Experimental study of wastewater treatment containing sulfuric acid solutions using freezing and thawing method

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ABSTRACT

The aim of this work is to study an industrial wastewater treatment process using freezing. A synthetic solution of water/sulfuric acid was chosen as a simulated wastewater sample. Firstly, the solid–liquid equilibrium of the sulfuric acid/water binary system was studied to determine the range of concentration values and their corresponding temperatures that are suitable for freezing. Secondly, freezing tests were conducted to evaluate the effect of the freezing step on the separation performance of water and acid recovery. The total block flowed by fractionated thawing was shown to be an efficient method that allows a deep purification by a gradient temperature effect, thus removing the solute that incorporates into the ice during the prior freezing step. A statistical model of concentrated sulfuric acid and purified water was developed and used to find the most significant parameters on the process performance. The main parameters studied are the initial sulfuric acid concentration, the freezing temperature, and the thawed ice fraction. The results show that the freezing process performance depends on the concentration of the initial solution and fractionated thawing. However, the freezing temperature did not show any effect neither on the concentrated thawed solutions nor on the purity of the last fraction of melted ice. The higher concentrated fraction of sulfuric acid that could be reached was about 28.9%, it was obtained with an initial sulfuric acid concentration of about 20%. The highest purified fraction was about 0.045%, it was obtained with an initial sulfuric acid concentration of about 0.1%. Generally, the results confirmed the feasibility of the technique and gave a good idea about the operating conditions that can be used for the treatment of wastewater containing sulfuric acid.

Keywords: Acidic wastewater treatment; Sulfuric acid solutions; Freezing; Thawing; Experimental design

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1. Introduction

The drive for zero discharge plants is desirable nowadays and could become a mandatory requirement in the future; therefore the industries must operate under increasingly stringent ethical and legislative restrictions for the removal of harmful compounds. Note that these compounds could rather be used in suitable production or marketed after further purification. Wastewaters generated by the chemical industries cause problems because they contain hazardous substances. Such wastewaters can be classified according to their chemical composition and their pH in acid waters, alkaline waters, and neutral waters. Among these wastewaters types, acidic waters are those that require prior treatment before their disposal because they present a greater environmental risk compared to others.

Sulfuric acid is one of the most important chemicals, which has large-scale industrial uses, especially in the manufacturing of phosphoric acid. Many industries release significant volumes of waste sulfuric acid. For instance, the factories for the production of titanium dioxide (which are used especially in the manufacture of paints and surface coatings) generate eight tons of waste sulfuric acid (with a sulfuric acid concentration of about 20% by weight) per one ton of titanium dioxide [1]. The treatment and valorization of such wastewater are currently unavailable and thus imposes proper management. Until recently, the most traditional management approach of acidic solutions is neutralization. Such a technique does not produce sufficient volume and quality of water, thus it does not offer the selectivity necessary to create streams of precious products that can be recycled or reused. In addition, it has issues related to the high cost of alkaline compounds used and the sludge formation, which consequently requires another management. Several methods were proposed by researchers to recover sulfuric acid. The most established techniques are evaporation [2], and liquid–liquid extraction based on the use of solvents such as alcohols [3], methyl diphenyl phosphate [4] and tris(2-ethylhexyl)amine [5]. Despite the inexpensive and easy implementation of liquid–liquid extraction method, it has the disadvantages of being long,

difficult to automate, often consuming toxic solvent, and less effective for compounds with high polarities. As regard evaporation, the treatment of dilute acid solutions using this technology is energy-intensive and associated with corrosion issues. Kesieme et al. [6] have studied a new application of the direct contact membrane distillation process for the recovery of water and acid from acidic waste solutions generated in the mining industry, however, the use of this technology requires more energy consumption compared to conventional evaporators.

Freeze concentration is a particular type of cooling crystallization from solution or the melt, in which water is separated from the liquid by crystallizing ice at low temperatures. It is a solid–liquid separation process that can provide an efficient alternative process to recover sulfuric acid and produce pure water from dilute sulfuric acid waste. To assess the thermal energy consumption of wastewaters treatment, an overview of the different methods studied is summarized in Table 1. As shown, freezing is the least energy-consuming process compared to vaporization and membrane distillation, because it consumes less energy during the phase transition which makes the melting heat of the ice seven times lower than the vaporization heat of the water. In terms of energy consumption, 335 kJ/kg of heat is needed to freeze water while 2,248 and 2,495 kJ/kg is needed to evaporate water at 100°C and 0°C, respectively [15]. In addition, freezing causes less corrosion and scaling problems than evaporation and does not generate thermal discharges [16]. On other side, the general interest in water treatment by freezing opposite to membranes technologies such as nanofiltration [17], comes from the possibility of freezing to treat strongly acidic or basic solutions and to work in relatively wide concentration ranges and compositions of feed water.

Crystallization has shown its efficiency in several industrial applications, especially in agro-food industries [18]. The performance of crystallization was studied and its efficiency was established in the desalination of seawater and spent ion-exchange resin regeneration solutions [19–23]. The process was also applied in wastewater treatments to eliminate tetrahydrofuran and chromium (VI)

Table 1
Energy consumption of water treatment through different processes

Methods	Thermal energy consumed (kWh/m^3)	Type of water	References
Multi-effect distillation	60	Water desalination	[7]
Membrane distillation	100	Sulfuric acid solutions	[6]
Integration of the falling film technique, fractional thawing and block freezing	10.3	Sucrose solutions	[8]
	11.5	Saline solutions	[9]
	23.33	Coffee and orange juice	[10]
Cryoconcentration	21.3	Wastewater treatment	[11]
HybridICE technology	21–29	Brine solutions	[12]
Hybrid method: coupling freezing and reverse osmosis	5.171	Seawater	[13]
Freeze concentration system with tubular heat exchanger	9–11	Seawater	[14]

Table 2
Variables and responses for the experimental design obtained using Minitab software [45,46]

