

# Freeze Desalination as Point of Use Water Treatment Technology: A Case of Chromium (VI) Removal from Water †

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**Abstract:** Options to develop tanning industries could be hindered even in the presence of huge leather industry raw materials due to the requirements of high-tech contaminant removal technologies, especially in developing countries. This study was initiated to investigate the efficiency of freeze desalination for Cr(VI) removal using freezers to generate fresh water. Simulated water as well as deionized water to which known concentrations of Cr(VI) spiked into it were studied. The effects of parameters such as initial concentration, freeze duration, ice nucleation, ice volume, and influence of co-occurring ions were evaluated in relation to meltwater. The physicochemical characteristics of the produced meltwater were also evaluated. A high total water recovery of up to 85% V/V of initial water was achieved for the freeze separation rate of 90% in the experimental evaluation. Cr(VI) removal efficiency of up to 80% from simulated tap and 93 to 97% for deionized water spiked with Cr(VI) were found in this batch partial freezing. Freeze desalination was found to be relatively viable desalination technology in terms of quality of water produced, options on the use of cost effective refrigerants and technologies which could have a pertinent importance to save energy consumption of freezers.

**Keywords:** ice nucleation; freeze desalination; freezer; refrigerant; progressive freezing

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## 1. Introduction

Chromium is one the priority pollutants list under clean water act of United States Environmental Protection Agency (US EPA) which can be released into natural waters due to the discharge of a variety of industrial wastewaters. Wastewater generated by leather tanning, electroplating, textile, metal finishing industries, and wood preservatives are among the major contributing sources. Uncontrolled solid and liquid waste discharges into open water systems from domestic use and industries with minimal or no treatment are common in developing countries [1]. Globally, more than 90% of the leather industries used chrome tanning. Consequently, about 30–50% of the Cr used in the tanning process leached into the environment [2]. Various water sources in developing countries are highly polluted with Cr(VI) [3]. In the water bodies of Ethiopian rift valley, for instance, in Koka, Ziway, and Awassa lakes and their major inflows, rivers and their inflows, and in effluents were shown to occur up to 0.269 mg/L [4–6] which is a value exceeding 0.05 mg/L, the maximum permissible level for drinking water set by the World Health Organization (WHO 2011).

Chromium is among the naturally occurring trace elements. It occurs in different valence states. Cr(VI) and Cr(III) being common in the natural environment. Cr(VI) is toxic due to its powerful oxidizing nature; it is even evidenced as being mutagenic and carcinogenic [7]. Alternatively, Cr(III) is important to maintain balanced glucose metabolism in humans and animals [8]. The existence of Cr in different oxidation states has a significant consequence on the transport and fate of Cr species, varying in their treatment capabilities and costs [9]. Considerable efforts, therefore, have been made to treat mostly Cr(VI) containing water/ wastewater.

Widely employed methods for Cr(VI) removal include chemical precipitation (primarily by reducing Cr(VI) to Cr(III)), ion exchange, membrane, and adsorption processes [10]. Moreover, it is often not feasible to apply high-tech membrane-based solutions in semi-urban and rural areas of developing countries [11–14]. Sludge production, cost unaffordability, and unpleasant tests are among the challenges encountered for most of the methods especially in developing countries. The main drawbacks for membrane separation processes, however, are membrane fouling, and cake layer formation on the membrane by the pollutants. Especially, the high organic content of tannery effluents leads to rapid scaling and biofouling of reverse osmosis membranes with a consequent reduction in flux rates and performance. Thermal processes which involve phase changes, such as membrane distillation and freezing processes, are frequently employed for the removal of soluble pollutants [15–17]. However, such thermal treatments are suffered from high treatment costs. Treating industrial wastewater by segregation of waste pools is a very important step in tannery pollution prevention. Application of freezing is a promising method if applied based on natural freezing process in cold regions. In such circumstances, energy is required only for ice melting and transportation.

