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# Freezing-accelerated removal of chromate by biochar synthesized from waste rice husk



Separation Purification

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#### ABSTRACT

The application of biochar has been considered a promising method for remediating contaminated water, as biochar exhibits a redox activity for environmentally relevant redox reactions. Although the mechanisms of various redox reactions by biochar in water have been widely investigated, investigations of reaction in ice have not been attempted. In this study, the freezing-accelerated removal of chromate (Cr(VI)) by biochar synthesized from waste rice husks (RH-BC) was investigated in water (25 °C) and ice (-20 °C). The reduction of Cr(VI) with RH-BC was insignificant in water, whereas an enhanced reduction efficiency of Cr(VI) was observed in ice due to the freeze concentration phenomenon. The enhanced redox reaction between Cr(VI) and dissolved organic matter (DOM) is primarily responsible for the accelerated Cr(VI) reduction in ice, wherein DOM is a primary component of RH-BC. Experiments on various conditions of pH and RH-BC concentrations reveal that Cr(VI) is heavily reduced at low pH values and an aggregation of RH-BC in ice can inhibit the reduction efficiency of Cr (VI) due to a decrease in active sites. The removal of Cr(VI) by RH-BC was successfully achieved with real Cr(VI) contaminated wastewater in ice; this elucidated the environmental relevance of freezing-assisted Cr(VI) removal in cold regions.

#### 1. Introduction

Biochar (BC) is a carbon-rich and porous solid product produced by thermal decomposition (pyrolysis) under O<sub>2</sub>-limited conditions [1]. Owing to its unique properties, such as large amounts of functional groups and high contents of organic carbon and ash [2,3], BC has received significant attention as a cost-effective material for environmental applications; these include carbon sequestration, greenhouse gas reduction, improvement of soil fertility, and immobilization and remediation of contaminated water and soil [4]. As a field that extensively utilizes BC, research on the usage of BC as a sorbent and/or reductant has been extensively performed for the removal of environmental pollutants such as dyes [5,6], phenols [7], pesticides [8], and heavy metal ions [9] in water and soil.

According to the literature, BC has specifically shown a strong affinity for heavy metals because of its properties such as its porous structure and the existence of several functional groups on its surface [3,10,11]. Among heavy metal ions, chromium is a common element in Earth's crust, which is widely used in various industries such as metallurgy, dye and pigment, corrosion inhibition, leather tanning, and electroplating [12]. Trivalent chromium (i.e., Cr(III)) and hexavalent chromium (i.e., Cr(VI), chromate) are the most stable oxidation states of chromium. In addition, Cr(VI) is approximately  $500 \sim 1,000$  times more hazardous than Cr(III) in terms of its carcinogenic and mutagenic effects on biological systems [13]. Thus, Cr(VI) is widely restricted based on the European Restriction of Hazardous Substances (RoHS) Directive and the removal and/or reduction of Cr(VI) by BC has been extensively explored [14-18]. Dong et al. [15] proposed a two-step removal mechanism of Cr(VI) under acidic media by using sugar beet tailing (SBT)-BC, wherein Cr(VI) was preferentially reduced to Cr(III) via electrostatic attraction between negatively charged Cr(VI) (i.e., HCrO<sub>4</sub><sup>-</sup>) and positively charged BC; this was followed by the complexation of Cr(III) with functional groups on SBT-BC. Li et al. [3] reviewed several articles to provide insights for the adsorption mechanisms of metal ions by BC; they also proposed the following Cr(VI) sorption mechanisms according to the literature: (1) electrostatic attraction and reduction of Cr(VI) and (2) complexation of Cr(III) on BC surface. Moreover, they reported that the reduction pathways of Cr(VI) in an aqueous solution could be divided into direct (i.e., reduction by solubilized BC components) and indirect (i.e., reduction on a biochar

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#### surface) pathways.

Although BC is considered as a promising material for Cr(VI) reduction and adsorption from water, its actual performance is significantly lower than those of conventional sorbents [19]. To solve technical issues, numerous studies designed to enhance the performance of BC have been extensively performed via chemical modifications and physical modifications [20-23]. Typical chemical modification methods include methanol and amino modifications and acid/base treatments to enhance the adsorption capacity by modifying the surface functional groups of BC [21]. Impregnating BC with metal oxide is another chemical modification method. The nanosized metal oxide particles on the BC surface can act as active sorption sites, which results in an improvement of the sorption ability for heavy metal ions [19,24]. Meanwhile, physical modification methods such as steam activation and gas purging use oxidizing agents (CO<sub>2</sub>, steam, and air) without any chemicals to enlarge the surface area, pore volume, and structure of microporous BC [25]. Although these modification techniques increase the efficiency of the BC as a sorbent, reductant, and soil conditioner, additional costs for the modification process are required. Further, incorrect modification can cause the abilities of BC to diminish, such as the reduction in porosity and the decrease in surface area.

