	O ^b	39.20
	N	2.07
	S	–
Higher heating value (kcal/kg) ^a	6339	

^a On a dry basis.

^b By difference.

tubes containing the adjusted solution (10 mL) were simultaneously placed in a rack in pre-adjusted ethanol baths (i.e., 25 °C for the aqueous phase reaction, and –20 °C for the frozen phase reaction). At fixed time intervals, samples were collected and thawed in warm water (45 °C) in a beaker. Thereafter, to eliminate SCG particles, the solutions were filtered using a 0.45- μm syringe filter, and immediately analyzed to determine Cr(VI) concentrations using the calorimetric 1,5-diphenylcarbazide (DPC) method [34]. To confirm the data reproducibility, experiments were performed at least twice.

Analytical methods

To determine Cr(VI) concentrations, a mixture of 3 mL of the Cr(VI)-containing aqueous solution and 100 μL of the DPC reagent (DPC 0.05 g + acetone 25 mL + sulfuric acid 250 μL) was stored in the dark for 30 min. Thereafter, absorbance measurements were performed at 540 nm using a UV–vis spectrophotometer (UV-2600, Shimadzu).

Given that cresol red (CR) exhibits a unique speciation under different pH conditions, it was used as an indicator. Each form of CR has a different maximum absorption wavelength (i.e., 434, 518, and 573 nm for monoprotonated, diprotonated, and deprotonated CR, respectively) [38]. Therefore, the absorbance of the frozen solution was determined using a UV–vis spectrometer coupled with an integrating sphere (Cary 5000, Agilent Technologies) to calculate the pH of the frozen solution as previously described [34]. The detailed procedure for the measurement of the pH of the frozen solution is presented in the supplementary information.

The chemical analysis of the SCG to determine the concentrations of its main components, such as caffeine, chlorogenic acid, and ferulic acid [32] was performed using a liquid chromatography–Orbitrap mass spectrometer (LC–MS, Vanquish UHPLC combined with a Q Exactive Focus; Thermo Fisher Scientific Inc., Bremen, Germany). To separate the components, a C18 column (Hypersil GOLD VANQUISH aQ, 100 mm \times 2.1 mm, 1.9 μm ; Thermo Fisher Scientific Inc.) with two mobile phases, (A) and (B), consisting of water with 0.1% (V/V) formic acid and acetonitrile with 0.1% (V/V) formic acid (B), respectively, were used. The gradient elution of the LC under a flow rate of 0.3 mL/min was initially 0.5% (B) at 2 min, and at 15 min, it increased to 99%, and was maintained for 2 min. Thereafter, between 17 and 18 min, the elution was readjusted to the initial condition (0.5% B), and maintained for 2 min. The MS detector was operated in the positive electrospray ionization (ESI) mode for caffeine, and in the negative ESI mode for chlorogenic and ferulic acids. Specifically, the MS operating parameters were: spray voltage = 3.8 and 2.5 kV for the positive and negative modes, respectively, sheath gas flow rate = 40 arbitrary unit, capillary temperature = 320 °C, S-lens RF level = 50, and auxiliary gas heater temperature = 350 °C. The mass spectra were obtained for m/z in the range 50–700 at a resolution of 70,000. Each compound was then identified using Compound Discoverer ver. 3.1 (Thermo Fisher Scientific Inc.), and each compound had high $mzCloud$ match score (> 70).

The optical image of the frozen sample containing Cr(VI) and SCG at –20 °C was also obtained using a stereoscopic microscope (SZX16 with SZX2-TR30, Olympus) equipped with a temperature-controlled stage (THMS600, Linkam Scientific).

Results and discussion

Reduction efficiency of Cr(VI) using spent coffee ground in water and ice

To compare the efficiency of Cr(VI) reduction using SCG in the aqueous (25 °C) and frozen (–20 °C) phases, the residual

concentrations of Cr(VI) in both phases were measured (Fig. 1). Cr(VI) reduction using SCG in the aqueous phase was very slow ($k = 49.1 \times 10^{-3} \text{ h}^{-1}$); however, in the frozen phase, it proceeded rapidly ($k = 556.0 \times 10^{-3} \text{ h}^{-1}$), and reached equilibrium ($\sim 1.89 \mu\text{M}$) after 3 h of reaction. Table S1 shows the residual concentrations of total Cr and Cr(VI) after 3 h, which indicates that the decrease in Cr(VI) concentration could be mainly due to the redox reaction but not adsorption by SCG (i.e., only 1.86 μM and 1.75 μM of total Cr were removed by SCG in water and ice after 3 h, respectively). We compared the rate constant of Cr(VI) reduction in the SCG/freezing system with that in other systems (Table 2) [15–17]. The reduction rate of Cr(VI) by SCG/freezing ($556.0 \times 10^{-3} \text{ h}^{-1}$) was higher than that by gallic acid at the same pH value ($103.6 \times 10^{-3} \text{ h}^{-1}$). Although the pH of the systems differed, it was found that the value of SCG/freezing was usually higher than those for the biochar/organic acid system, except for the BC700/oxalic system.