Freeze desalination which involves three steps: ice formation, ice washing, and ice melting to obtain fresh water with subsequent removal of contaminants is an alternative physical process which can be used for desalting, based on the different freezing points of fresh and salt waters. It has been reported as being effective to remove various organic and inorganic contaminants from water/wastewater [18,19]. When freeze concentration is performed to purify water or liquid waste, impurities are separated from the ice phase during formation of the ice crystals. Two basic freeze desalination methods are available: suspension and progressive freeze crystallization. In both processes, inclusion of most compounds in the ice crystal lattice is impossible due to the small dimensions of ice crystal lattice. In progressive freeze crystallization, the separation of ice crystals formed from the concentrated mother liquor is much easier than in the conventional suspension crystallization, in which many small ice crystals are formed [17,20]. In the current study, we focused on indirect and progressive freeze desalination to assess the potential of home-use freezers to generate Cr(VI) free water.

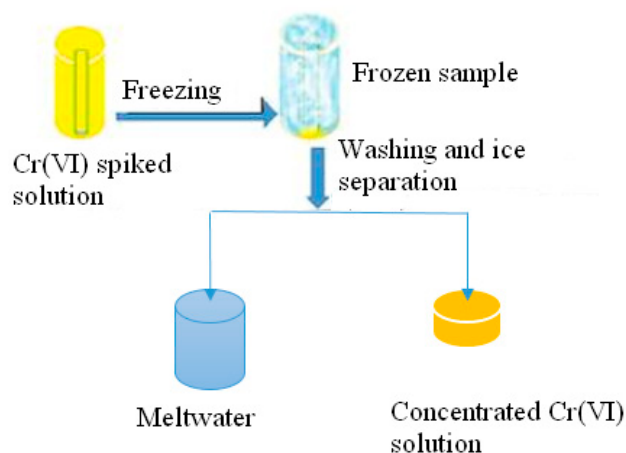
## 2. Materials and Methods

### 2.1. Reagents

A 1000 mg/L Cr(VI) were prepared from potassium dichromate (Riedel-de Haen, Seelze, Germany) in double-distilled water. Working solutions were prepared by diluting Cr(VI) stock solutions. 1000 mg/L Cr(VI) standard (Merck KGaA, Darmstadt, Germany) was employed for calibration by appropriate dilution. Series of standard solutions were prepared by pipetting suitable volumes of Cr(VI) using a Thermo Scientific FJ40512 Finnpiquette automatic dilutor. Fresh solutions were prepared prior to each experiment. Moreover, simulated tap water considering an example of drinking water specifications from AquaVital with major ions ( $\text{Ca}^{2+}$  58.64 mg/L,  $\text{Mg}^{2+}$  29.26 mg/L,  $\text{Na}^+$  92.67 mg/L,  $\text{K}^+$  20 mg/L,  $\text{HCO}_3^-$  470 mg/L, and  $\text{SO}_4^{2-}$  60 mg/L) spiked with 5 mg/L of Cr(VI) was prepared and tested.