The freezing process is a possible method for enhancing BC performance. It is commonly accepted that chemical reactions slow down as temperature drops and ice crystal is inert as reaction media. However, some reactions such as redox conversions and the dissolution of solid particles can be accelerated by freezing [12,13,26–28]. This is because solutes, protons, and/or solid particles dramatically accumulate in ice grain boundaries, which are the liquid compartments between ice crystals by exclusion from solid ice crystals during freezing; this is termed as the freeze concentration effect. Numerous studies have continuously investigated enhanced redox conversions in the ice phase between Cr(VI) and some species such as arsenite (As(III)) [12], dissolved organic matter (DOM) [29], hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) [30], phenolic compounds [13], and nitrite (NO<sub>2</sub><sup>-</sup>) [31]. However, a drawback in the reduction of Cr(VI) is that the concentration of total chromium remains in the system.

Therefore, the freezing-induced reduction and adsorption of Cr(VI) by BC was attempted to achieve the enhanced Cr(VI) removal efficiency in the ice phase. In this study, we used the BC synthesized from waste rice husks (RH-BC), and investigated the reduction and adsorption efficiency of Cr(VI) by RH-BC in the ice phase (i.e., at -20 °C) in comparison with its counterpart in the water phase (i.e., at 25 °C). The redox conversion of Cr(VI)/RH-BC was accelerated in ice; however, it was negligible in water. To elucidate the freezing-enhanced reduction of Cr(VI) by RH-BC in ice, the redox conversion kinetics of Cr(VI) with dissolved organic matter (DOM) derived from raw RH-BC as well as washed RH-BC in both ice and water were also explored as a function of various experimental conditions. By understanding the combination results, this research will be able to provide fundamental data for the actual commercialization of the RH-BC/freezing system.

## 2. Materials and methods

#### 2.1. Material and chemicals

The waste rice husks (RH), which was collected from a rice mill company in the Republic of Korea, was cryo-milled and dried at 105 °C. To minimize the heat and mass transfer inhibition effect, particle sizes below 500 µm were collected and used for each experiment. The real Cr (VI)-containing wastewater was obtained from a local electroplating plant in the Republic of Korea. All chemicals and reagents were used without further purification in this study including as follows: sodium dichromate dihydrate (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O, Cr(VI), Sigma-Aldrich,  $\geq$  99.5%), 1,5-diphenylcarbazide (C<sub>6</sub>H<sub>5</sub>NHNHCONHNHC<sub>6</sub>H<sub>5</sub>, DPC, Sigma-Aldrich,  $\geq$  99.95%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, Kanto,  $\geq$  96.0%), acetone (CH<sub>3</sub>COCH<sub>3</sub>, Kanto,  $\geq$  99.5%), cresol red (C<sub>2</sub>1H<sub>18</sub>O<sub>5</sub>S, Sigma-

Aldrich,  $\geq$  95.0%).

#### 2.2. Thermogravimetric and product analysis

The thermogravimetric (TG) analyzer (Pyris Diamond, PerkinElmer Co.) was used to establish the thermal properties of RH and determine the reaction temperature for the RH-BC production. For TG analysis, the sample (5 mg) was heated from ambient temperature to 700 °C at a heating rate of 20 °C/min under nitrogen flow (100 mL/min). Multishot gas chromatography/mass spectrometry (GC/MS) (7890A/5975C inert, Agilent Technologies) analysis *via* pyrolyzer (Py; EGA/Py-3030D, Frontier Laboratories Ltd.) was also carried out to determine the detailed information on the evolved chemicals in each thermal zone [32]. The detailed Py-GC/MS operational conditions are given in the supplementary information section (Table S1).

#### 2.3. Sample preparation and characterization

To produce RH-BC, 20 g of dried RH was heated non-isothermally from ambient temperature to 300 °C at a heating rate of 10 °C/min, under a nitrogen flow rate of 500 mL/min using fixed-bed reactor. RH-BC was cryo-milled with liquid nitrogen using a milling machine and sieved to make its particle size below 63 µm, which is hereafter referred to as raw RH-BC. Washed RH-BC and DOM separated from raw RH-BC were also prepared to deeply investigate Cr(VI) conversion pathways. For DOM preparation, 10 g of raw RH-BC was placed into the reaction vessel with 1 L of the ultrapure deionized (DI) water (18.3 M·cm, Human-Power I + water purification system, Human Co.) for 24 h, and then filtered by a membrane (0.22 µm, Durapore membrane filters, Millipore Co.). The residual raw RH-BC was washed four additional times using the same method for DOM preparation to sufficiently remove DOM; this process is hereafter referred to as washed RH-BC. All of the samples were dried at 105 °C for at least 24 h before each experiment.