	Run	C_0 (wt.%)	T (°C)	$F1$ (%)	C_{F1} (wt.%)	Standard deviation	IF3 (%)	C_{IF3} (wt.%)	Standard deviation
Experimental design	1	0.10	−16	10	0.59	0.01	20	0.05	0.01
	2	20.00	−16	10	28.64	0.41	20	10.50	0.06
	3	0.10	−24	10	0.61	0.03	20	0.05	0.01
	4	20.00	−24	10	28.91	0.31	20	10.39	0.11
	5	0.10	−16	30	0.25	0.02	40	0.08	0.01
	6	20.00	−16	30	25.45	0.20	40	16.04	0.28
	7	0.10	−24	30	0.25	0.01	40	0.08	0.02
	8	20.00	−24	30	25.69	0.22	40	15.40	0.17
	9	0.10	−20	20	0.38	0.02	30	0.07	0.02
	10	20.00	−20	20	26.91	0.27	30	13.58	0.16
	11	10.05	−16	20	16.85	0.23	30	3.63	0.19
	12	10.05	−24	20	16.28	0.25	30	3.79	0.29
	13	10.05	−20	10	19.79	0.27	20	2.20	0.14
	14	10.05	−20	30	15.12	0.36	40	4.93	0.30
Repetition at the center of the domain	15	10.05	−20	20	16.47	0.23	30	3.34	0.11
	16	10.05	−20	20	16.58	0.15	30	3.52	0.22
	17	10.05	−20	20	16.63	0.25	30	3.75	0.12
Check point	18	5.00	−20	10	11.52	**	20	5.48	**
	19	5.00	−20	20	9.08	**	30	7.55	**
	20	5.00	−20	30	8.94	**	40	9.32	**
	21	15.00	−20	10	24.82	**	20	5.10	**
	22	15.00	−20	20	22.33	**	30	7.21	**
	23	15.00	−20	30	21.41	**	40	9.18	**

[24,25], to remove pharmaceutically active compounds [26], to treat acetone solutions, electroplating wastewater, organic compounds wastewater coming from cutting oil waste, and urban wastewater plant [27–29] and to recover sulfate [30]. However, the technology has never been applied at a commercial scale, because of higher fixed investment capital costs and higher operating costs for the ice separation step. Considering the progress of current research on renewable energy sources, the efficiency/cost ratio of freezing could be improved by integrating it to liquefied natural gas cold energy [31] or the use of hybrid techniques by coupling freezing and membranes desalination processes [13]. By the use of combining freezing and membrane desalination processes, approximately 25% of the energy consumed could be saved when compared to conventional reverse osmosis desalination [13]. Rane and Padiya [14] suggested a freeze concentration system for seawater desalination using a heat pump system. The energy consumption was expected to consume 9 to 11 kWh/m³.

Freeze concentration can be carried out either by direct or indirect freezing. In the direct contact system, the solution is in direct contact with the refrigerant used to reduce the temperature. The refrigerant in the liquid form under pressure is expanded and vaporized at low pressure to produce a cooling effect. The indirect process: in which the cooling is operated by mobilizing the refrigerant through the walls of some form of heat exchangers, it can be classified into three groups: suspension, block freezing, and progressive freeze concentration. Block freezing can be classified into two kinds, partial and total block. In the partial block, the sample is partially frozen and the unfrozen liquid is recovered after a previously defined time. Treatment by total block freezing is operated in two steps; the first one consists to cool the feed water in a cold room until germination and solidification of the water present in the solution. During this step, a degree of supersaturation exceeding the limit saturation must be achieved to obtain the first crystalline seeds. The second step consists to separate the solid–liquid phases by thawing the ice layer in different fractions in order to melt the impure zones trapped into the ice during freezing. This technique does not require seeding or washing and other unit operations [32], it was chosen for its simplicity and its high efficiency compared to the suspension method.

In this paper, industrial wastewater treatment by freezing and thawing process was studied. The aim is to assess the influence of freezing parameters in order to obtain pure ice and concentrated sulfuric acid. The influence of initial concentration, freezing temperature, and thawing fraction was evaluated.

2. Experimental methods

2.1. Thermodynamic study of the solid–liquid equilibrium

The determination of the solid/liquid equilibrium of the sulfuric acid/water binary system is important to determine the operating conditions of the freezing process in

terms of concentrations and temperatures. In this study, the solid/liquid equilibrium was determined experimentally using a method of cryoscopy [33,34].

Fig. 1 shows the description of the experimental apparatus used to determine the solid/liquid equilibrium of synthetic solutions. The apparatus of cryoscopy used in this study is from PHIWE. It consists of two cylindrical glass vessels of DURAN glass, one of which fits in the other and is held in position in it by a GL 45 screw-top connector. The inner cylindrical glass vessel has a capacity of 60 mL, a flat bottom to accommodate magnetic stirrer bars, and a lateral inlet for the introduction of the substance to be tested. The outer jacket glass was filled with 35–40 mL of ethyl alcohol in order to ensure a uniform heat transport from the inner vessel to the freezing mixture. The set of two cylindrical tubes was plunged inside a 1,000 mL glass beaker filled with an appropriate freezing mixture of crushed ice and sodium chloride in order to reach temperatures close to –22°C. The whole equipment was placed under agitation using magnetic stirrer with heater MR Hei-Standard. The measure of the temperature inside the inner cylindrical glass vessels and in the cooling bath was performed by two temperature probes immersion type Pt100 (5) connected to a data acquisition system (6) (temperature meter digital, 4–2).

1. Cylindrical crystallizer
2. Magnetic stirrer
3. Jacketed vessel
4. Cooling bath
5. Thermocouple
6. Data aquisition system
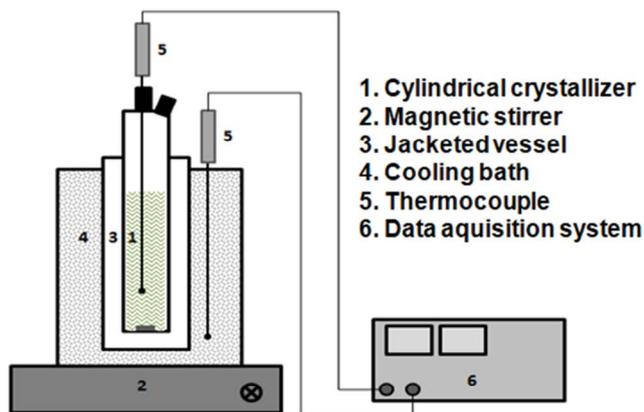
Fig. 1. Experimental setup used for the study of the solid–liquid equilibrium.

The experimental study of the solid–liquid equilibrium was carried out for the synthetic H_2SO_4–H_2O system in concentrations ranging from 0.1% to 25% of H_2SO_4 and the temperatures range between 272.64 and 252.15 K. The sulfuric acid used (97%) was provided by Sigma-Aldrich (82024 Taufkirchen, Germany).

The procedure of the solid–liquid equilibrium consists of introducing a solution of known composition into the inner cylindrical crystallizer. The solution is slightly cooled until the appearance of the solid. The temperature of the solution is then monitored over time.