## 2.2. Experimental Setup

Prior to the experiment, smooth plastic containers with volume 250 mL were selected to avoid entrainment of contaminants into the ice crystals. The influence of surface roughness of containers involved was previously described [21]. Concentration variations were studied in the range of 1 to 300 mg/L. To reject the concentrated Cr(VI), a plastic tube with ca. 20 mm diameter was inserted being upside down in each plastic beakers (Figure 1). After each different partial freezing steps (until freeze removal rate of 90%), three beakers were taken from the freezer and ice crystals were separated from the remaining water by rejecting the concentrated liquid. The whole procedure was repeated after different time intervals until only a small volume of (10–15% V/V) concentrated solution remained unfrozen. To desorb Cr(VI) weakly adsorbed into the ice crystal, the ice surface was washed three times by rinsing with small cold deionized water set at 278.15 K. Subsequently, the ice crystals were melted letting to room temperature and analyzed for Cr content using a colorimetric method. Thus, 250 mg chelating agent, 1,5-Diphenylcarbazide (BDH, Poole, UK), was dissolved in 50 mL acetone (Himedia, India) and stored in an amber bottle. The pH of samples was adjusted to  $2.0 \pm 0.5$  using 0.5 M sulfuric acid. Then, 2 mL of the diphenylcarbazide solution was added to each sample (100 mL) and the mixture was allowed to stand for 10 min. to obtain full color development. Absorbance was measured at 540 nm using a Janway 6051 colorimeter. Background correction was performed by analyzing blanks. Calcium, magnesium, potassium and sodium concentrations were measured in the melted ice using an inductively coupled plasma optical emission spectrometer (VISTA-MPX CCD, Varian, Palo Alto, CA, USA). Conductivity and pH were measured using conductivity meter (WTW LF 537) and pH meter ORION star A211, respectively.



**Figure 1.** Overview of the experimental setup with ca. 20 mm diameter plastic tubes being inserted upside down in plastic beakers containing Cr(VI) contaminated water.

The efficiency of freeze separation ( $\eta$ ) and removal rate were evaluated through Equations (1) & (2), respectively.

$$\eta = \left(1 - \frac{C_s V_s}{C_o V_o}\right) \times 100 \quad (1)$$

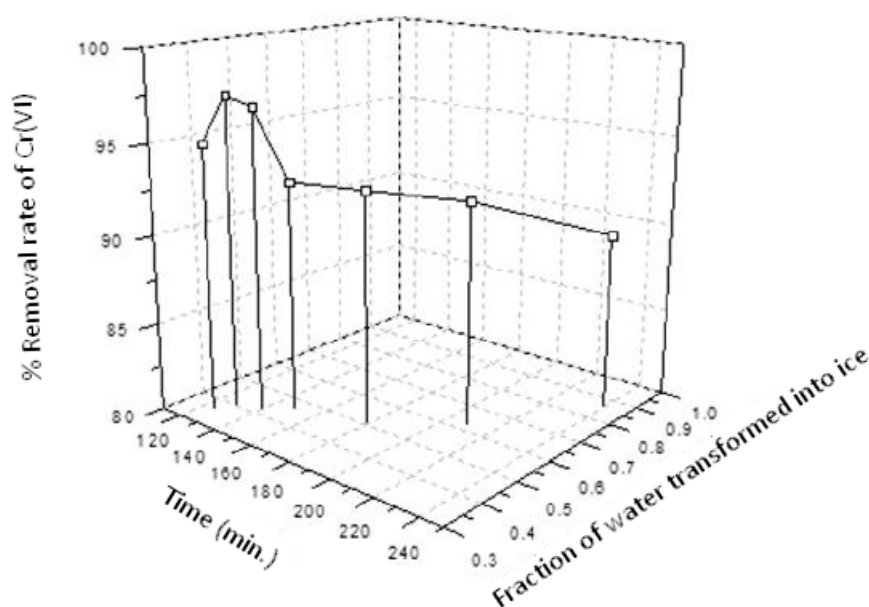
$$\%R = \left[\frac{C_o - C_s}{C_o}\right] \times 100 \quad (2)$$

where,  $C_o$  and  $C_s$  (mg/L) are the Cr concentrations in the initial feed solution and in the melted ice, respectively, and  $V_o$  initial volume of Cr(VI)-containing solution/simulated water,  $V_s$  volume of the solid phase (ice) after melting (mL).