Proximate, ultimate analysis, and higher heating value (HHV) measurements were conducted to investigate the physico-chemical properties of RH and RH-BC according to established procedures reported elsewhere [32]. The physico-chemical properties of RH and RH-BC are summarized in Table S2 (Supplementary Information). To determine the qualitative characterization of DOM, a fluorescent excitation-emission matrix (EEM) measurement was performed using a fluorescence spectrophotometer (FLS-1000, Edinburgh Instruments Ltd.); this process used excitation wavelengths from 240 to 450 nm with scanning emission spectra from 250 to 580 nm at 5 nm intervals. The DOM concentrations were measured by a total organic carbon (TOC) analyzer equipped with a nondispersive infrared sensor (NDIR) (TOC-VCSH, Shimadzu Co.). For the analysis of RH-BC functional groups, the Fourier transform infrared spectroscopy (FTIR) spectrum was also analyzed via a FTIR instrument (NICOLET iN10 MX, Thermo Fisher, Co.) using the attenuated total reflection (ATR) mode.

## 2.4. Experimental procedure

The reduction of Cr(VI) by raw RH-BC, washed RH-BC, and DOM applied in this study were classified depending on the adding substance types. In case of experiments for the reduction of Cr(VI) by raw and washed RH-BC, 10 mL of solution containing the desired amount of RH-BC (1 g/L ~ 10 g/L) and concentration of Cr(VI) (usually, 20  $\mu$ M) was prepared in a conical tube (15 mL). The pH value of solution containing RH-BC was adjusted to the desired experimental values (3.0 ~ 5.0) using a HClO<sub>4</sub> (1 M) and NaOH (1 M). For the redox conversion of Cr (VI) by DOM, 10 mL of Cr(VI) containing solution with the same concentration of DOM as raw RH-BC was prepared with the conditions of [Cr(VI)]<sub>i</sub> = 20  $\mu$ M, [DOM]<sub>i</sub> = 6.553 mg C/L, and [pH]<sub>i</sub> = 3.0 ~ 5.0. The prepared conical tubes were located at the same time (t = 0) in a rack in a cryogenic ethanol bath, which were pre-adjusted at 25 °C (for

the reaction in water) and -20 °C (for the reaction in ice). At each fixed time interval, the samples collected from each ethanol bath were thawed in lukewarm water (40 °C). Then, the solution containing raw and washed RH-BC was filtered using a 0.45 µm syringe filter to remove RH-BC particles. The filtered solution (i.e., the solution separated from Cr(VI)/RH-BC) and DOM containing solution (i.e., Cr(VI)/DOM) were immediately analyzed to determine the residual concentrations of Cr (VI) and total chromium. To measure the concentrations of Cr(VI) and total chromium in the solution, we used the 1, 5-diphenylcarbazide (DPC) method and inductively coupled plasma-optical emission spectroscopy (ICP-OES; iCAP 6300 Duo, Thermo Fisher Co.), respectively, according to established procedures reported elsewhere [30]. All data were obtained from the average values of three replicates to confirm data reproducibility.

## 2.5. pH measurement of frozen solution

To estimate the pH of the frozen solution, a UV–visible spectrometer equipped with an integrating sphere (Cary 5000, Agilent Technologies) was used, and the pH value of the frozen solution was calculated according to the procedure reported by Ju et al. [13]. Cresol red (CR) was used as a pH indicator because CR exists in three different forms depending on the pH, and each form has a different maximum absorption wavelength ( $\lambda$ max = 518 nm for diprotonated CR,  $\lambda$ max = 434 nm for monoprotonated CR, and  $\lambda$ max = 573 nm for deprotonated CR). To determine the relative concentrations of two CR forms (i.e., [monoprotonated CR]/[diprotonated CR] or [deprotonated CR]/[monoprotonated CR]) in the frozen solution, the *lsqnonneg* function of Matlab was used as follows:

$$\sum_{\lambda=400\text{nm}}^{\lambda=650\text{nm}} (A \cdot a + B \cdot b - X)^2 = \text{minimum value}$$
(1)

where X is the absorbance of the frozen solution, A and B donate the absorbance of pure deprotonated and monoprotonated CR (or the absorbance value of pure monoprotonated and deprotonated CR), respectively, and a and b (non-negative parameters) are the relative concentrations of diprotonated and monoprotonated CR (or the relative concentrations of monoprotonated and deprotonated CR) in the frozen solution, respectively. The pure ice was used as a reference. The pH of the frozen solution was estimated by Eq. (2), where  $pK_{a1} = 1.10$  and  $pK_{a2} = 8.15$  [13].

$$pH = pK_{a1} + \log \frac{[monoprotonated CR]}{[diprotonated CR]} \text{ or}$$

$$pK_{a2} + \log \frac{[deprotonated CR]}{[monoprotonated CR]}$$
(2)

#### 3. Results and discussion

## 3.1. Characterization of RH and RH-BC

Fig. 1a shows the TG and derivative TG (DTG) curves for RH at a heating rate of 20 °C/min. Lignocellulosic biomass, which consists of hemicellulose, cellulose, and lignin, decomposes typically at the temperature zone between 200 °C and 400 °C. The DTG curve in Fig. 1a shows that RH decomposition involves complex reaction patterns (i.e., shoulder, main, and tailing peaks) owing to the unique thermal stability of each component (hemicellulose: ~200–400 °C, cellulose: ~300–400 °C, and lignin: ~200–600 °C) [33]. The detailed pyrolysis behavior of RH with respect to its major components (hemicellulose, cellulose, and lignin) is explained in the supplementary information.