2.2. Experimental procedure of total block freezing

The process of total block freezing was carried out with solutions of initial concentration ranging between 0.1 and 20 wt.% of H_2SO_4. The solutions were placed into cylindrical containers filled with 0.2 L. The process was conducted in two steps: the first one consists of cooling the solutions in a cold room until producing an ice block. The cold room used in this study is from Robert Bosch Hausgeräte GmbH (81739 München, Germany) (E-Nr (KGN36VL21/17)) with a cooling capacity of 14 kg/24 h. The second step consists of thawing the ice block; it was carried out by partial melting of the ice block at room temperature (25°C). This step consists of purifying in depth the ice block by melting the impure areas and draining the solute. As illustrated in Fig. 2, three levels of fractionated thawing were operated.

The different solutions collected after fractionated thawing are weighed. These concentrations were determined by conductivity and by measuring the melting temperature. The relationship between the concentration and the melting temperature is presented in the section of the solid–liquid equilibrium of the H_2SO_4–H_2O binary system. The structure of the ice was observed using an optical microscope from Olympus with a magnification of ×11.

The conductivity (σ) was measured using a portable conductivity meter (HANNA edgeEC, HANNA Instruments Woonsocket RI USA). The relationship between the conductivity and the concentration C_0^{i0} is presented by Eqs. (1) and (2). The correlations coefficients of by Eqs. (1) and (2) are 0.998 and 0.993, respectively.

$$C_0^1 (\text{wt.\%}) = 6 \times 10^{-9} \times \sigma^4 + 7 \times 10^{-6} \times \sigma^3 + 5 \times 10^{-4} \times \sigma^3 + 9.1 \times 10^{-3} \times \sigma^3 + 0.004, \quad \text{For } 0 < C_0^1 < 1\% \tag{1}$$
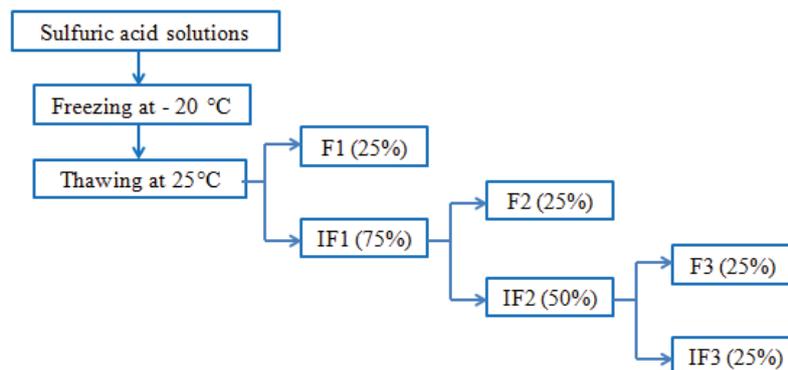
Fig. 2. Schematic layout of block freezing process.

$$C_0^2 (\text{wt.\%}) = 10^{-6} \times \sigma^2 + 0.0192 \times \sigma, \quad \text{For } 1 \leq C_0^2 \leq 25\% \quad (2)$$

where C_0^1 and C_0^2 are the concentrations of H_2SO_4 in weight percent (wt.%) and σ is the conductivity in mS cm^{-1}.

2.3. Calculation of block freezing parameters

2.3.1. Thawing fraction (F).

The thawing fraction was defined as the ratio between the thawed volume and the volume of the initial solution, as indicated in Eq. (3):

$$F = \frac{V_{\text{liq}}}{V_0} \times 100 \quad (3)$$

where F is the thawing fraction, V_{liq} is the volume in milliliters of the liquid fraction, and V_0 is the initial volume in milliliters.

2.3.2. Concentration index (CI)

The concentration index was calculated as the ratio between the concentration of the recovered liquid fraction and the concentration of the initial solution [10,32].

$$CI = \frac{C_{\text{liq}}}{C_0} \quad (4)$$

where CI is the concentration index, C_{liq} is the weight percent (wt.%) of H_2SO_4 in the recovered liquid fraction and C_0 is the initial weight percent (wt.%) of H_2SO_4.

2.3.3. Removal efficiency (RE)

The removal efficiency can be considered as the ratio between the concentration of sulfuric acid entrapped in the solid phase and the total concentration of the acid in the initial solution as written in Eq. (5) [9,32,35].

$$RE = \left(1 - \frac{C_{\text{ice}}}{C_0}\right) \times 100 \quad (5)$$

where RE is the removal efficiency, C_{ice} is the weight percent (wt.%) of H_2SO_4 in the ice fraction and C_0 is the initial weight percent (wt.%) of H_2SO_4.

2.4. Statistical analysis

Statistical analysis was performed to quantify the role of the process variables on the concentration of sulfuric acid (C_{F1}) and ice purity (C_{IF3}). The main variables studied in this work were the initial solute concentration (C_0), the freezing temperature (T), and the thawed ice fraction (F). The statistical design was applied using a statistical software MINITAB version 18. The experimental design is given in Table 2.

The total number of design points needed (N) is determined by the formula $N = 2^k + 2k + S_0$, where k is the number of variables and S_0 is the number of center points. The experiences were repeated three times for a total of 54 runs. Each

variable has a low and high level, respectively –1 and +1. The low and high factor values chosen for this study were selected according to the preliminary experiments studied in section 3.2 and in the operating range covered by the variable. The initial concentration (C_0) was taken by weight between 0.1 and 20 wt.%, the temperature (T) between –16°C and –20°C and the thawed ice fraction (F) between 10% and 30% for C_{F1} and between 20% and 40% for C_{IF3}.

3. Results and discussion

3.1. Solid–liquid equilibrium of H_2SO_4–H_2O binary system

The experimental solid–liquid equilibrium study was performed using synthetic methods. Fig. 3 presents the comparison between the solid–liquid equilibrium temperatures obtained experimentally and the literature data [36]. We observed that the freezing temperatures obtained experimentally and the literature data are in good agreement. The average absolute deviation is 0.25 K; the average relative error is 0.15% compared to the data of Gable et al. [36]. The study of the solid–liquid equilibrium showed that there is an equilibrium between the ice and sulfuric acid solutions in a domain of concentration from 0.1 to 20 wt.%. The corresponding temperature range is between 272.64 and 252.15 K. This range of concentration and temperature shows the technical feasibility of treating sulfuric acid solutions by the freezing method. In this range of temperature and concentration, the experimental results can be expressed by the following equation.

$$T_{\text{eq}}(K) = -0.0224 C_{\text{sa}}^2 - 0.2733 C_{\text{sa}} + 273.15 \quad (6)$$

where C_{sa} is the weight percent (wt.%) of each sulfuric acid solution.

