



Water purification of aqueous nickel sulfate solutions by air cooled natural freezing



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HIGHLIGHTS

- Natural freezing is a potential treatment method for wastewaters containing NiSO₄.
- Suitable to replace expensive methods to treat dilute solution of heavy metals.
- Ice purity is determined by growth rate and solution concentration.
- Solution inclusion within ice crystallites is the main source of ice impurity.
- Solution concentration and freezing condition control ice characteristics.

ARTICLE INFO

Article history:

Received 22 January 2016

Received in revised form 25 February 2016

Accepted 27 February 2016

Available online 3 March 2016

Keywords:

Freeze crystallization
Distribution coefficient
Ice growth rate
Ice purity
Heat transfer
Wastewater treatment

ABSTRACT

Ni²⁺ in excess of maximum recommended limits must be removed from wastewater prior to discharge because of its persistent bio-accumulative and detrimental nature. Natural freezing is suggested as a purification technique to treat huge volumes of wastewater containing Ni²⁺ in a sustainable and energy efficient manner. In order to evaluate the feasibility of such a technique for purification of wastewater, natural freezing was simulated experimentally for ice crystallization from different NiSO₄ (aq) solutions. The impact of solution concentration at different freezing conditions such as different ambient air temperature, freezing time and freezing rate on the efficiency of the purification process was investigated. Experimental results demonstrated that at the growth rate (*G*) of 3.5×10^{-8} m/s, the ice layer formed from 1 wt.% ($\approx 10,000$ ppm) NiSO₄ (aq) solution incorporated only 0.0038 wt.% (≈ 38 ppm) NiSO₄ as impurity, i.e., the ice is more than 250 times pure than the original salt solution. In the case of freezing of very dilute solutions, e.g., 0.1 wt.% NiSO₄ (aq) solution, which is the dilution level of practical interest, the same growth condition is likely to produce an ice layer of even higher purity. For example, at *G* of 7.4×10^{-8} m/s, the ice layer impurity that had formed from 0.1 wt.% NiSO₄ (aq) solution was only 0.001 wt.% (≈ 10 ppm). For this reason, this purification technique has potential for implementation on the surface of wastewater ponds in cold climate regions where the temperature drops below 0 °C. In addition, inclusion formation within the ice matrix during freezing was investigated for various solution concentrations both macroscopically and microscopically.

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1. Introduction

Lack of access and deterioration in water quality are major problems all over the world. Industrial discharge exacerbates water scarcity by polluting both the environment and water resources [1]. Mining and heavy industry produce substantial volumes of wastewater contaminated with heavy metal [2,3]. Release of wastewaters laden with heavy metals above thresholds defined

in worldwide environmental legislation is harmful to the environment and deleterious to both flora and fauna [4].

It is common to find nickel (II) ion in excess of maximum allowable limits in many wastewaters discharged from electroplating, electronics, metal cleaning and textile industry sites and such wastewaters can cause serious water pollution if not treated before release [2]. Nickel is responsible for a number of pathological effects and is implicated in several severe and long-lasting disorders such as damage to lungs and kidneys, gastrointestinal distress, pulmonary fibrosis, renal edema and skin dermatitis [5]. In view of its toxicity, strict permissible limits have been set, e.g., the limit for potable water is 0.02 mg/L [6].

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List of symbols

G	growth rate (m/s)	T_a	air temperature inside the freezer ($^{\circ}\text{C}/\text{K}$)
SLE	solid–liquid equilibrium	ΔT	degree of undercooling from solution's freezing point ($^{\circ}\text{C}/\text{K}$)
C_s	solute concentration in solid (ice) phase (wt.%)	t	freezing time (s)
C_b	solute concentration in the bulk solution (wt.%)	δ	boundary layer thickness (m)
C_i	solute concentration at the ice–solution interface (wt.%)	δ_T	thermal boundary layer (m)
C_0	concentration of initial solution to freeze (wt.%)	δ_C	concentration boundary layer (m)
K	effective distribution coefficient	R_F	freezing ratio (%)
K^*	limiting distribution coefficient	E	separation efficiency (%)
DMTM	differential mass transfer model	V_s	volume of solid (ice) phase after mixing (m^3)
FPD	freezing point depression ($^{\circ}\text{C}/\text{K}$)	V_0	volume of initial solution to freezing (m^3)
ρ	density (kg/m^3)	X	ice layer thickness (m)
ν	kinematic viscosity (m^2/s)	h_{sol}	heat transfer coefficient of solution ($\text{W}/\text{m}^2/\text{K}$)
D	diffusion coefficient (m^2/s)	h_{air}	heat transfer coefficient of air ($\text{W}/\text{m}^2/\text{K}$)
C_p	heat capacity ($\text{J}/\text{kg}/\text{K}$)	k_{ice}	thermal conductivity of ice ($\text{W}/\text{m}/\text{K}$)
k	thermal conductivity ($\text{W}/\text{m}/\text{K}$)	ΔH	latent heat of freezing of impure ice (J/kg)
T_f	Freezing point of the solution ($^{\circ}\text{C}/\text{K}$)	ΔH_f	latent heat of freezing of pure ice (J/kg)
T_b	temperature of the bulk solution ($^{\circ}\text{C}/\text{K}$)	U	overall heat transfer coefficient ($\text{W}/\text{m}^2/\text{K}$)

