Applications of Freezing for the Removal of Cr(VI)

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1. Introduction

- About 748 million people across the globe are relied on unimproved drinking water sources (WHO 2014),
- Quality of drinking water is a big challenge due to: increased emerging pollutants including trace elements (Geissen et al. 2015)
- **Trace elements** are of public concern due to their variable effects
- E.g., As, Cd, and Cr

(Onda et al. 2012; Pan et al. 2015)

Cr contamination

- Chromium enter the water streams through:

– Leather tanning, metallurgy, electroplating, textile and pigment manufacturing, and wood preserving

e.g., wood preserving-Chromate Copper Arsenate (CCA)

- More than 90% of the leathers tanned globally, contain chromium, with 30–50% of the Cr used in the process leached

Naturally sources

- Soil parent material/processes of weathering and soil formation
- Natural inputs:
  - Aerial (volcanic and other dusts)
  - Flooding

Trace element contamination in Ethiopia

- Area of Ethiopia ~ 1.13 million Km^2
- Altitude: 120 m below sea level at the Danakil depression to 4,550 m above sea level, Ras Dashenin the NW highlands
- Deep river gorges
- Main Ethiopian Rift Valley, ca. **30%**
- 85% depends on agriculture

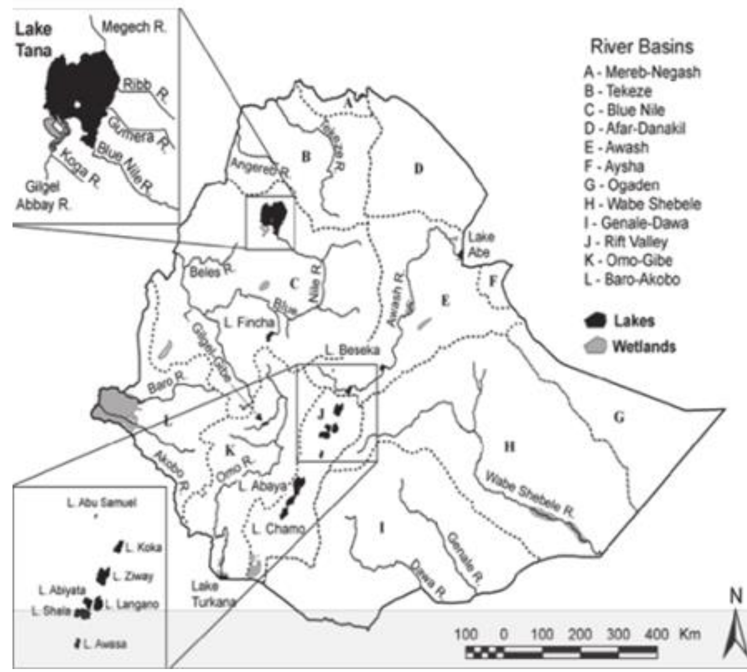


Fig.1.1 River Basins of Ethiopia and major rivers, lakes and wetlands (Moges *et al.*, 2010)

Trace elements: Ethiopia scenario

Fig. 1. 2 A snap shot of views of tannery wastes joining rivers (AMTV, 2015)

- Industrial effluents including trace metals are discharged with minimal or no treatments
- Illegal discharges of industrial wastes
- E.g., in MER area, in six rivers (their inflows), and in effluents from two factories, Cr reach 0.104-0.121 mg/L; up to 10 mg/L
- About 33 tannery industries with chrome tanning in Ethiopia
- 53.9 million cattle, 25.4 million sheep, 24.1 million goats

(Zinabu and Pearce, 2003; Haile, 2007; CSA, 2011, UNIDO2011b; Dsikowitzky et al., 2012; Mengistie et al. 2012016)

Fate of Cr in the environment

- Chromium exists in many different oxidation states
- Cr(VI) and Cr(III) being the most stable forms
- Cr(VI) exists in solution as monomeric species/ions:

  $H_2CrO_4^0$, $HCrO_4^{2-}$ (hydrogen chromate) and CrO_4^{2-} (chromate); or as the dimeric ion $Cr_2O_7$2- (dichromate)