3.2. Wastewater treatment containing sulfuric acid solutions by freezing and thawing

3.2.1. Kinetic study of the freezing step

The freeze duration is defined as the required time to obtain an ice block; it varies according to the solution concentration. This parameter influences the kinetics of freezing because it is related to the growth rate of the ice and the cooling rate. Therefore it influences the purity of the growing ice in the solid phase and also the solute concentration in the liquid phase. In order to study the effect of the freeze duration on the freezing process, the different synthetic sulfuric acid solutions prepared in the range of concentration between 0.1% and 20% were frozen at constant temperature (–20°C). The process of separation by freezing for different aqueous solutions of sulfuric acid and mass fraction of melted ice as a function of freeze duration is given in Fig. 4. When the freezing time increased the ice mass increased, however, the increase of ice mass allows the increase of the recovered liquid concentration because the partial freezing of the solution causes acid particle rejection [37]. From an initial concentration of 0.1 and 10 wt.%, the total ice freezing was reached within 8 h. However, for an initial concentration of 20 wt.%, only 73% of water was solidified during 24 h of freezing. In this case, in order to
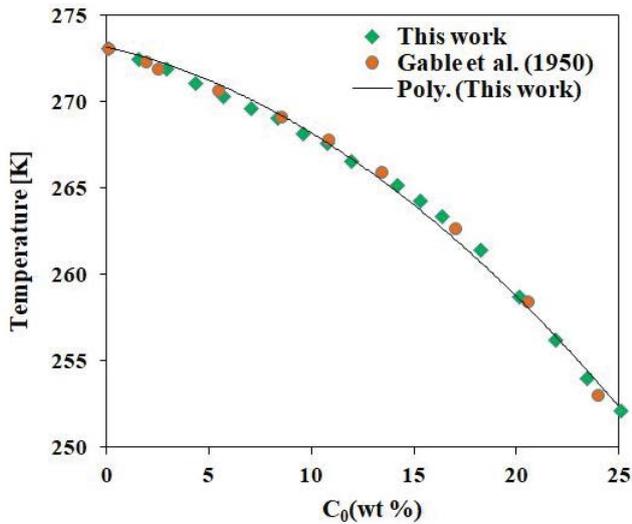
Fig. 3. Comparison between the solid–liquid equilibrium temperatures of sulfuric acid obtained experimentally and the literature data.
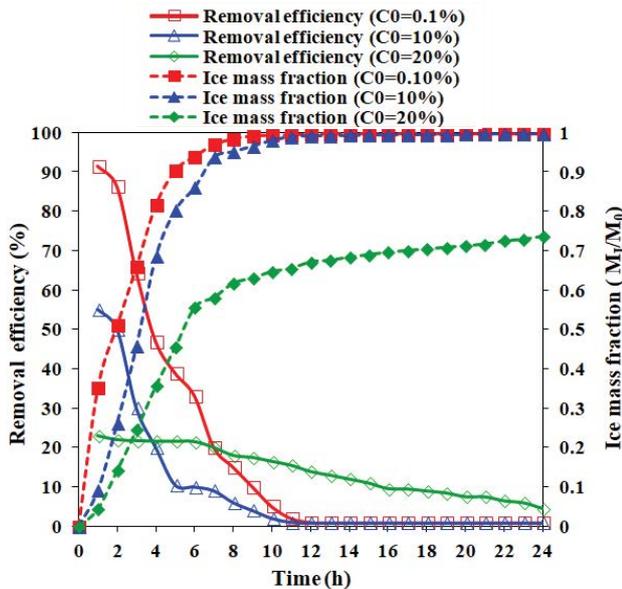
Fig. 4. Kinetic study of the effect of the freezing step on the sulfuric acid removal efficiency and the fraction of the ice produced from initial concentrations of sulfuric acid solutions of 0.1, 10, and 20 wt.%. The cooling temperature of the samples was applied at –20°C.

produce a large quantity of ice in less than 24 h, it is necessary to decrease the freezing temperature below –20°C.

It was shown that almost 91%, 55%, 23% of removal efficiency within 1 h of freezing was achieved from initial concentrations of 0.1, 10, and 20 wt.%, respectively. For these same initial concentrations, the efficiency was decreased until reaching 15%, 6%, and 18% within 8 h of freezing, respectively. A longer freezing time revealed the inclusion of high sulfuric acid contents in the ice produced. We can explain this behavior by the growth of the ice layers

which nearly filled the entire space inside the cylindrical container and by the saturation of solute in the remaining liquid after 1 h of the freezing process. Similarly, this behavior has been previously demonstrated by Jusoh et al. [38] and Chen et al. [39]; the authors have clearly stated that a high amount of solutes in the concentrated solution can easily be trapped in ice layers when the freezing process is longer. In contrast, several studies have demonstrated that the change in the growth mechanism leads directly to a change in the process of inclusions [20,40]. Indeed, a high growth rate or a high cooling rate results in a rapid cooling period which increases the incorporation rate of the solute into the ice under the form of solution pockets. As demonstrated by Rich et al. [20], using a dynamic layer pilot crystallizer, the incorporations of solutes in the ice depending on the high cooling rate which contrasts with our study. This contrast can be explained by the difference between the dynamic and the static freezing method and by the thermodynamic properties of the treated solution.

Including the duration effect, the incorporations of the solute in the ice can strongly be influenced by other parameters such as the container angle used and surface roughness [12,41].

3.2.2. Study of the thawing step

The different synthetic sulfuric acid solutions prepared in the range of concentrations between 0.1 and 20 wt.% were frozen at –20°C. The fractionated thawing step was operated by melting partially the ice in four equal fractions. As illustrated in Fig. 2, three levels were performed, in each level, 25% of the initial volume was thawed and analyzed. Three thawed fractions ($F1$, $F2$, and $F3$) were obtained and the final ice fraction is under the name IF3. The evolution of the sulfuric acid concentration of the different thawed fractions according to the initial concentration is presented in Fig. 5. In general, the highest concentrations were obtained for the first thawed fractions ($F1$ and $F2$) compared to the initial sulfuric acid concentrations. Furthermore, the fractions $F3$ and IF3 are the least concentrated. Similar results were obtained for the treatment of food products [10]. The concentration in weight percent (wt.%) of each liquid fraction obtained after the thawing stage (C_{F1}, C_{F2}, C_{F3}, C_{IF3}) can be predicted according to initial sulfuric acid concentration (C_0) by the polynomial Eqs. (7)–(10).