Notably, Cr(VI) reduction in the frozen phase proceeded gradually even in the absence of SCG, indicating that protons concentrate in the liquid during the freezing process. This results in a decrease in the pH, which favors the thermodynamic reduction of Cr(VI) [33]. To elucidate the accumulation of protons in the liquid regions, UV–vis absorbance measurements were performed on CR was under the conditions: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{CR}]_i = 6.67 \mu\text{M}$, $\text{pH}_i = 3.0$, and temperature = 25 °C and –20 °C, for the aqueous and frozen phases, respectively (Fig. 2). The results obtained showed that owing to the freezing process, there was a shift in the maximum wavelength from 434 nm (monoprotonated CR) to 518 nm (deprotonated CR), indicating that there was a decrease in the pH of the frozen samples; hence, a significant decrease in the calculated pH value (0.91) [34]. Even though the degree of Cr(VI) reduction in the absence of SCG in the frozen solution was higher than that in the aqueous solution, the efficiency of the reduction was negligible compared with that resulting in the presence of SCG in the frozen solution. This observation suggests that the main enhanced Cr(VI) redox conversion pathway is not proton-mediated, but SCG-assisted.

To clarify the enhanced reduction of Cr(VI) using SCG in the frozen phase, experiments were performed using washed SCG in both the aqueous and frozen phases. Relative to the absence of washed SCG, a faster Cr(VI) reduction rate was observed in both phases; however, the performance of the washed SCG was quite lower than that of the raw SCG (Fig. 1) because during the washing process, significant amounts of SCG extracts, which possibly act as reductants, were removed. Reportedly, phenolic compounds, which are the major components of SCG extracts alongside

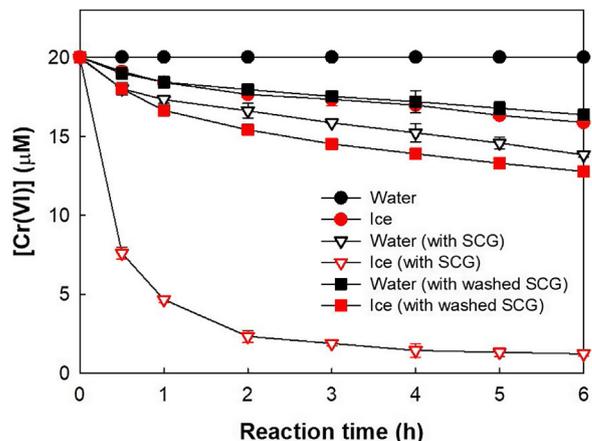


Fig. 1. Time profiles of Cr(VI) concentration during treatment with raw and washed SCG under the experimental conditions: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG or washed SCG}] = 0.1 \text{ g/L}$, $\text{pH}_i = 3.0$, and freezing temperature = –20 °C.

Table 2
Rate constant of Cr(VI) reduction under the SCG/freezing and other reported systems.

Cr(VI) reduction system	Condition		Reduction rate ($\times 10^{-3} \text{ h}^{-1}$) ^a	Refs.
SCG/freezing	[Cr(VI)] _i = 20 μM [SCG] = 0.1 g/L pH _i = 3.0	SCG (Water)	49.1 \pm 3.8 ($R^2 = 0.99$)	This study
		SCG (Ice)	556.0 \pm 58.7 ($R^2 = 0.93$)	
Gallic acid	[Cr(VI)] _i = 20 mg/L [Gallic acid] _i = 0.175 mM	pH = 2.0	951.6	[15]
		pH = 3.0	103.6	
		pH = 4.0	17.3	
		pH = 5.0	7.5	
Biochar (BC) with lactate	[Cr(VI)] _i = 100 mg/L [Lactate] _i = 1.7 g/L (15 mM) [Biochar] _i = 2.5 g/L pH _i = 2.0	BC	34.10	[16]
		Lactate	18.7	
		BC/Lactate	37.7	
Biochar (BC) with organic acids	[Cr(VI)] _i = 30 mg/L [Biochar] _i = 2.5 g/L [Organic acid] _i = 5.0 mM pH _i = 4.0	BC400	3.04	[17]
		BC400/Citric	2.00	
		BC400/Lactic	3.46	
		BC400/Tartaric	7.09	
		BC400/Oxalic	1.82	
		BC700	7.40	
		BC700/Citric	35.9	
		BC700/Lactic	191	
		BC700/Tartaric	138	
		BC700/Oxalic	864	