In terms of BC production, pyrolysis temperature is one of the key factors used to control the quantities of functional groups on BC surfaces [3]. At higher temperatures, the amounts of O-containing functional groups (carboxyl, alcohol and hydroxyl groups) are reduced with the production of large amounts of volatile oxygenated compounds

because of the acceleration of dehydration reactions of biomass components at higher temperatures [34]. These O-containing functional groups may not only participate in the adsorption of chromium (i.e., mainly Cr(III)), but they also can act as an electron-donor (ED) for Cr (VI) reduction [3]. Multi-shot GC/MS analysis results (Fig. 1b) confirmed that large amounts of functional groups on the BC surface could be removed together with producing a large quantity of volatile Ocontaining compounds (acids, anhydro-sugars, phenols and so on) when applying higher temperatures. Therefore, it is suitable that BC was produced at a lower temperature (300 °C) because BC having higher amounts of functional groups increases the reduction and/or adsorption of chromium [35].

Fig. 1c shows the FTIR spectrum of raw RH-BC, and the four functional groups characterize the raw RH-BC [15,36]. The broad band of  $3100-3700 \text{ cm}^{-1}$  was mainly assigned to the –OH stretching vibration. The peaks between 1400 and 1710 cm<sup>-1</sup> could correspond to C–O stretching (carbonyl –C=O and carboxyl –COOH; 1706 cm<sup>-1</sup>) and C=C stretching of the benzene ring skeleton from aromatics (1410–1680 cm<sup>-1</sup>). The final peak observed between 950 and 1200 cm<sup>-1</sup> represented –C–O vibrations of phenols. Among the functional groups, carboxyl and hydroxyl groups reportedly play important roles in metal sorption [3]. Specifically, in the case of Cr(VI) reduction and adsorption, these functional groups can be involved in reducing Cr(VI) to Cr(III), and in subsequent Cr(III) complexation on raw RH-BC [15].

## 3.2. Cr(VI) reduction by RH-BC in aqueous solution and ice

The reduction of Cr(VI) by RH-BC in ice (-20 °C) and water (25 °C) were investigated, and the results were compared. Fig. 2a which shows the time profiles of Cr(VI) concentrations in water and ice, revealed that the reduction of Cr(VI) was negligible in the water phase. However, in the ice phase, it was significant in the ice phase and it proceeded even in the absence of raw RH-BC owing to the enhanced proton-mediated reduction process (i.e.,  $4\text{HCr}(\text{VI})\text{O}_4^- + 16\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 3\text{O}_2 + 10\text{H}_2\text{O}; \text{E}_0 = 0.15 \text{ V}_{\text{NHE}}$ ) in the liquid grain boundary during the freezing process [30,31]. However, the degree of reduction in the absence of raw RH-BC (i.e., after a 6 h reaction, 19.64  $\mu$ M of Cr (VI) was reduced in the presence of raw RH-BC. This finding indicates that the raw RH-BC mediated reduction process is the main reduction pathway for Cr(VI) reduction in ice.

The enhanced RH-BC-mediated Cr(VI) reduction observed in ice possibly resulted from the DOM that eluted from raw RH-BC and/or from RH-BC itself. To further understand the RH-BC-mediated Cr(VI) reduction pathway, experiments on Cr(VI) reduction by washed RH-BC and DOM separated from raw RH-BC were also performed in the water and ice phases (Fig. 2b). The DOM concentration was adjusted to be the same as the DOM concentration associated with 1 g/L of raw RH-BC. The reduction kinetics of Cr(VI) by DOM during freezing were dramatically accelerated compared with those in the water phase. However, the reduction efficiency of Cr(VI) by washed RH-BC in the ice phase quite decreased compared with those of raw RH-BC. This result implies that the enhanced Cr(VI) reduction by raw RH-BC in the ice phase was most likely due to the redox reaction between Cr(VI) and DOM.