Cr toxicity…

Lung cancer

- Cr(VI) enters cells via anion transporters
- Undergoes metabolic reductions forms Cr(V) and (IV) to form Cr(III)
- Cr(V) and Cr(IV) , and free radicals can bind with DNA and result in mutagenic effects
- Cr(III) affects DNA replication, causes mutagenesis, and alters the structure and activity of enzymes, reacting with their carboxyl and thiol groups

▪ The speciation of a metal is the key to understand the toxic effects

(Kelly, 1988; WHO 2003; Santos-Echeandía et al, 2008)

Desalination techniques

- Precipitation-Coagulation–filtration (with and without prior reduction)
  - Coagulant use
  - Suspension-posing secondary pollutant
- Adsorption
  - Not well commercialized
  - Adsorbent regeneration capacity or the disposal
- Ion exchange- restricted due to its higher cost

Desalination …

- Membrane technology is effective in removing both hexavalent and trivalent species of chromium
- High investment and operational costs
- Fouling of membrane

❖ Hybrid methods- like freezing-RO and adsorption-membrane showed promising in cost savings

Freeze desalination

- Freeze desalination is an alternative method, based on salt rejection from water during freezing.
- The small dimensions of the ice crystal lattice excludes the salt ions during partial freezing
- It is highly related to the hydration free energy and hydrated or ionic radius of the salt ions

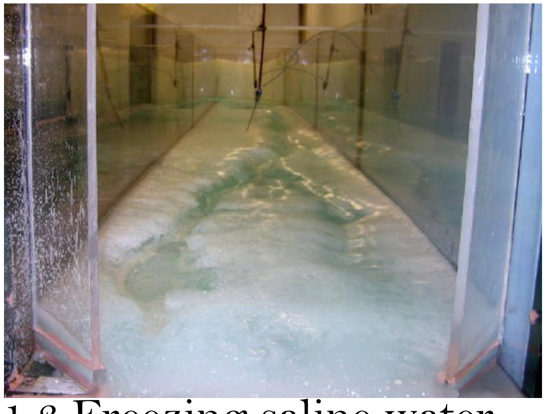
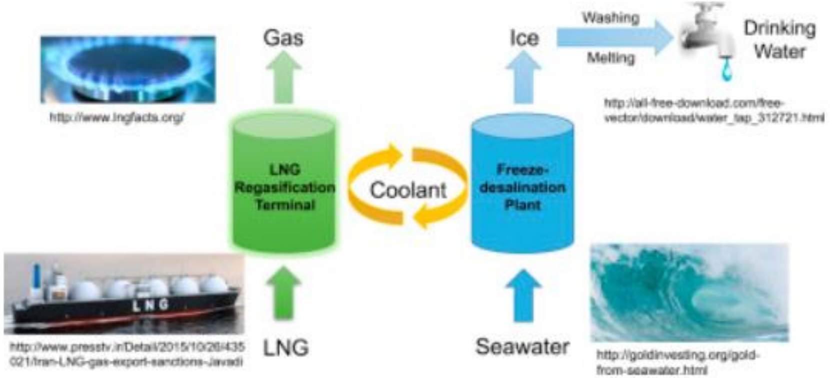


Fig. 1.3 Freezing saline water (Beier *et al.* 2006)

Freeze desalination

- Less scaling or fouling and corrosion problems
- The use of low cost and energy sources like cold energy, liquefied natural gas (LNG)
- Renewable refrigerant options
- Energy efficiency Vs distillation
- No additives of chemicals



(Miyazaki et al. 2000;Wang and Chung 2012; Chang et al 2016)