$$C_{F1}(\text{wt.\%}) = 0.0027\,C_0^3 - 0.1035\,C_0^2 + 2.3233\,C_0 \quad R^2 = 0.9998 \quad (7)$$

$$C_{F2}(\text{wt.\%}) = -0.0022\,C_0^3 + 0.0651\,C_0^2 + 0.8472\,C_0 \quad R^2 = 0.9979 \quad (8)$$

$$C_{F3}(\text{wt.\%}) = 0.0011\,C_0^3 + 0.0045\,C_0^2 + 0.6214\,C_0 \quad R^2 = 0.9989 \quad (9)$$

$$C_{IF3}(\text{wt.\%}) = 0.002\,C_0^3 - 0.0217\,C_0^2 + 0.2899\,C_0 \quad R^2 = 0.9977 \quad (10)$$

The concentration index (CI) defined in Eq. (3), was calculated to evaluate the thawing process (Fig. 6). When C_0 increases, the CI of the fractions $F2$, $F3$, and IF3 increase. The values of CI > 1 represent the more concentrated thawed fractions and the values of CI < 1 represent the purified thawed fractions. The values at which CI crosses
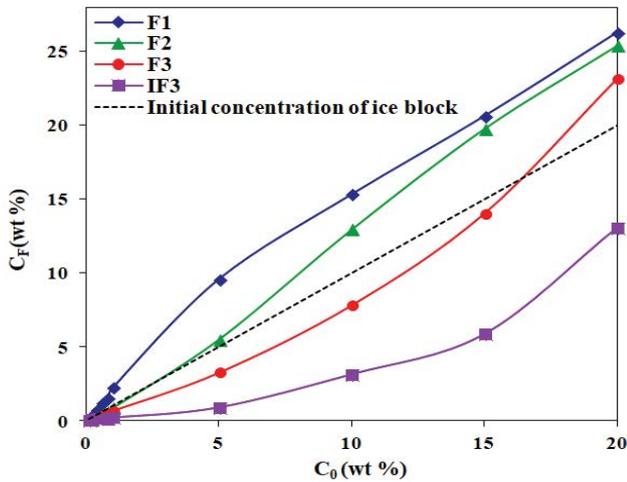
Fig. 5. Sulfuric acid concentration obtained in the different thawed fractions (*F*1, *F*2, *F*3, IF3) for initial concentration of sulfuric acid solutions varied between 0.1 and 20 wt.%.
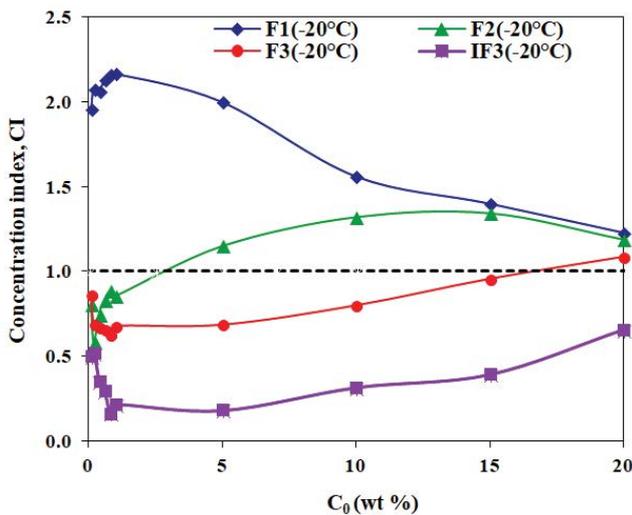
Fig. 6. Concentration index obtained in the different thawed fractions (*F*1, *F*2, *F*3, IF3) for initial concentration of sulfuric acid solutions varied between 0.1 and 20 wt.%.

the horizontal line of CI = 1 correspond to the moment at which the thawing process must be completed to avoid the dilution of the sample and to recover the maximum yield of concentrated sulfuric acid. In our study, the obtained results indicate that the most concentrated solutions were recovered in the first fraction (*F*1). In contrast, the concentration index of the IF3 has a value lower than the standard value CI = 1. The concentration index values of the two fractions *F*2 and *F*3 are near to 1, in this case, it would be preferable to treat their mixture a second time by the block freezing process in order to recover the maximum yield of the acid. By referring to previous work, the greater sulfuric acid concentration in the first fraction can be explained by the supercooling effect [42]. Such a phenomenon allows rapid crystallization of the first layer of the ice; consequently, sulfuric acid was trapped in this ice layer which

was the first thawed. On other hand, the IF3 was the purest because of the low growth rate of the ice in the center of the container which was due to the delay of the formation and thawing of the ice center. As suggested by Glen [43], a lower freezing rate allows the development of ice crystals in the form of a layer with a flat solid–liquid interface which improves the purity of the ice. For initial concentration less than 15 wt.% of sulfuric acid, the concentration index of the first thawed fraction varies between 1.6 and 2.2. The concentration index was decreased until reaching a value of 1.28 for the initial concentration of 20 wt.%. These results indicate that the occlusion of sulfuric acid in the outer layer of the ice increases with the initial concentration.

The efficiency of the acid separation during the fractionated thawing process was evaluated (Fig. 7). For the initial concentration between 0.1 and 1 wt.%, respectively only about 13.35% and 37.66% of amount acid were recovered during the first thawed fraction. For the same range of initial concentrations, the elimination of the last separation is 50% and 74%, respectively. The final elimination was not complete because during the formation of the ice block, the solute was trapped in the ice in the form of bags or grain boundaries. Fig. 8a illustrates the ice crystal morphology for the initial sulfuric acid concentration of 0.1 wt.%. The image confirms the existence of acid pockets inside the ice with a mono-crystalline ice structure. In the initial concentration range from 1 to 15 wt.%, the separation rate was 37.66% and 15.63% for the first fractionated thawing and increased until reaching 74% and 70% respectively. For an initial composition of 20%, the elimination rate varies between 2% and 34%.

These results indicated that the last separation rates for the initial concentration range between 1 and 15 wt.% were more effective than those below 1 wt.%. In addition, the separation rates remained almost constant for the range between 1 and 15 wt.%. By comparing this behavior with those reported for food fluids, in which the concentration efficiency decreased considerably with the initial concentration of solute, we found absolutely the opposite. Probably, even at high acid concentrations, the size of the acid allows relatively easy elimination. Moreover, because of the supercooling required by high acid concentration solutions, the fraction of ice decreased with the decrease of concentration. According to the study performed by Chen et al. [39], the accumulation of solute at the solid–liquid interface lowers the freezing point of the solution and increases the difficulty of crystal formation. As previously mentioned, a decrease in freezing temperature must be applied to produce the maximum amount of ice by continuously supplying the system with cooling energy [44]. Otherwise, the structure of ice observed for an initial solution of 10 wt.% (Fig. 8b) is polycrystalline. In this case, sulfuric acid was trapped in the gaps between the crystals which allowed an elution of the acid with efficiency much higher than that of initial concentration less than 1 wt.%. The gaps were multiplied when the ice was formed from a high initial concentration (20 wt.%). The high initial concentration solution implies the increase of the concentration of these impure zones. In addition, it is known that the viscosity of sulfuric acid increases with the increase of concentration, probably this factor has slowed the rate of the fluid

movement during the thawing process, and therefore the acid particles adhered easily on the surface of the ice.