### 3. Results and Discussion

#### 3.1. Deionized Water Spiked with Cr(VI)

It was presented in Figure 2 that, the removal of Cr(VI) from aqueous solutions of 5 mg/L Cr(VI) as function of freeze duration and fraction of water transformed into ice was illustrated. It could be concluded that initially the removal rate increased up to nearly 97% as the freezing time and volume of ice increased. About 40% meltwater recovery afterwards, the entrapment of Cr(VI) in the ice phase increased and the removal percentage started decreasing, making the separation of ice more difficult than before. Such trend has been observed for the removal of other soluble pollutants as well [22,23]. It was shown in literature that, as the residual liquid volume got too small, the removal efficiency decreased, due to the impossibility to maintain regular contact between the liquid and solid phases [24]. Long freeze duration results an entrained of impurities into ice crystals relative to the volume of the solution remained unfrozen [25]. That is, as the volume of liquid water remains relatively small, the solid-liquid interface became more labile and ice crystal forms dendrites with more advanced ice branches gradually [23].



**Figure 2.** Relation between the fraction of water transformed into ice (V/V), percent Cr(VI) removed and freeze duration (conditions: deionized water with spiked Cr(VI) at initial concentration of 5 mg/L & freeze temperature of 249.15 K, initial volume 250 mL) [26].

Experimental data and literature search results have shown that the surface roughness plays a very crucial role in the rate of ice nucleation. A preliminary experiment illustrated that the use of rough surface plastics resulted an enhanced inclusion of Cr(VI) into the ice crystals. The impact of surface roughness on the freeze duration was previously described [27]. The effective partition constant (K) in between the ice and liquid phases can be defined according to literature [28].

$$K = C_s/C_L \tag{3}$$

where  $C_s$  (mass %) and  $C_L$  (mass %) are chromium concentrations in ice and solution phases, respectively. The value of K is situated between 0 and 1, revealing meanings of no salts in solid phase and no freeze concentration, respectively. In observation of the mass balance, a small volume increase in the ice phase results in a small decrement of the volume of the solution phase ( $-dV_L$ ), whereas the concentration of the solute increases in the solution phase by  $dC_L$ . Assuming complete mixing in the solution phase and no mixing in the ice phase, the mass balance of solutes can be presented as follows [28]:

$$C_L V_L = -C_S dV_L + (C_L + dC_L)(V_L + dV_L) \tag{4}$$

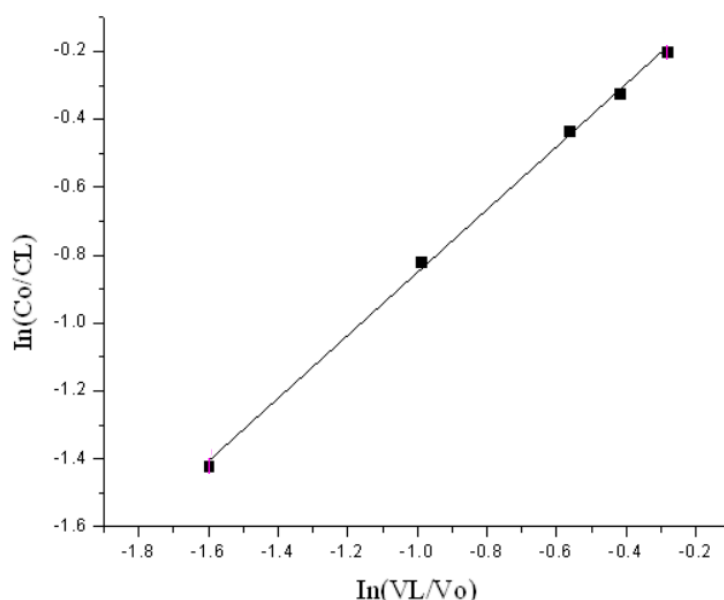
By substituting Equation (3) in Equation (4):

$$(dC_L + C_L/C_L)/(dV_L/V_L) = K - 1 \tag{5}$$

Integrating Equation (5):

$$(1 - K) \log(V_L/V_0) = \text{Log}(C_0/C_L) \tag{6}$$

where  $C_0$  (mass %) is the initial concentration of chromium (VI) before freezing,  $C_L$  (mass %) is the concentration of the concentrated residue, and  $V_0$  is the initial volume used. Figure 3 shows a linear plot of experimental data used to calculate the effective partition constant,  $K$ , for the progressive freeze desalination of aqueous solution spiked with 5 mg/L Cr(VI). Using Equation (6),  $K$ -value of 0.064 was obtained from the slope of the linear plot, which indicates the effectiveness of the progressive freeze concentration process.