Fig. 3 shows the EEM spectrum for the qualitative characterization of DOM. The region can be assigned as humic acid-like matter (polyphenolic compounds consisted of quinone, phenol, catechol, sugar moieties and so on) [37,38]. This means that DOM is an effective ED for Cr(VI) reduction because polydentate ligands can more easily form a precursor (chromate ester intermediate) for the reduction of Cr(VI) [12,39]. After 6 h of reaction in the presence of DOM, the residual concentrations of DOM were 6.051 mg C/L and 4.723 mg C/L in water and ice, respectively. Similarly, larger amounts of DOM were oxidized and removed in the ice phase during the experiments with raw and



Fig. 1. Characterization of RH and RH-BC: (a) TG and DTG curves of RH, (b) Pyrograms obtained from multi-shot GC/MS analysis of RH, and (c) FTIR spectrum of RH-BC.

washed RH-BC. The initial concentrations of DOM were 6.553 mg C/L for raw RH-BC and 4.415 mg C/L for washed RH-BC, respectively. The residual concentrations of DOM ( $[DOM]_f$ ) after the 6 h reaction were 5.844 (raw RH-BC) and 4.273 mg C/L (washed RH-BC) in water, whereas the concentrations in ice were  $[DOM]_f = 4.568$  (raw RH-BC) and 2.471 mg C/L (washed RH-BC). Therefore, the enhanced redox reaction between Cr(VI) and DOM in the ice phase was the main pathway of the accelerated Cr(VI) transformation by raw RH-BC (i.e., the simultaneous reduction of Cr(VI) and oxidation of DOM).

Notably, the reduction efficiency of Cr(VI) by raw RH-BC was higher than that by DOM in both water and ice. The consumption amount of DOM in the Cr(VI)/raw RH-BC system was also higher than that in Cr (VI)/DOM system. This means that the redox reaction of Cr(VI)/DOM increased in both water and ice when DOM co-existed with RH-BC. Ocontaining functional groups in BC act as an ED, and BC acts as electron shuttle for Cr(VI) reduction under co-exist system of BC and other ED compounds, and it results in the enhanced Cr(VI) transformation [18]. Therefore, the synergistic effect on Cr(VI) reduction by raw RH-BC might occur because BC can act as an electron shuttle to electron transfers between DOM and Cr(VI) with the role as an ED.

## 3.3. Reduction of Cr(VI) in water and ice under various conditions

## 3.3.1. The effect of $pH_i$ on Cr(VI) reduction in water and ice

Fig. 4a and 4b show the effect of  $pH_i$  on Cr(VI) reduction by DOM in water and ice. The rate of Cr(VI) reduction by DOM in ice (Fig. 4a) was higher than that in water (Fig. 4b). Fig. 4c–4f, which show the pH-dependent reduction of Cr(VI) by RH-BC revealed that the difference in the rates of Cr(VI) reduction by RH-BC in water (Fig. 4c and 4e) and ice (Fig. 4d and 4f) was negligible. Additionally, there was an increase in

the Cr(VI) reduction efficiencies of DOM and RH-BC in water as  $pH_i$  decreased, indicating that the  $pH_i$  of the system has a significant effect on Cr(VI) removal efficiency, which was enhanced to a greater extent by lower  $pH_i$  values. This behavior is expected given that the reduction of Cr(VI) to Cr(III) requires protons ( $HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$ ). The enhanced reduction of Cr(VI) during freezing could be attributed to the lowering of the pH values of the grain boundary *via* the freeze concentration phenomenon [13,30]. The concentration of protons under acidic condition increases by 2 ~ 4 orders of magnitude in ice compared with water [40,41].

To verify the pH decrease during freeze process, the solution containing these solutes was prepared under the conditions of [Cr (VI)]<sub>i</sub> = 20  $\mu$ M, [DOM]<sub>i</sub> = 6.553 mg C/L and [pH]<sub>i</sub> = 3.0. The pH of the frozen solution was estimated by measuring the UV-vis absorption spectra of CR as a pH indicator [13]. As shown in Fig. 5, the maximum absorption of CR in water at pH = 3.0 was observed at 434 nm (monoprotonated form of CR), whereas that in ice changed from 434 nm to 518 nm (deprotonated form of CR). Therefore, this result confirms that the pH of the frozen solution was approximately 0.55.

Even though the Cr(VI) reduction rates in ice were higher than those in water, in the ice phase, the conversion efficiency of Cr(VI) by DOM observed at  $pH_i = 2.0$  was lower than that observed at  $pH_i = 3.0$ , possibly owing to Cr(VI) speciation as a function of pH. During the freezing process, there was a decrease in the pH value of the reaction system (Fig. 5); thus, the concentration of the solid form of Cr(VI) (i.e., Cr(VI)O<sub>3</sub>, equilibrium solid-state of H<sub>2</sub>Cr(VI)O<sub>4</sub>) increased at the grain boundary, bringing about a hindering effect on Cr(VI) reduction owing to the diffusion limitation between Cr(VI) and DOM [13]. Meanwhile, it is worth noting that in ice at pH<sub>i</sub> values in the range of 2.0 ~ 3.0, the



**Fig. 2.** Time profiles of Cr(VI) concentration with (a) raw RH-BC and (b) DOM and washed RH-BC in water and ice. Experimental conditions were as follow: (a)  $[Cr(VI)]_i = 20 \ \mu\text{M}$ , [raw RH-BC] = 1 g/L, and  $[pH]_i = 3.0$ ; (b-1) experiment on Cr(VI) reduction by DOM:  $[Cr(VI)]_i = 20 \ \mu\text{M}$ ,  $[DOM]_i = 6.553 \ \text{mg C/}$ L, and  $[pH]_i = 3.0$ ; (b-2) experiment on Cr(VI) reduction by washed RH-BC:  $[Cr(VI)]_i = 20 \ \mu\text{M}$ , [washed RH-BC] = 1 g/L, and  $[pH]_i = 3.0$ .