^a The rate constant was obtained from first-order reaction model.

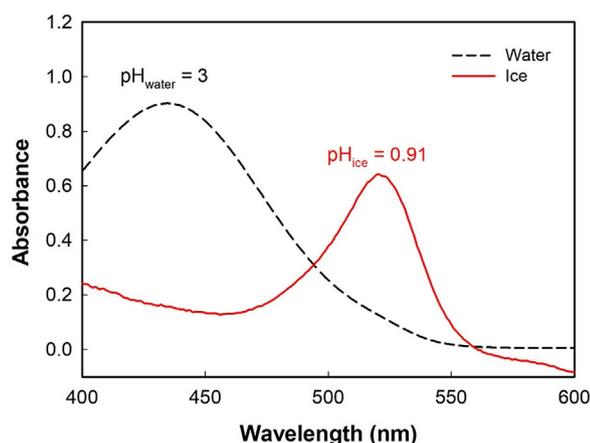


Fig. 2. UV-vis absorption spectra of CR in the aqueous and ice phases under the experimental conditions [Cr(VI)]_i = 20 μM , pH_i = 3.0, and freezing temperature = -20°C .

caffeine, can act as reducing agents for Cr(VI) reduction [32,39]. As shown in Fig. 3, SCG particles did not accumulate in the ice grain boundaries owing to their relatively larger particle sizes (~ 63 – $250 \mu\text{m}$) compared with the thickness of the liquid layer (approximately a few angstroms to tens of micrometers), which depends on the freezing temperature [40]. Thus, the results showed that the accelerated reduction of Cr(VI) using SCG in the frozen solution could be attributed to the accumulation of Cr(VI), protons, and SCG extracts in the ice grain boundaries during the freezing process.

Table 3 shows the MS peak areas for caffeine, chlorogenic acid, and ferulic acid, which are the main components of SCG extracts, after 6 h of reaction [32], and chromatograms are shown in the

supplementary information. Even though Cr(VI) reduction proceeded in the aqueous and frozen solutions, the change in the peak area of caffeine was negligible (i.e., only 0.4% after 6 h of reaction in the frozen solution). However, the peak areas of chlorogenic and ferulic acids for the reaction in the aqueous phase were significantly reduced (approximately 66.3 and 10.4%, respectively, after 6 h of reaction). However, in ice, the compounds were not observed, confirming that the phenolic compounds in the SCG extracts predominantly acted as electron donors for the reduction of Cr(VI) to Cr(III) [30,39,41]. Therefore, the accelerated reduction observed in ice could possibly be attributed to the enhanced reduction of Cr(VI) by the phenolic compounds in SCG extracts in the liquid regions.

Reduction of Cr(VI) using spent coffee ground in water and ice under different conditions

In this study, the effect of pH_i on Cr(VI) reduction using SCG was also investigated, and the variation of the Cr(VI) reduction rates with the pH_i values is shown in Fig. 4. Particularly, there was an increase in the rates of Cr(VI) reduction using SCG in the aqueous phase as pH_i decreased (Fig. 4(a)). This observation shows that pH_i values have a significant effect on Cr(VI) reduction using SCG, i.e., the lower the pH_i value, the faster the reduction rate [33,39]. As mentioned in the previous section, during the freezing process, there was a dramatic decrease in pH (pH_{water} = 3 \rightarrow pH_{ice} = 0.91) (Fig. 2); thus, the reduction rates of Cr(VI) using SCG in ice were significantly enhanced. Therefore, this accelerated reduction of Cr(VI) (Fig. 4(b)) could be attributed to the increased concentration of protons, coupled with the action of the phenolic compounds in the SCG extracts at the ice grain boundaries.