2. Materials and methods

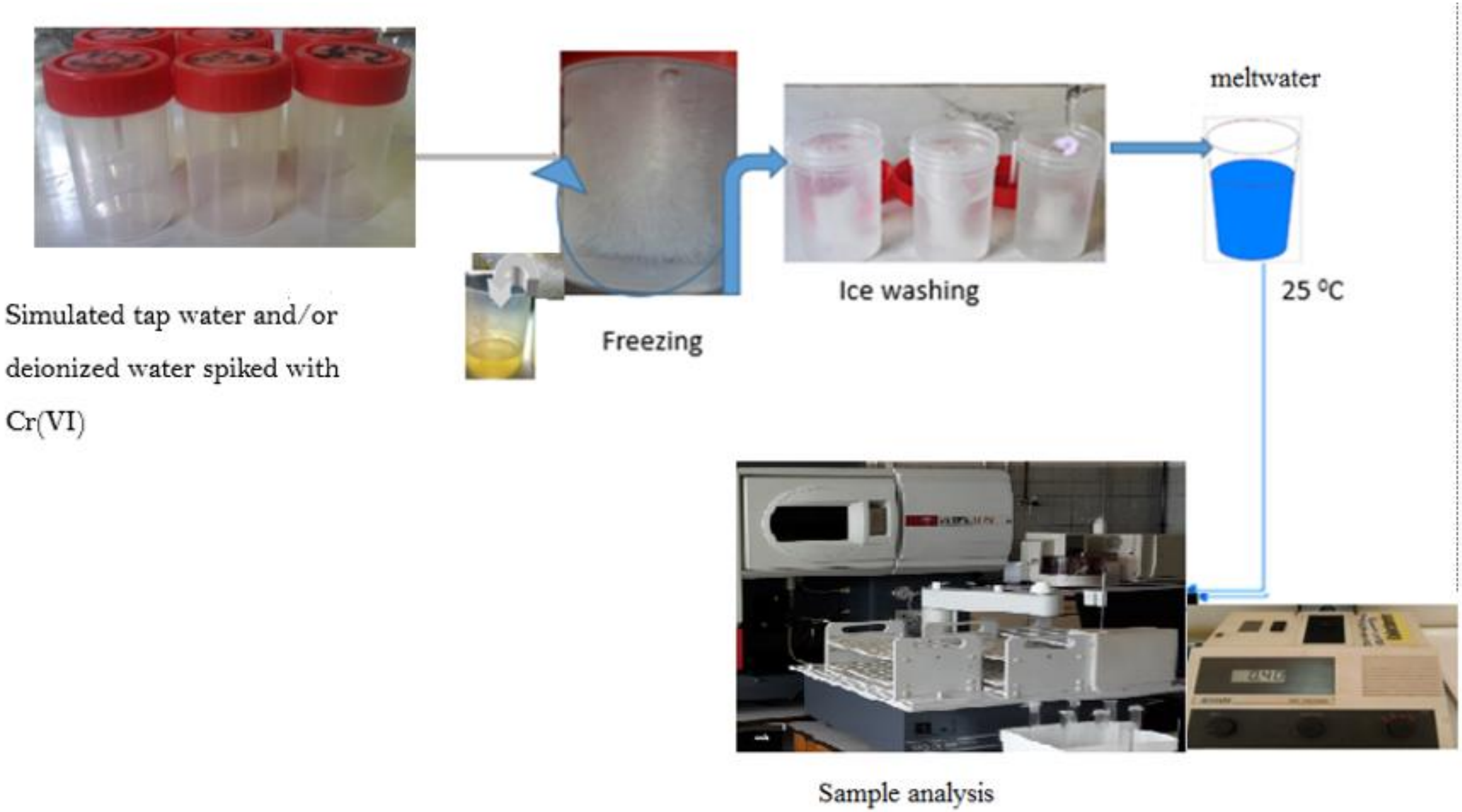


Fig 2.1 Batch experimental set up view for C(VI) freeze removal

Results and discussion

- Chromium removal efficiency

  ~ 93 to 97% removed form deionized water spiked 5 mg/L Cr(VI)

- Meltwater recovery ~85%
- As the freezing time and volume of ice increases
- The ice appearance changes sharply