Fig. 3. Excitation-emission matrix (EEM) fluorescence spectroscopy of DOM.

rates of Cr(VI) reduction by raw RH-BC were higher than those brought about by DOM, suggesting that the synergistic effect on Cr(VI) reduction by raw RH-BC in ice can be realized by accumulating RH-BC particles together with Cr(VI) and DOM at the grain boundary. As a result, a larger reduction of Cr(VI) in ice by RH-BC can be achieved due to the freeze concentration effect under the acidic solution. In addition, the real Cr(VI)-containing wastewater is usually acidic, which means that the reduction of Cr(VI) in ice is suitable [42].

## 3.3.2. The effect of RH-BC dosage on Cr(VI) reduction in water and ice

Fig. 6 shows the residual concentration of Cr(VI) in water and ice with respect to the RH-BC dosage after the 6 h reaction. In the water phase, the final concentration of Cr(VI) slightly decreased as the concentration of washed RH-BC increased (17.93  $\sim$  16.14  $\mu$ M, Fig. 6a); however, the degree of Cr(VI) reduction was negligible even at 10 times of the washed RH-BC dosage (Fig. 6a). Enhanced reduction efficiencies of Cr(VI) by washed RH-BC in ice were observed due to the freeze concentration effect, and the maximum efficiency of Cr(VI) reduction was achieved in the ice phase at 3 g/L of washed RH-BC. In the Cr(VI) reduction by raw RH-BC (Fig. 6b), the reduction efficiencies of Cr(VI) in water were also lower than those in ice, and residual concentrations of Cr(VI) in water reached the equilibrium (ca. 12  $\mu$ M) above 2 g/L of the raw RH-BC dosage.

Although the residual concentrations of Cr(VI) were very similar  $(0.40 \sim 1.01 \,\mu\text{M})$ , the lowest concentration of Cr(VI) was observed at 3 g/L of raw RH-BC. Notably, this behavior was only observed in the ice phase. This can be explained by the inhibitory effects for Cr(VI) reduction caused by BC particle aggregation, which are clearly visible at higher RH-BC concentrations [43,44]. Solid particles are highly aggregated in ice grain boundaries by freezing [26]. The RH-BC particle aggregation in ice reduces available active sites (i.e., O-containing functional groups on BC surface) and ability as electron shuttle for Cr (VI) reduction [45,46]. In addition, the aggregation can be enhanced by DOM [47]. DOM tends to sorb to the BC surface, and the aggregation of BC particles is accelerated at a high concentration of DOM [47]. As expected, the initial DOM concentration increased (raw RH-BC:  $6.553 \sim 41.565 \text{ mg C/L}$ , washed RH-BC  $4.415 \sim 9.162 \text{ mg C/L}$ ) with the RH-BC dosage (Table 1). However, the concentration of DOM did not follow proportionally as the RH-BC concentration increased. For example, measured [DOM]<sub>i</sub> values at 10 g/L of washed and raw RH-BC were 9.162 mg C/L and 41.565 mg C/L, respectively; these values were lower than the theoretical DOM values of washed RH-BC (44.15 mg C/ L) and raw RH-BC (65.53 mg C/L). The results imply that a significant amount of DOM was attached on the RH-BC's surfaces, which resulted in the enhancement of RH-BC aggregation. In addition, the consumption amount of DOM ( $\Delta$ [DOM]) in ice was also higher than that in water.  $\Delta$ [DOM] values in the range of 4–10 g/L of RH-BC in the ice phase were higher than  $\Delta$ [DOM] values at 3 g/L of RH-BC; however, the reduction efficiencies of Cr(VI) in ice were maximized at 3 g/L of RH-BC. This means that DOM will likely sorb on the RH-BC surface to form the RH-BC/DOM complex rather than participate in the redox reaction with Cr(VI) when the RH-BC aggregation begins acceleration. Therefore, the decreased reduction efficiency of Cr(VI) by RH-BC in ice at above 3 g/L of RH-BC was likely due to the hindering effects caused by RH-BC aggregation [44-47].

The effect of RH-BC dosage on the adsorptive removal of chromium was also investigated in water and ice (Fig. 7). Although the reduction efficiency of Cr(VI) in the ice phase was maximized at 3 g/L of RH-BC, the adsorption capacity in ice positively correlated with the RH-BC dosage. This can be explained by an increase of the total amount of adsorption sites [43], and an increased adsorption capacity by forming RH-BC/DOM complexes at a high concentration of RH-BC [48]. DOM attached on a BC surface can increase the adsorption capacity due to connection role of DOM between chromium and BC [46,48]. Therefore, the aggregation of RH-BC as the RH-BC concentration increases does not affect the adsorption capacity of chromium on RH-BC; rather, the adsorption efficiency increases due to the increase of total adsorption sites and increased connecting ability of DOM between chromium and RH-BC.