However, the reduction capacity of Cr(VI) using SCG at pH_i = 2.0 in the ice phase was slightly lower than that observed at pH = 3.0. This is because of the limited diffusion between the solid form of

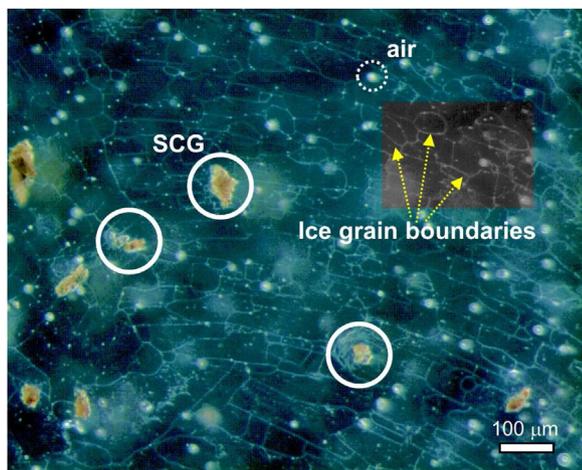


Fig. 3. Optical image of frozen solution [obtained using a stereoscopic microscope under the experimental conditions: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}] = 0.1 \text{ g/L}$, $\text{pH}_i = 3.0$, and freezing temperature = -20°C].

Table 3

LC–MS peak areas for caffeine, chlorogenic acid, and ferulic acid before and after the reaction in water and ice.

Compound	Caffeine (MS Count $\times 10^{-6}$)	Chlorogenic acid	Ferulic acid
Before reaction	1238.53 ± 35.54	76.38 ± 2.60	4.34 ± 0.01
Reaction in water	1238.87 ± 33.58	25.75 ± 0.14	3.89 ± 0.06
Reaction in ice	1233.88 ± 2.74	–	–

Cr(VI) and the phenolic compounds [34]. Additionally, solutions with low pH values can also be expected given that the freezing process results in more acidic environments [36]. It already reported that the solid form of Cr(VI) (CrO_3) increases, as H_2CrO_4 (equilibrium state of CrO_3) increases, when pH values fall below 1.0 ($\text{H}_2\text{CrO}_4 \leftrightarrow \text{CrO}_3 + \text{H}_2\text{O}$) [20,34].

Fig. 4(c) shows the residual Cr(VI) concentrations as a function of the SCG dosage after 3 h of reaction. The residual concentration of Cr(VI) decreased as the SCG dosage increased for both phases; however, the reduction efficiency in the aqueous phase at an SCG dosage of 0.5 g/L in the aqueous solution was lower than that in the frozen phase at a dosage of 0.05 g/L. After 3 h of reaction, the residual Cr(VI) concentration in the aqueous phase with an SCG dosage of 0.5 g/L was $9.11 \pm 0.20 \mu\text{M}$ of Cr(VI), while that in the frozen solution was $4.73 \pm 0.28 \mu\text{M}$ at an SCG dosage of 0.05 g/L. This observation indicates that the enhanced reduction of Cr(VI) via freezing can be achieved when all solutes (i.e., Cr(VI), protons, and the phenolic compounds in SCG extracts) are simultaneously accumulated in the ice grain boundaries [34].

In this study, the effect of temperature on Cr(VI) reduction using SCG was also investigated for temperatures between 25 and -196°C (Fig. 4(d)). It was observed that the efficiency of the Cr(VI) reduction process increased with decreasing temperature for temperatures in the range 20 to -30°C . However, the residual concentration of Cr(VI) at -196°C (i.e., rapid freezing using liquid nitrogen) was much higher than those obtained at temperatures between -10 and -30°C owing to differences in freezing behavior [33,40]. The ice crystals formed between -10 and -30°C gradually increase in size as the solutes move towards the ice grain boundaries. However, the ice crystals rapidly formed at -196°C , leaving no time for the exclusion of the solutes. This finding indicates that the freezing method (i.e., freezing rate) is another key factor that influences Cr(VI) reduction.