Thawing time is another parameter which varies as a function of the initial concentration. Fig. 9 presents the evolution of the thawing time and the ice fractions concentration according to the initial concentration for the freezing temperature realized at –20°C. It shows a strong ice thawing time effect, the higher the concentration of the initial solution, the shorter the time of the ice thawing. For example, for a solution with an initial H_2SO_4 concentration of 20 wt.%, the thawing time is the shortest. The production of 25% of the liquid fraction was obtained after about 7 min of fusion and 75% of the liquid fraction was obtained after about 30 min of fusion. The longest
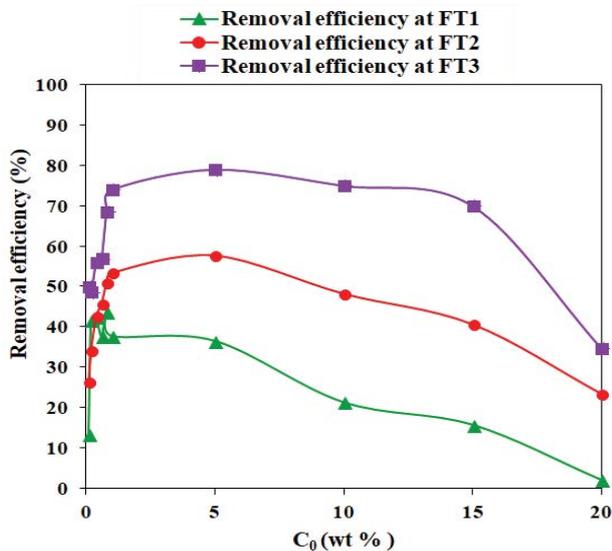
operation was obtained for an initial concentration solution of 0.1 wt.%. For this initial concentration, the first concentrated fraction melt after 69 min, and the last fraction melt after about 191 min. It should be noted that the ice layer obtained at the end of the shortest operation was fragile, while the ice resulting from low concentration is more compact. Visual observations of the ice appearance during experience showed a highly cracked ice for the high initial concentration which explains the in depth purified layer.

Based on this result, we confirm that the first fraction recovered via the freezing-thawing process increased about two-fold from initial concentration below 5 wt.%, and the treated water decreased to about 2–4-fold from initial concentrations between 0.1 and 20 wt.%. This shows the significant effect of the fractionated thawing step on the concentration of sulfuric acid and on the purification of acidic water. In order to assess the separation fraction effect, a statistical study has been carried out; the results will be discussed later in the experimental analysis section.

3.3. Experimental design analysis

According to the study carried out in the previous section, we have shown that the main key variables that could affect the performance of the block freezing-thawing system are the initial concentration (C_0), the temperature (T), and the ice thawed fraction (F). In order to better understand the effect of each factor on the concentration of sulfuric acid in the first thawed fraction (C_{F1}) and the last melted fraction (C_{IF3}), statistical processing was performed. This method provides assistance in interpreting the results. In our case, the statistical analysis consists of estimating, using the least-squares method, the coefficients of the model, and the different residues (the difference between the observed values and the values predicted by the model). The model was validated taken into account the variance analysis which indicates the significance of the model (p-value). In fact, coefficients with a low p-value indicate a positive effect.

Fig. 7. Removal efficiency obtained in the different level of fractionated thawing (FT1, FT2, FT3) for initial concentration varied between 0.1 and 20 wt.% of sulfuric acid.
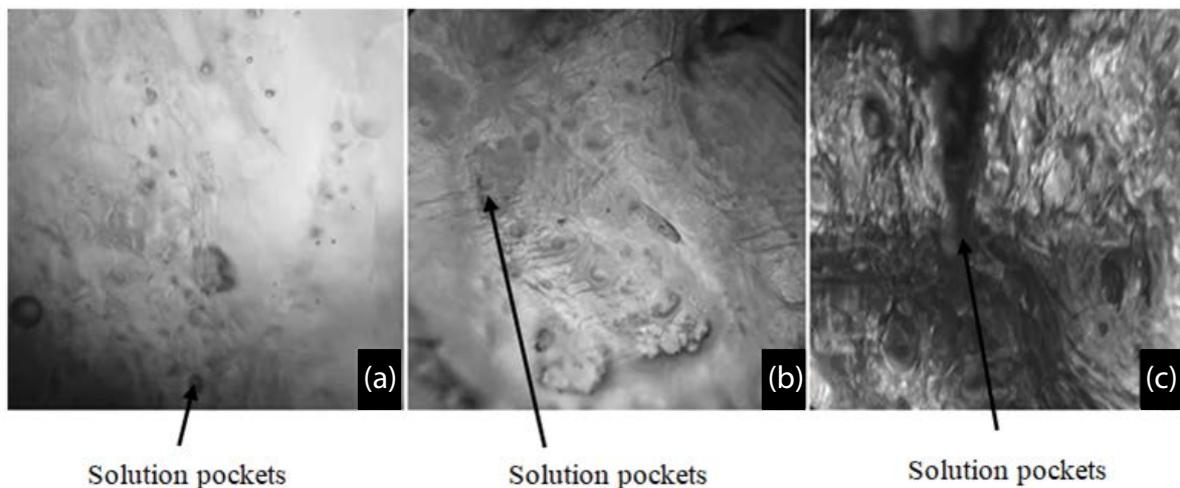
Fig. 8. Ice crystal morphology depending on the initial sulfuric acid concentration: (a) $C_0 = 1$ wt.%, (b) $C_0 = 10$ wt.%, and (c) $C_0 = 20$ wt.%. The captures were taken a magnification of ×11 using optical microscope.

Three experiments (corresponding to runs 15, 16, 17) were repeated at the center domain in order to validate the experimental error variance and to test the reproducibility of the responses. To complete the study, six experiments (corresponding to runs 18, 19, 20, 21, 22, 23) were performed in order to validate the accuracy of the model with experimental data.