**Fig. 4.** Effect of  $pH_i$  on the redox conversion of Cr(VI) by DOM (for a and b), raw RH-BC (for c and d) and washed RH-BC (for e and f) in water and ice. Experimental condition were as follow:  $[Cr(VI)]_i = 20 \ \mu$ M; (a and b),  $[DOM]_i = 6.553 \ mg \ C/L$  and  $[pH]_i = 2.0 \sim 5.0$ ; (c and d)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (e and f) [washed \ RH-BC] = 1 \ g/L, and  $[pH]_i = 2.0 \sim 5.0$ ; (e and f) [washed \ RH-BC] = 1 \ g/L, and  $[pH]_i = 2.0 \sim 5.0$ ; (c and d)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (e and f) [washed \ RH-BC] = 1 \ g/L, and  $[pH]_i = 2.0 \sim 5.0$ ; (e and f)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and d)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and f)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and f)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and f)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and f)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and f)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and f)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and f)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and f)  $[raw \ RH-BC] = 1 \ g/L$ , and  $[pH]_i = 2.0 \sim 5.0$ ; (c and f)  $[raw \ RH-BC] = 1 \ g/L$ ; (c and f)  $[raw \ RH-BC] = 1 \ g$ 

#### 3.4. Freeze concentration effect on the Cr(VI) reduction by RH-BC

The enhanced reduction of Cr(VI) by raw RH-BC in ice should be due to the freeze concentration effect. To verify the freeze concentration effect, the reduction of Cr(VI) in water at a high concentration of raw RH-BC (10 g/L) and/or low pH (2.0) was investigated to compare the results at the reference conditions ([raw RH-BC] = 1 g/L and pH = 3.0 in water and ice). As shown in Fig. 8, the reduction of Cr(VI) by raw RH-BC positively correlated with the RH-BC and proton concentration in the water phase. Although the reduction efficiencies of Cr (VI) in water positively correlated with the RH-BC dosage and proton concentration, the reduction efficiencies of Cr(VI) were lower than that of the reference condition for ice when both the concentrations of raw RH-BC and protons increased by 10 times. This result implies that protons and/or RH-BC might be concentrated in ice grain boundaries more than 10 times (Fig. 5). 3.5. Reduction of Cr(VI) in real Cr(VI)-contaminated wastewater by RH-BC

Small residual concentrations of Cr(VI) and DOM in the solution after 6 h reaction are considered to be optimal from the perspective of reducing harm to humans and the environment because Cr(VI) is more harmful than Cr(III), and DOM also could be considered as an organic pollutant. According to the legislation of the Korea Ministry of Environment, only effluents with a TOC level below 15 mg C/L will be discharged from a wastewater treatment facility at region I (clean area) after 2020. In general, the TOC levels of rivers and lakes range from 2 to 10 mg C/L [49]. Therefore, we selected the reaction conditions with the highest Cr(VI) reduction and DOM concentration below 10 mg C/L after 6 h reaction in the ice phase, and applied these conditions to the real Cr (VI)-contaminated wastewater (electroplating wastewater) containing Cr(VI) and various metals (Table S3). Fig. 9 shows the residual concentration of Cr(VI) in artificial Cr(VI) wastewater and real Cr(VI)-



Fig. 5. UV-vis absorption spectra of CR before and after freezing. Experimental conditions were as follow:  $[Cr(VI)]_i = 20 \ \mu\text{M}$ ,  $[DOM]_i = 6.553 \ \text{mg C/L}$ , and  $[pH]_i = 3.0.$ 



Fig. 6. Effect of RH-BC dosage on Cr(VI) reduction by (a) washed RH-BC and (b) raw RH-BC in water and ice. Experimental condition were as follow: reaction time = 6 h,  $[Cr(VI)]_i$  = 20 µM, [RH-BC] = 1 ~ 10 g/L, and  $[pH]_i$  = 3.0.

contaminated wastewater after the 6 h reaction in water and ice. The reduction of Cr(VI) in Cr(VI)-contaminated wastewater by raw RH-BC was also negligible in water, whereas it was dramatically enhanced in ice. These results imply that enhanced reductions of real Cr(VI)-containing wastewater by raw RH-BC may be feasible via the freezing process.