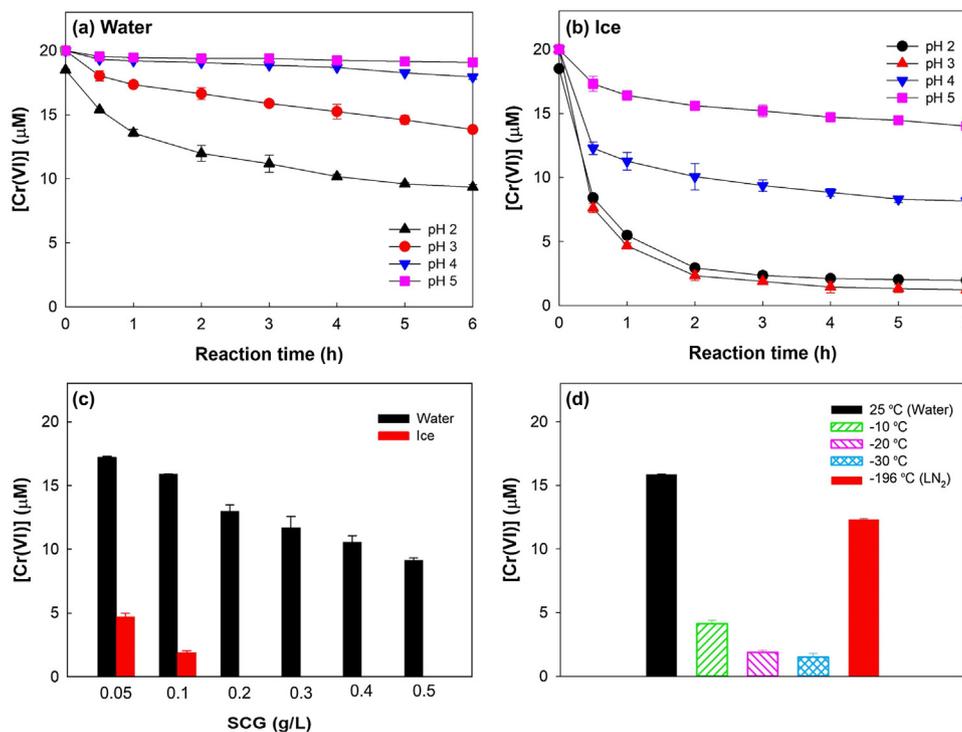


Fig. 4. Effect of (a and b) pH_i , (b) SCG dosage, and (c) freezing temperature on Cr(VI) reduction under experimental conditions: (a and b) $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}] = 0.1 \text{ g/L}$, $\text{pH}_i = \sim 2.0\text{--}5.0$, and freezing temperature = -20°C , (c) $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}] = \sim 0.05\text{--}0.5 \text{ g/L}$, $\text{pH}_i = 3.0$, reaction time = 3 h, and freezing temperature = -20°C , and (d) $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}] = 0.1 \text{ g/L}$, $\text{pH}_i = 3.0$, reaction time = 3 h, and freezing temperature = ~ 25 to -196°C .

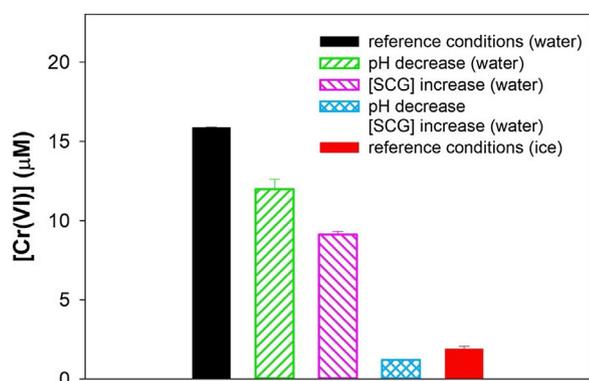


Fig. 5. Effect of increase in SCG dosage and/or decrease in pH_i on Cr(VI) reduction using SCG (reaction time and freezing temperature were 3 h and -20°C , respectively). Reference conditions: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}] = 0.1 \text{ g/L}$, $pH_i = 3.0$; pH decrease: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}] = 0.1 \text{ g/L}$, $pH_i = 2.0$; [SCG] increase: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}] = 0.5 \text{ g/L}$, $pH_i = 3.0$; and pH decrease and [SCG] increase: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}] = 0.5 \text{ g/L}$, $pH_i = 2.0$.

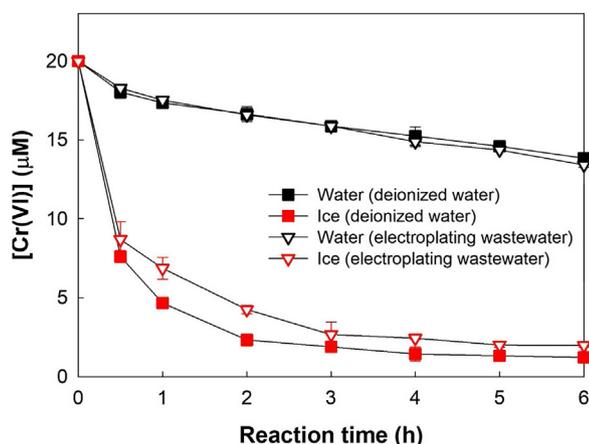


Fig. 6. Time profiles of Cr(VI) in real Cr(VI)-contaminated wastewater and synthesized Cr(VI)-containing wastewater in water and ice under the experimental conditions: $[\text{Cr(VI)}]_i = 20 \mu\text{M}$, $[\text{SCG}] = 0.1 \text{ g/L}$, and $pH_i = 3.0$.