The polynomial regression equations in uncoded units of both responses C_{F1} (wt.%) and C_{IF3} (wt.%) are developed using Minitab software. Therefore the model equations are shown in Eqs. (11) and (12), all significant and insignificant points have been taken into account.

$$C_{F1}(\text{wt.\%}) = -3.7 + 2.106\,C_0 - 0.71T - 0.284\,F1 - 0.03243\,C_0^2 - 0.0181\,T^2 + 0.00601\,F1^2 - 0.00152\,C_0T - 0.00716\,C_0F1 + 0.00013\,TF1 \quad (11)$$

With a mean absolute error MAE = 0.349%. MAE is the average value of the residuals.

$$C_{IF3}(\text{wt.\%}) = -2.50 - 0.3194\,C_0 - 0.071\,T + 0.1240\,IF3 + 0.03139\,C_0^2 - 0.00031\,T^2 - 0.00150\,IF3^2 + 0.00238\,C_0T + 0.013177\,C_0IF3 + 0.00165\,T\,IF3 \quad (12)$$

With a mean absolute error MAE = 0.114%.

The central composite design study with the Pareto diagram (Fig. 10) allows analyzing the effect of each parameter on the responses. Fig. 10 illustrates the predominant effect of the initial concentration followed by the ice thawed fraction for the two responses. The analysis of the first response results (Table 2) showed that the sulfuric acid concentration (C_{F1}) varies between 0.248% and 28.64% for an initial concentration range between 0.1% and 20%. Statistical analysis of the (C_{F1}) response (Table 3) confirms that the initial concentration C_0 is the predominant factor with a positive impact ($P < 0.05$). The correlation coefficient (R^2) and the adjusted correlation coefficient (R^2_{Adj}) prove the existence of a good accuracy of the model which confirms that the model is significant with the absence of systematic error.

The ice thawed fraction (F) showed a significant impact ($P < 0.05$). However, the effect of the freezing temperature was not significant ($P > 0.05$); moreover, the interaction between the temperature and the concentration was not significant as well as the temperature and the fraction interaction. The response of ice purity (C_{IF3}) shows that major factors influencing the ice purity are the initial concentration and the ice thawed fraction, which is consistent with the C_{F1} response.

The extrapolation of the models and experimental results at different thawed fractions is presented in Fig. 11, it shows that the thawed fraction of 10% lead to the maximum concentration of sulfuric acid (Fig. 11a). This confirms that the first liquid melted from ice is the most concentrated. Moreover, the response of C_{IF3} proves that when ice is thawed under 80% of the initial volume the maximum of ice purity can be reached (Fig. 10b). Therefore, each time the superficial layers have melted, the ice was deeply purified and the incorporated solute was eliminated simultaneously. However, the downside
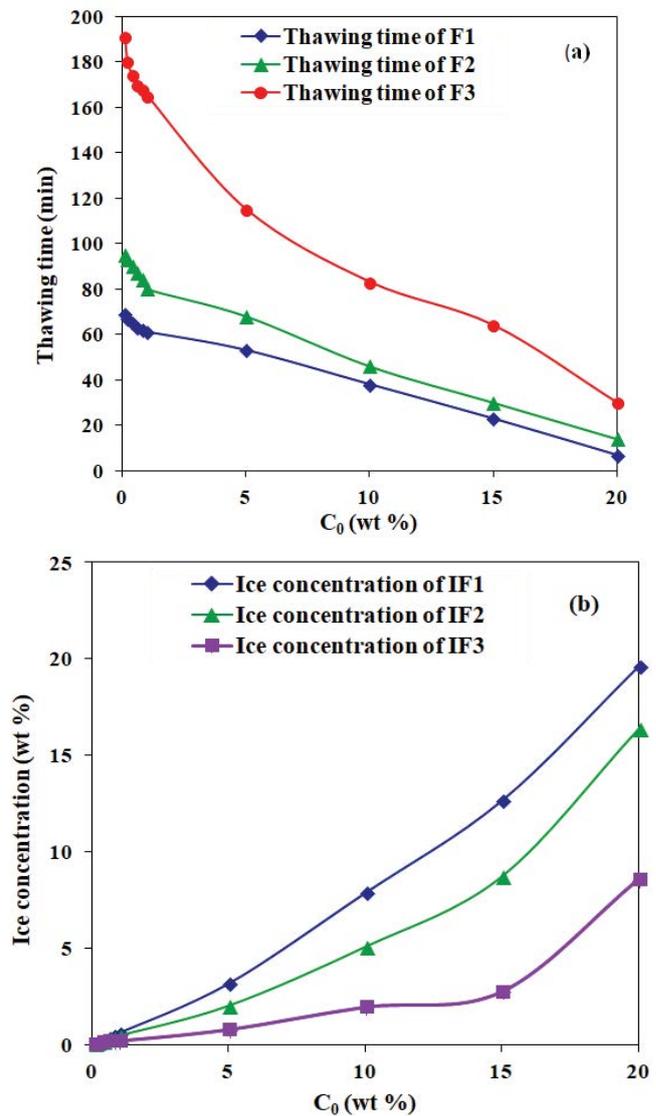
Fig. 9. Thawing time (a) of the thawed fractions (*F*1, *F*2, *F*3) and concentration (b) of the ice fractions (IF1, IF2 and IF3) obtained during thawing the ice block (realized at –20°C) at room temperature (for initial sulfuric acid concentrations varied between 0.1 and 20 wt.%).

of reducing the ice thawed fraction is the decrease of the mass recovered.

Despite the effect of decreasing the ice thawed fraction, the elimination did not reach the maximum. If we refer to the work of Petzold and Aguilera [47], to have an effective separation with a high concentration of recovered solute, it is necessary to perform several stages of freezing or to integrate this method with another technique of freezing like suspension freezing or falling film freezing.

Regarding the temperature, it was expected that there would be a significant temperature effect on the first fraction recovered and the last fraction of ice because of the temperature influences the ice growth rate and obviously the concentration of the melted fractions. In our case, the effect was insignificant, indeed the amount of the ice block

Table 3
Estimated coded coefficients for responses C_{F1} and C_{IF3}

NOM	C_{F1} (wt.%)		C_{IF3} (wt.%)	
	Coefficient	p-value	Coefficient	p-value
Constant	16.728	0.000	3.639	0.000
C_0	13.351	0.000	6.560	0.000
T	0.005	0.982	0.058	0.428
F	–1.177	0.001	1.334	0.000
$C_0 \cdot C_0$	–3.211	0.000	3.108	0.000
$T \cdot T$	–0.289	0.539	–0.005	0.972
$F \cdot F$	0.601	0.222	–0.150	0.300
$C_0 \cdot T$	–0.061	0.822	0.095	0.262
$C_0 \cdot F$	–0.712	0.029	1.311	0.000
$T \cdot F$	0.005	0.984	0.066	0.422
R^2	99.800		99.900	
R^2_{Adj}	99.500		99.800	