**Figure 3.** Relationship between  $C_0/C_L$  and  $V_L/V_0$  when subjecting 5 mg/L Cr(VI) in deionized water to freeze desalination at a temperature of 249.15 K.

### 3.2. Validating Cr(VI) Removal from Simulated Tap Water

Drinking water contains several substances that can affect particular ion removal/water purification process. The removal of Cr(VI) from simulated water and aqueous solutions has been illustrated in Table 1. The influence of presence of dissolved ions for Cr(VI) removal by freeze desalination was also investigated. In the simulated tap water, the Cr(VI) removal efficiency was lower as compared to the removal efficiency in deionized water spiked with Cr(VI). In case of tap water, TDS played an inverse role in the Cr(V) removal efficiency. The effect of common ions existing in drinking water and inverse relation of TDS with ion removal was also observed for other soluble pollutants using freezing [23,29].

When evaluating the impact of Cr concentration on its removal from simulated tap water, a slight decrement was observed for a wide range of concentrations, up to 100 mg/L Cr(VI). However, at concentrations above 100 mg/L Cr(VI) in the system, an abrupt decrement on percent separation efficiency (Table 1) was observed. When the initial Cr(VI) concentration increased 100 mg/L Cr(VI) onwards, the solute concentration could remain even more concentrated near the ice-water interface, resulting more labile and ice crystal dendrites with more ice branches. The fact that the freezing process is relatively insensitive to a wide range of contaminants' concentrations were also observed

in literatures as an advantage of freeze desalination [20,22,29]. The removal of the ions involved in the experiment for simulated water decreased in the order:  $K^+ > Na^+ > Mg^{2+} \approx Ca^{2+}$ . Previously, Kang et al. (2014) [29] found similar results except that the removal of  $Na^+$  being nearly the same as the removal of divalent ions. It seems that the removal efficiency is related to the hydration free energy and the hydrated radius of the ions. Ions in water are found in hydrated forms which can be described as  $M^+(H_2O)_n$ , with  $n$  water molecules coordinated with the cation in a geometrically defined hydration shell. The size of hydrated ions (e.g.,  $Ca^{2+}$  0.82 nm,  $Mg^{2+}$  0.86 nm) was reported in literature [30]. The hydrated radius of ions varies depending on the coordination number of the ion acting as central ion. For instance, the hydrated radius of  $Mg^{2+}$  was shown to increase by about 25% if its coordination number increased from four to six. Besides the size exclusion properties of the ice crystals for larger sized ions, these ions with higher ionic radius bind with adjacent water molecules more weakly as compared to smaller size ones [31,32]. Hydration free energy shows the stability of the hydrated ions in reference to their unhydrated counterpart. The magnitude of hydration free energy for the studied ions is provided in the order:  $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ . Ions having a strong interaction with water molecules are more easily incorporated in the ice phase during freezing. Thus, ions with smaller energy of hydration have less association with water and hence high removal percentage [29,31,33]. As the surface charge density of the ions decreased from  $Na^+$  to  $K^+$ , ions with strongly hydrated ones (e.g.,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ) contributed to the stability of nearest water-oxygen binding [29] hence more accommodation of these ions into the ice phase relative to the weakly hydrated  $K^+$ , hence rejection of  $K^+$  found greater.