Verification of the freeze concentration effect on Cr(VI) reduction using spent coffee ground

Based on the results obtained, the accelerated reduction of Cr(VI) using SCG in ice could be attributed to the freeze concentration of Cr(VI), protons, and the phenolic compounds in the SCG extracts at the ice grain boundaries. To illustrate this freeze concentration effect, the residual concentrations of Cr(VI) in the aqueous solution under either high SCG dosages or low pH_i conditions were determined, and the results are shown in Fig. 5. Even though the residual concentrations of Cr(VI) at low pH_i ($11.98 \pm 0.62 \mu\text{M}$) or high SCG dosages ($9.11 \pm 0.20 \mu\text{M}$) were lower compared with the reference condition in the aqueous phase ($15.88 \pm 0.03 \mu\text{M}$), the residual concentrations of Cr(VI) were quite higher than the reference conditions in the frozen phase ($1.89 \pm 0.16 \mu\text{M}$). It should be noted that the efficiency of Cr(VI) reduction in the aqueous solution was comparable with that obtained under the reference condition in the frozen solution, when both the SCG and proton concentrations were increased. Therefore, the freeze concentration phenomenon was responsible for the accelerated reduction of Cr(VI) in the frozen solution using SCG.

Practical application of spent coffee ground for Cr(VI) reduction in real Cr(VI)-containing wastewater

To check the feasibility of employing SCG as reducing agent in the freezing-mediated reduction of Cr(VI) in real Cr(VI)-containing wastewater (e.g., electroplating wastewater), the rate of the reduction processes in the aqueous and frozen phases were investigated (Fig. 6). The results showed that in the ice phase, the efficiency of the reduction of Cr(VI) in electroplating wastewater using SCG was comparable with that observed with the synthesized Cr(VI)-containing wastewater (i.e., the reduction rates (k) were $473.1 \times 10^{-3} \text{ h}^{-1}$ and $556.0 \times 10^{-3} \text{ h}^{-1}$ for the real Cr(VI)-wastewater and synthesized wastewater in ice, respectively). After 3 h of reaction, the concentration of Cr(VI) was 1.89 ± 0.16 and $2.67 \pm 0.81 \mu\text{M}$ in the real Cr(VI)-containing wastewater and the synthesized wastewater, respectively.

Even though these results suggest that the freezing-mediated reduction of Cr(VI) using SCG can be applied in the remediation of real Cr(VI)-polluted wastewater, the process may be uneconomical given that external energy is required to freeze all the Cr(VI)-contaminated wastewater at the proposed system site. Thus, the proposed system will be economically feasible only in regions where low temperatures are latitudinally and/or seasonally maintained. It is well known that polar regions, high latitudes, and mid-latitudes are usually characterized by very low temperatures during the winter season, i.e., below -10°C [36]. Therefore, the application of this freezing/SCG system can be economically feasible in these regions, where an external energy source is not needed for freezing. Regarding the design of commercial scale plants for this system and the optimization of the process parameters, it would be necessary to perform Cr(VI) reduction experiments using SCG in different types of reactors and further compare the results obtained given that these factors significantly influence the efficiency of the Cr(VI) reduction process.

Conclusions

The feasibility of freezing-assisted reduction of Cr(VI) was investigated using SCG. The results showed that there was an accelerated reduction of Cr(VI) owing to the freeze concentration effect, indicating that the main Cr(VI) reduction pathway in the frozen phase can be attributed to the enhanced redox conversion of Cr(VI) by the phenolic compounds in SCG extracts at the ice grain boundaries. The freezing method employed is a key factor to achieve the enhanced reduction of Cr(VI). The enhanced reduction of Cr(VI) in real Cr(VI)-containing wastewater (i.e., electroplating wastewater) was successfully achieved in ice, highlighting the applicability of this method.

Declaration of interests

None.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jiec.2021.05.008>.

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