A number of conventional physical–chemical separation methods, such as ion exchange, adsorption, chemical precipitation, electrochemical treatment, evaporative recovery, pressure driven membrane filtration, etc. have been used in recent years to treat Ni^{2+} containing wastewater.

Application of chemical precipitation, adsorption and ion exchange technologies is limited to small-scale. Membrane process is highly energy intensive, prone to fouling and efficient only for dilute solution. Inefficient metal removal, low separation efficiency, high costs for chemical reagents, high-energy requirements and the production of high volumes of secondary wastewater are shortcomings of these technologies [2,7]. On the other hand, due to toxicity the presence of high concentration of Ni^{2+} in the effluents impedes the direct application of biological methods in the treatment of nickel-containing wastewaters [8]. Due to aforementioned reasons, none of these methods is suitable for treatment of dilute and voluminous wastewater. For instance in Finland mine water effluents are usually very dilute and annual effluent volume in some mines can be even up to 10 million tons. Therefore, this huge volume of wastewater needs to be treated in an energy efficient manner rather than using conventional methods.

Ice formation from aqueous solutions by freeze crystallization has a wide range of applications in solute concentration and wastewater purification processes [9]. Freeze crystallization can overcome some of the limitations associated with the above-mentioned technologies. The approach provides high product quality at good separation efficiency [10] and low energy requirements [11]. Of the two possible freeze crystallization methods, layer crystallization and suspension crystallization, the former is more advantageous in terms of ease of separation ability, based on density difference between the ice layer and residual solution [3].

Natural freezing can be used to treat wastewaters in ponds by ice crystallization in regions where ambient temperatures drop below 0°C during winter time. The use of natural freezing in wastewater treatment facilitates volume reduction by forming pure ice layer and thus concentrate pollutants in the residual wastewater.

This work introduces ice crystallization as a purification technique to treat NiSO_4 -laden wastewaters. Natural freezing was simulated experimentally for ice crystallization from unsaturated NiSO_4 (aq) solutions. The influence of solution concentration and different growth conditions on the efficiency of the purification process is also addressed in the present work.

Inclusion of concentrated solution within the ice layer during freezing is an important feature influencing the ice characteristics. With the exception of natural sea ice inclusion [12,13], the mechanisms of inclusion formation in the ice layer have not been studied extensively. From photomicrographs of sea ice, it is apparent that brine incorporates in the ice matrix as pockets [14,15]. The probable reason behind the difference in appearance and characteristics between sea ice and lake ice is the difference between the chemical compositions of water from these two sources [16]. Therefore, we also focus in this work on how the ice layer formed by freezing NiSO_4 (aq) solutions differs both macroscopically and microscopically with the variation of initial solution concentration.

2. Theoretical considerations

Ideal conditions for purification through freezing include (1) that the impurities do not form solid–solution with ice, (2) that the growth rate of ice layer is low enough to avoid occlusion of impurities, and (3) that the ice crystallites are large enough to minimize the amount of solution retained on their surfaces. For the attainment of any solid–liquid equilibrium (SLE), the chemical potential of the solvent must be equal between the liquid and solid phases [17]. During ice crystallization from a solution, redistribution of solute occurs and the extent of the redistribution is greatly influenced by the growth kinetics of the ice front and the ability of the solute to diffuse away from the ice–solution interface [18]. Usually, solute molecules/ions are unable to integrate into the ice crystal lattice owing to constraints imposed by their size/charge [16]. Thus, ions are mostly rejected by the progressing ice–solution interface.

The purity of the ice crystals formed from the solution relies on the growth rate of the ice crystallization [18]. At very low growth rates, only a very small portion of the solute gets incorporated into the ice layer and the major portion of the solute diffuses away from the advancing ice front into the bulk of the solution. Thus, the purity of the ice layer becomes very high and the remaining solution becomes solute – enriched. On the other hand, if the growth rate is too high for the solute to diffuse from the ice–solution interface, the solutes become entrapped in the ice layer, which eventually leads to impure ice crystals and no enrichment of the solution.

During freezing of the solution, the incorporation of solute in the crystal can be characterized by the redistribution of solute in

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