**Table 1.** Physicochemical properties of water tested (initial conditions) and melted ice [27].

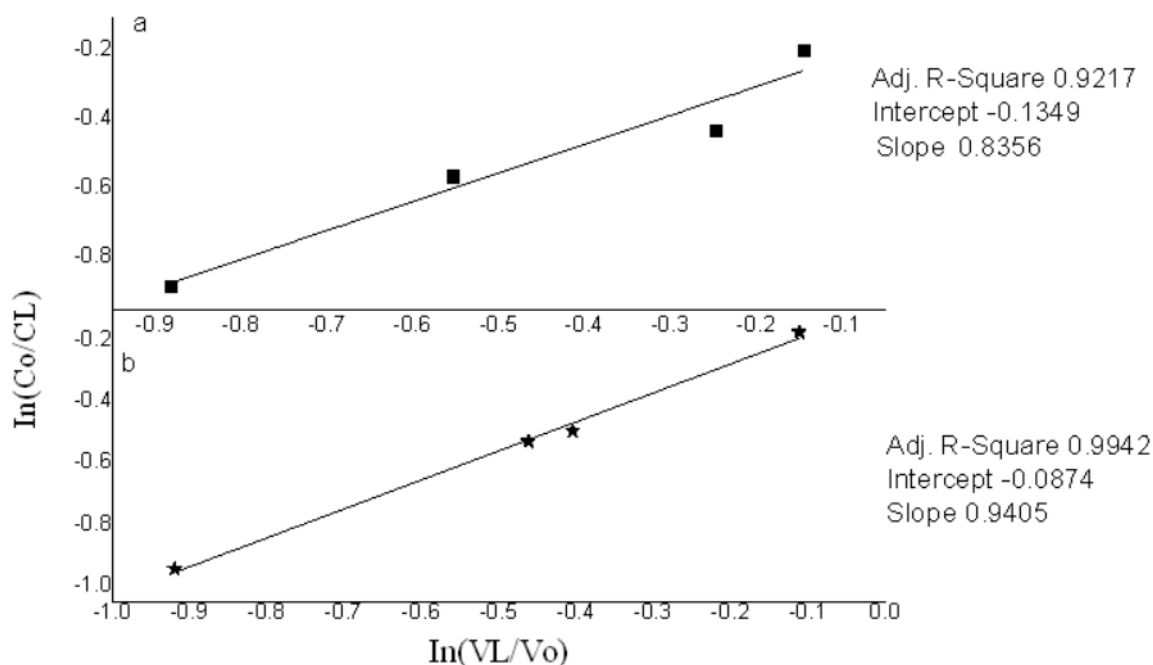
Parameters	Melted Ice obtained from Simulated tap water	Melted Ice obtained from frozen deionized water spiked with Cr	Simulated tap water	Deionized Water Spiked with Cr
Conductivity ( $\mu S/cm$ )	46.8	2.6	99.6	2.5
pH	7.4	6.5	7.9	6.4
DO (mg/L)	6.8	6.83	6.81	6.9
$Ca^{2+}$ (mg/L)	28.5		58.6	
$Mg^{2+}$ (mg/L)	14.4		29.3	
$Na^+$ (mg/L)	32.4		92.67	
$K^+$ (mg/L)	5.59		19.98	
	1.75	0.16	5	5
	3.54	0.41	10	10
$Cr^{+6}$ (mg/L)	14.1	1.28	40	40
	31.2	6.4	80	80
	41	9	100	100
	100	30.3	200	200
$HCO_3^-$ (mg/)	NM		470	
$SO_4^{2-}$ (mg/L)	NM		60	

Temperature 295.65 K during measurement of pH, conductivity and DO. NM = Not measured.