	Washed RH-BC						Raw RH-BC					
Biochar (g/L)	1	2	3	4	5	10	1	2	3	4	5	10
[DOM] <sub>i</sub> Water ∆[DOM] <sup>a</sup> Ice ∆[DOM] <sup>a</sup>	$\begin{array}{c} 4.415\pm \ 0.106\\ 0.142\pm 0.021\\ 1.944\pm \ 0.101 \end{array}$	$4.713\pm 0.064$ $0.34\pm 0.220$ $2.196\pm 0.045$	$5.339\pm 0.035$ $0.815\pm 0.015$ $2.609\pm 0.066$	$\begin{array}{l} 6.024\pm\ 0.042\\ 0.940\pm\ 0.030\\ 3.073\pm\ 0.027 \end{array}$	$\begin{array}{c} 6.832 \pm \ 0.094 \\ 1.792 \pm \ 0.210 \\ 3.261 \pm \ 0.015 \end{array}$	$9.162\pm 0.065$ $1.886\pm 0.016$ $3.353\pm 0.045$	$6.553\pm 0.062$ $0.709\pm 0.060$ $1.985\pm 0.030$	$10.641\pm 0.304$ $1.163\pm 0.215$ $4.354\pm 0.245$	$14.060\pm 0.072$ $1.523\pm 0.040$ $5.149\pm 0.039$	$\begin{array}{l} 18.383 \pm \ 0.013 \\ 2.185 \pm \ 0.009 \\ 7.947 \pm \ 0.467 \end{array}$	$22.432\pm 0.408$ $2.356\pm 0.134$ $8.265\pm 0.045$	$\begin{array}{l} 41.565\pm \ 0.085\\ 6.730\pm 0.765\\ 25.255\pm 0.003 \end{array}$
<sup>a</sup> mg C/L: [DO	M] <sub>I</sub> - [DOM] <sub>f</sub> , wł	tere [DOM] <sub>f</sub> is f	inal concentratio	on of [DOM] in s	olution after 6 l	1 reaction.						

**Table 1** 

Reduced concentration of DOM ( $\Delta$ [DOM]<sup>a</sup>) in water and ice after 6 h reaction.



**Fig. 7.** Effect of RH-BC dosage on adsorptive removal of chromium ( $\mu$ M) by (a) washed RH-BC and (b) raw RH-BC in water and ice. Experimental condition were as follow: reaction time = 6 h, [Cr(VI)]<sub>i</sub> = 20  $\mu$ M, [RH-BC] = 1 ~ 10 g/L, and [pH]<sub>i</sub> = 3.0.



**Fig. 8.** Effect of increase in raw RH-BC concentration and/or decrease in pH on the reduction of Cr(VI) in water (reference conditions:  $[Cr(VI)]_i = 20 \ \mu\text{M}$ , [raw RH-BC] = 1 g/L, and [pH]<sub>i</sub> = 3.0; [raw RH-BC] increase:  $[Cr(VI)]_i = 20 \ \mu\text{M}$ , [raw RH-BC] = 10 g/L, and [pH]<sub>i</sub> = 3.0; pH decrease:  $[Cr(VI)]_i = 20 \ \mu\text{M}$ , [raw RH-BC] = 1 g/L, and [pH]<sub>i</sub> = 2.0; [raw RH-BC] increase and pH decrease: [Cr (VI)]<sub>i</sub> = 20 \ \mu\text{M}, [raw RH-BC] = 10 g/L, and [pH]<sub>i</sub> = 2.0.



**Fig. 9.** Residual concentration of Cr(VI) in artificial Cr(VI) solution and real Cr (VI)-contaminated wastewater in water and ice after 6 h reaction. ([Cr (VI)]<sub>i</sub> = 20  $\mu$ M, [raw RH-BC] = 1 g/L, and [pH]<sub>i</sub> = 3.0).

#### 4. Conclusions

We investigated the enhanced reduction of Cr(VI) by BC in ice in comparison with its counterpart in water. To this end, the BC synthesized by waste rice husks (RH-BC) were used because these husks are one of the most abundant types of biomass worldwide. The reduction efficiency of Cr(VI) by RH-BC in ice was dramatically enhanced, whereas it was extremely slow in water. This reveals that DOM was main reductant for Cr(VI) reduction and RH-BC acted as an electron shuttle. During freezing, Cr(VI), DOM, and protons accumulated in the grain boundary due to the freeze concentration effect, which accelerated the redox reaction between Cr(VI) and DOM. The application of RH-BC in the reduction and removal of Cr(VI) seems to be beneficial because the reductive transformation of Cr(VI) by ions or soluble chemicals via redox reactions cannot reduce the total amounts of chromium. In addition, the reduction of Cr(VI) in real Cr(VI)-contaminated wastewater by RH-BC was also dramatically accelerated in ice and was comparable to that in the artificial Cr(VI) wastewater. Therefore, the freezing process combined with RH-BC application is an effective and practical treatment method for the reduction and removal of Cr(VI)containing wastewater. In addition, the proposed freezing-assisted Cr (VI) removal by RH-BC might be feasible in real cold environments such as permafrost, polar regions, and mid-latitudes during the winter season.

### CRediT authorship contribution statement

**Tae Uk Han:** Investigation, Writing - original draft. **Jungwon Kim:** Writing - review & editing. **Kitae Kim:** Conceptualization, Writing review & editing, Supervision.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

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