Effects on sulfuric acid concentration in the first thawed fraction (F1)
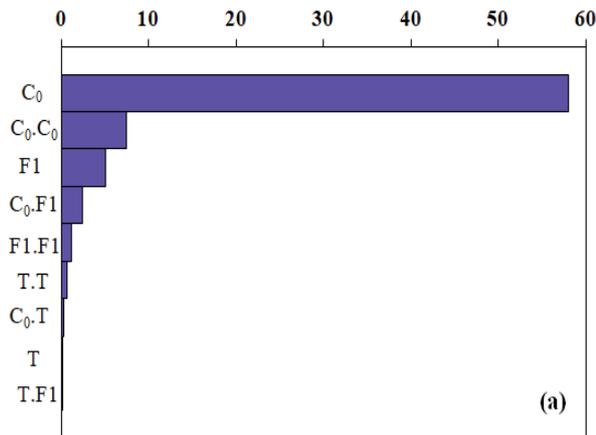
Effects on sulfuric acid concentration in ice (IF3)
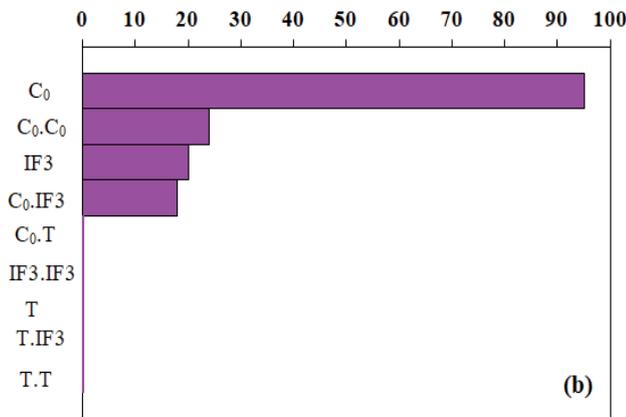
Fig. 10. Pareto chart on concentrated solution (a) and ice purity (b).
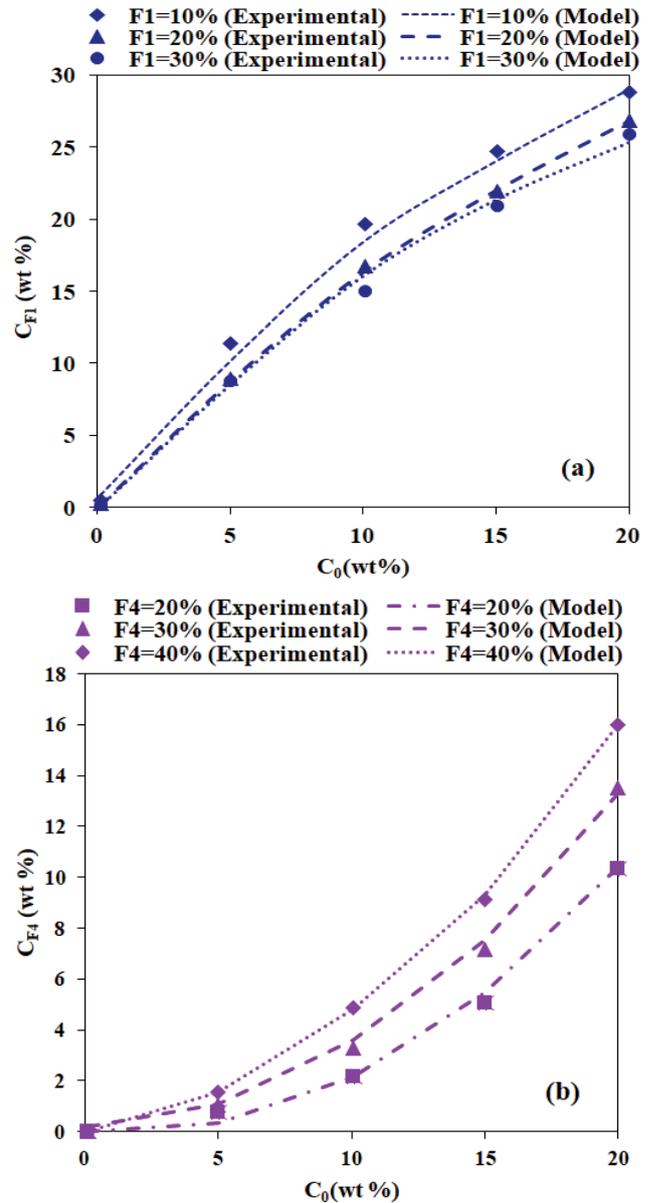
Fig. 11. Comparison between experimental data and modeling: (a) modeling results at different first fractions ($F1 = 10\%$; $F1 = 20\%$ and $F1 = 30\%$) and (b) modeling results at different last fractions (IF3 = 20%; IF3 = 30% and IF3 = 40%).

thawed in each fraction was identical for the three temperatures (–16°C, –20°C, –24°C). As the fractions were thawed at the same volume fractions, we can deduce that the temperature exerted on the solute during the ice block growth did not have an impact on the thawing of the solutes incorporated in the ice.

Similar behavior was expected by Aider and de Halleux [18].

4. Conclusion

This study demonstrated the feasibility of treating sulfuric acid wastewater using the freezing-thawing process

in a one-stage operation. The results of the solid–liquid equilibrium have shown the feasibility of practicing block freezing in a range of temperatures below –16°C. A freezing process has been applied for the sulfuric acid wastewater model. The total block technique followed by subsequent thawing showed acid removal rates of 50%, 70%, and 34% from initial concentrations of 0.1, 10, and 20 wt.% respectively. The study of freezing time showed that a longer freezing time revealed the inclusion of high sulfuric acid contents in the ice produced. An experimental design was developed to quantify the effects of the interaction of the initial concentration, the freezing temperature, and the ice thawed fraction on sulfuric acid concentration in each separated fraction. The results showed that in our conditions, the temperature did not influence the concentration parameters, while the initial concentration and the thawing stage had a very significant impact. The higher concentrated fractions of sulfuric acid that could be reached were about 0.6, 19.79, and 28.9 wt.%, they were obtained with initial sulfuric acid concentrations of about 0.1, 10.05, and 20 wt.%, respectively. The highest purified fractions were about 0.045, 2.2, and 10.39 wt.%, they were obtained from initial sulfuric acid concentrations of about 0.1, 10.05, and 20 wt.%, respectively. The results of this study show the feasibility of treating water containing sulfuric acid and recovering sulfuric acid which can be used in various industrial applications.

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