### 3.3. Effect of Sodium Chloride Application

The impact of presence of salt ions was evaluated in this freezing experiment by adding sodium chloride (250 mg/L  $Cl^-$ ) into deionized water containing 5 mg/L Cr(VI). The change in ice crystal morphology obscured the feasibilities of ice washing steps when NaCl was added relative to the solution of Cr(VI) spiked with deionized water alone. It has been also observed that the rate of ice formation, and inclusion of Cr(VI) into ice is higher for solutions containing Cr(VI) in the presence of sodium chloride salt as compared to solutions containing Cr(VI) alone (Figure 4a,b). The inclusion of impurities upon progressive freezing has been described by Halde (1980), who illustrated that variables such as freezing rate and added chemicals strongly affect the impurity migration. The possible existence of the salt as crystalline hydrates of  $NaCl \cdot 2H_2O$  at temperatures below 250.15 K as

well as the detection of solutes being more concentrated near the water-ice interface, enhancing depression of the freezing point temperature, could be reasons in the reduction of freeze removal of Cr(VI)[34,35].



**Figure 4.** Effect of chloride addition on Cr(VI) removal using freeze desalination at a temperature of 249.15 K: (a) deionized water spiked with 5 mg/L Cr(VI), (b) deionized water spiked with 5 mg/L Cr(VI), and 250 mg/L Cl<sup>-</sup>.

### 3.4. Energy Efficiency Views

The cost of desalination technologies depends mainly on the type of physical process (thermal or separation processes e.g., membrane process) involved, but also on other parameters such as plant capacity, feed water quality, pretreatment, plant condition, plant life, and investment assets. As a result, several strategies were proposed and are being implemented to improve the energy efficiency of desalination [15]. It is reported that the basic advantage of freeze desalination is the lower energy requirement compared to other thermal processes. For example, freeze desalination systems require six times lower energy to obtain 1 kg of fresh water compared to multi stage flash evaporation. Since compression work is a major cost parameter in freezing, renewable resources may be used to make the technology cost-efficient [36,37]. Furthermore, according to Attia (2010), the cost of freeze desalination using an auto-reversed R-22 vapor compression heat pump is 50% lower than most efficient methods reviewed previously [38]. Rice and Chau also elaborated the idea of using hydraulic refrigerant in freeze desalination plants, stating that freeze desalination is much more attractive than it has been in the past and should be reconsidered and compared with other means of desalination with regard to energy efficiency and other operating parameters [39]. Table 2 shows the total average costs and energy consumption of different desalination methods. Actual energy consumption using freezers is affected by several factors. For example, it depends on how the appliance is used and where it is located, temperature and others. Recently, the use of natural freezing, and waste energy applications such like LNG is showing freezing as promising future technology in water purification [25,40,41].

**Table 2.** Energy consumption and total average costs of large scale commercial desalination plants.

Methods	Total Energy kWh/m <sup>3</sup>	Total Average Costs	Remark	References
Thermal: Multistage flash evaporation (MSF)	10–16	1.0 \$/m <sup>3</sup>	Second largest installed desalting capacity in the world next to RO	[42]
Thermal: Multiple effect evaporation (ME)	5.5–9	about \$1.0/m <sup>3</sup>		[43]
Membrane processes: Reverse osmosis(RO)	6.95	less than \$0.5/m <sup>3</sup>	For seawater	[44,45]
Electrodialysis (ED)		less than \$1.0/m <sup>3</sup> about \$0.6/m <sup>3</sup>	For seawater For brackish water	[42]
Hybrid method: Coupling freezing and reverse osmosis (RO)	5.17		For seawater	[44]

#### 4. Conclusions

Our study confirmed that freeze separation process seems to have potential for Cr(VI) removal from water, revealing that water rejection was small and relatively efficient, producing 85% (V/V) of melted ice as desalted water when the removal rate was 90%. The freezing process revealed that Cr(VI) removal efficiency as high as 97% and 85% for deionized and simulated tap water spiked with 5 mg/L Cr(VI), respectively. However, technical challenges related to washing off the chromium adhered to the ice surface after freezing and separation of ice from water under real conditions outside the laboratory will need special attention when further developing the technology for practical use.

**Conflicts of Interest:** The authors declare no conflict of interest.

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