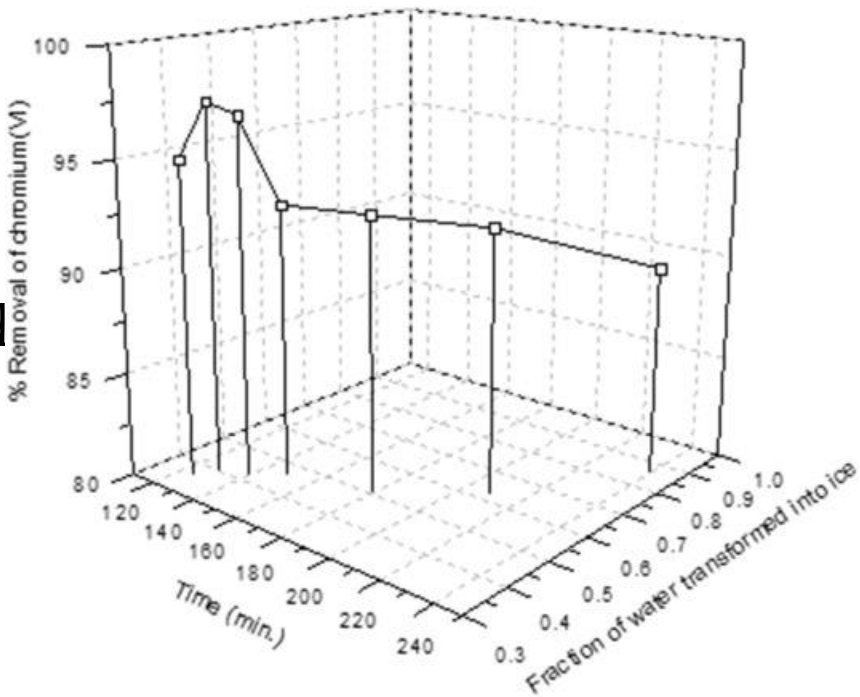
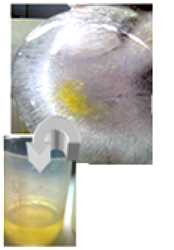


Fig.2.2 Relation between the fraction of water transformed into ice (V/V), percent Cr(VI) removed and freezing time (conditions: deionized water spiked with 5 mg/L Cr & freeze temperature of − 24 ± 2 °C, initial volume = 250 mL)



Freeze duration

- Cr(VI) compounds being colored –feasible for targeted washing
- The stability of ice at longer duration enhance the opportunity of washing effectively and rejection
- washing water has been overlooked in most of past studies

The effective partition constant (K):

$$K = C_S / C_L$$

where C_S and C_L are chromium concentrations in ice and solution phases,

Considering the mass balance it can be expressed by:

$$(1-K)\log(V_L/V_o) = 1og(C_o/C_L)$$

- K-value of 0.064 was calculated from the slope of the linear plot, which indicates the effectiveness of freeze concentration process

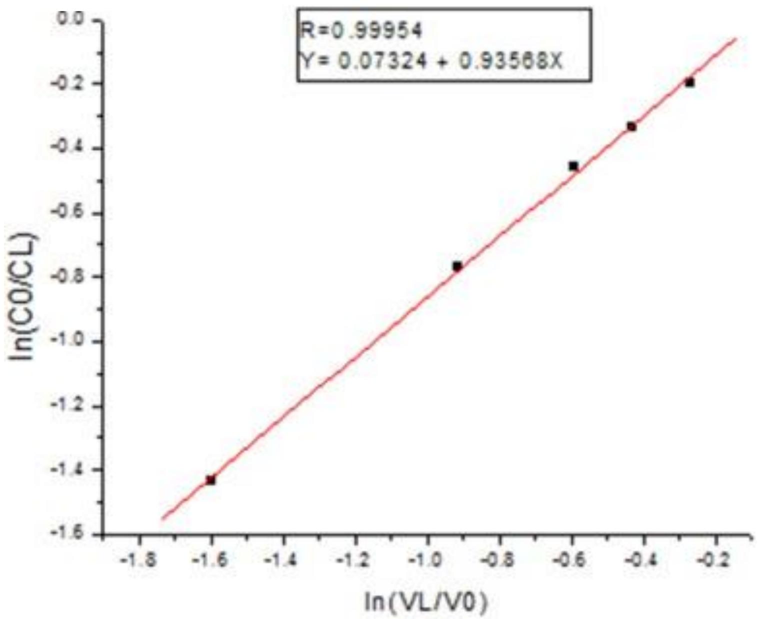
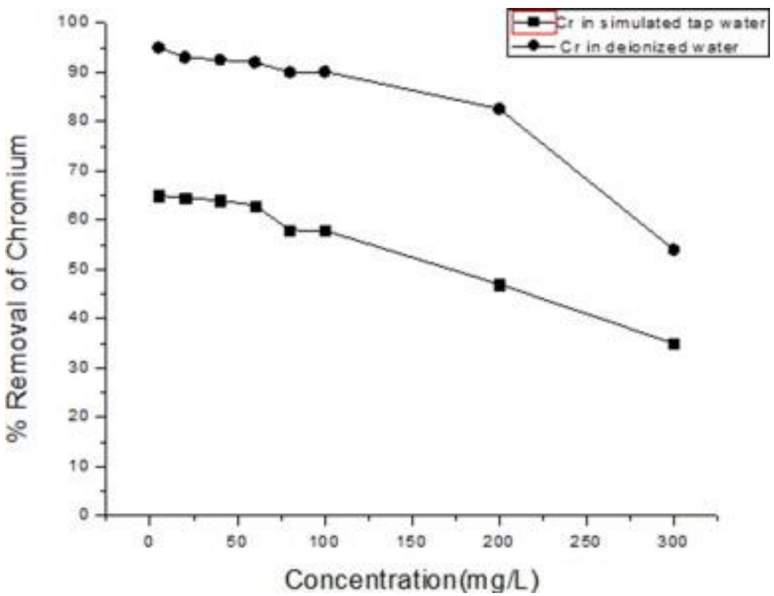


Fig. 2.3 Relationship between C0/CL and VL/V0 when subjecting 5 mg/L Cr(VI) in deionized water to freeze desalination at a temperature of − 24 ± 2 °C.

Effect of initial Cr(VI) concentration



Inclusion of solute in the ice occurred at high concentrations of solution relative to the volume involved

Fig. 2.4. Effect of initial Cr concentration on Cr removal (% separation) using aqueous solution and simulated tap water when applying freeze desalination at a temperature of − 24 ± 2 °C (initial volume = 250 mL).

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Effect of multi-ion system

Table 1.
Physicochemical properties of water tested (initial conditions) and melted ice.

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 (μS/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	
Cr^{+6} (mg/L)	1.75	0.16	5	5
HCO^{-}_{3} (mg/L)	NM		470	
SO_4^{2-} (mg/L)	NM		60	

Temperature 22.5 ± 0.4 °C during measurement of pH, conductivity and DO.

NM-Not measured

Effect of multi-ion system

- The removal of the ions for simulation water decreased in the order: $K^{+} > Na^{+} > Mg^{2+} \approx Ca^{2+}$
- Removal efficiency is related to the hydration free energy and the hydrated radius of the ions
- The magnitude of hydration free energy: $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$
- Ions having a strong interaction with water molecules are more easily incorporated in the ice phase during freezing

$\Delta T_f = i K_f m$

Effect of multi-ion system

- The size of ice pores can be varied in presence of many ions
- Ice could form an entire chunk if volume is very small and high ion concentrations
- Water does not freeze in the same manner when many ions are present-**freezing point depression**

(Tleimat 1980; Lorain et al. 2001)

Important aspects in Cr(VI) removal

- Feasibility in washing- due colored compounds of Cr(VI)
- The stability and nature of ice appearance as freeze duration increased
- Water rejected during freeze separation was small:

R(rejection, %)= $1 - \frac{Cm}{Co} X100$

Cm- meltwater

Co-initial sample solution

Conclusion

✓Separation of Cr(VI) using freezing is promising technique-foreseeing POU water treatment

✓Relatively efficient, 85% meltwater recovery from melted ice

✓Up to 97% removal efficiency of Cr(VI) for deionized water spiked with 5 mg/L Cr(VI)

✓85% removal for simulated tap water spiked with 5 mg/L Cr(VI)

❖ Technical challenges related to washing of the chromium adhered to the ice surface need special attention


Thank you