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Experimental study of industrial wastewater treatment by freezing

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ABSTRACT

This work aims to study an industrial wastewater treatment process by melt crystallization on a cold wall. A binary solution of water/acetone was chosen as model effluent. A parametric study of the wastewater treatment process was performed by means of an experimental design. The process was conducted in a static mode and the impurity concentration in the ice was analyzed after each freezing cycle. The process required applying very precise conditions and the ice concentration mainly depended on the initial solution concentration and on the applied cooling rate. The ice microstructure was also characterized by optical microscopy in a cold chamber and gave insights into the mechanism of impurity incorporation: the liquid inclusions were localized under the form of solution pockets at low growth rate or between the polycrystals at higher growth rate.

1. Introduction

Melt crystallization technology is well-known and has proved its efficiency in many industrial applications, particularly for freeze concentration in food industries [1], where the product flavors are temperature sensitive and for isomeric separation [2]. A recent review proposes discussion on the different freeze crystallization that can be applied for the treatment of reverse osmosis brines [3]. However, the technique has not yet been applied at industrial scale for wastewater treatment. This absence is probably due to misconceptions about this technique, especially concerning water purity or energy consumption. One of the first studies dealing with melt crystallization applied for wastewater treatment was done by Halde [4]. The author demonstrated the feasibility of freeze wastewater treatment of solutions and suspensions, but the process could not be extrapolated to industrial scale. Since this study, the improvement of melt crystallization technology [5] helps to bring out the advantages of the treatment [6] with batch [7] or continuous [8] pilot scale processes.

Moreover, the environmental hazards are now better apprehended and the standards for effluent discharge are getting more and more restricted. In this context, wastewater treatment by freeze concentration appears to be an interesting technology with low environmental impact [9]. Indeed, energy consumption is low compared to distillation process (latent heat of water vaporization is seven times higher than latent heat of ice fusion), no additional chemical products are needed and the produced ice crystals can be used as cold storage [10]. In addition, the implementation of a freezing step in wastewater treatment units presents two main advantages: (i) the high concentration in pollutants reached in the liquid effluent allows an easier post treatment of this effluent (either by advanced oxidation process or by incineration with a strong reduction of energy consumption) and (ii) the purity of the recovered aqueous effluent gets closer to the discharge standards.

The freeze crystallization can be classified into two groups, direct freezing and indirect freezing. In direct freezing, the refrigerant used to cool the solution is mixed directly with the brine. In indirect freeze concentration (i.e. with cooling performed across the wall of a heat exchanger), two main techniques have been investigated in the literature: (i) the process can work with suspensions of ice crystals, generally formed by scraping the ice layer deposited on the heat exchanger surface [11] or (ii) it can consist in the formation and growth of an ice layer on the exchanger surface, which is melt in a following step, to recover the purified aqueous solution [12–15]. The first technique has several advantages, as it can be operated in continuous mode and generally gives good ice crystal purity. However, two additional steps of filtration and washing are required to achieve the treatment. The second technology has retained our attention, because the separation between ice and concentrated wastewater is easier and does not require other unit operations. Crystallization on cold surface can be achieved in stagnant [16] solution (static melt crystallization) or in dynamic mode [17]; [18] with a falling film of solution or a circulation of solution. Cold surfaces can be flat [19] or cylindrical. Nucleation is a stochastic process and requires obviously to reach the metastable zone limit [20]. The material and the surface state are thus key factors of the nucleation [21]. If the influence of the operating parameters has widely been studied [22] the phenomena occurring during the crystallization have not yet been accurately explained.

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Nomenclature

C_0	Initial solution concentration (% wt)
C_a	Impurity (acetone) concentration in ice ($g\,L^{-1}$)
M_{ice}	Mass of ice produced (g)
T_{eq}	Equilibrium temperature (K)
V_R	Cooling ramp ($°C\,h^{-1}$)
V_{CR}	Ice growth rate ($mm\,h^{-1}$)
ΔT	Temperature difference between the cold tube and the tank double jacket (°C)
$w_{acetone}$	Mass fraction of acetone in the solution (% wt)

This work aims to operate with very precise conditions the process in order to understand the intrinsic phenomena, particularly the impurity incorporation mechanism. In that purpose the nucleation was overcome by forming a seed layer to avoid the rapid uncontrolled growth that occurs immediately after nucleation. The solid-liquid phase diagram was firstly established, in order to define the working domain, in terms of concentrations and temperatures. The second part of the work was focused on the static melt crystallization process, using a mixture of water and acetone as wastewater model. This model system is not linked to immediate practical application but the methods and findings developed in the paper can be extended to any system. An experimental design was used to quantify the influence of the parameters and their interactions on the acetone concentration in the ice layer. Finally, optical microscopic analyses of the ice structure were carried out to visualize the incorporation mechanisms.

2. Experimental methods

2.1. Thermodynamic data

The determination of the solid/liquid phase diagram of the binary system water/acetone is essential to define the operating conditions of the crystallization process and to delimit the working domains which avoid the formation of undesired solid forms. The phase diagram was achieved using two methods, the Differential Scanning Calorimetry (DSC) and a synthetic method, as described in a previous work dedicated to the establishment of the binary water/propionic acid phase diagram [23].

The calorimeter used in this study was a Thermal Analysis instruments (TA Q200). Samples (10–20 mg) of mixtures prepared at varying composition were weighed with a METTLER balance with an accuracy of 0.01 mg and then placed in sealed aluminum pans. To determine the phase change temperature, the experiments were performed according to the following program: (a) isotherm at 5 °C, (b) cooling rate at 10 °C min^{-1}, (c) isotherm at −70 °C during 5 min, (d) heating rate at 1 °C min^{-1}, (e) idem steps a, b and c, (f) heating rate at 5 °C min^{-1}, (g) idem steps a, b and c, (h) heating rate at 10 °C min^{-1}. The results reported in this work correspond to data during the heating phase (step d, f and h). All DSC curves were normalized with respect to the sample mass.

For the synthetic method, solution was cooled until solidification and heated until crystals fusion by analyzing the evolution of the solution temperature. The solution in the double jacketed vessel was homogenized with a magnetic stirrer. Solid − liquid phase diagram was then determined by monitoring temperature using a calibrated Pt100 resistance.

The synthetic method was used to consolidate the liquidus temperatures measured by Differential Scanning Calorimetry. Our experimental results were then compared to the literature data [24].

2.2. Experimental setup

Fig. 1 shows the scheme of the experimental setup and a photo focused on the crystallizer used for wastewater treatment. The apparatus consisted of a vertical stainless steel tube (1) plunged inside a cylindrical glass tank (5) filled with 0.3 L of solution (3). The freezing layer (4) developped on the wall of the vertical tube. The temperatures inside the tube and in the double jacket of the tank (5) were controlled by means of two thermostatic baths (6 and 7) filled with a water-ethylene glycol mixture (ethylene glycol mass fraction of 40% w/w).

The temperatures of the bulk solution and of the coolant inlet and outlet were measured with a set of six Pt100 sensors and were recorded via a data acquisition system (National Instrument) in a computer. After calibration, the error in temperature measurements was within the ± 0.05 K range.

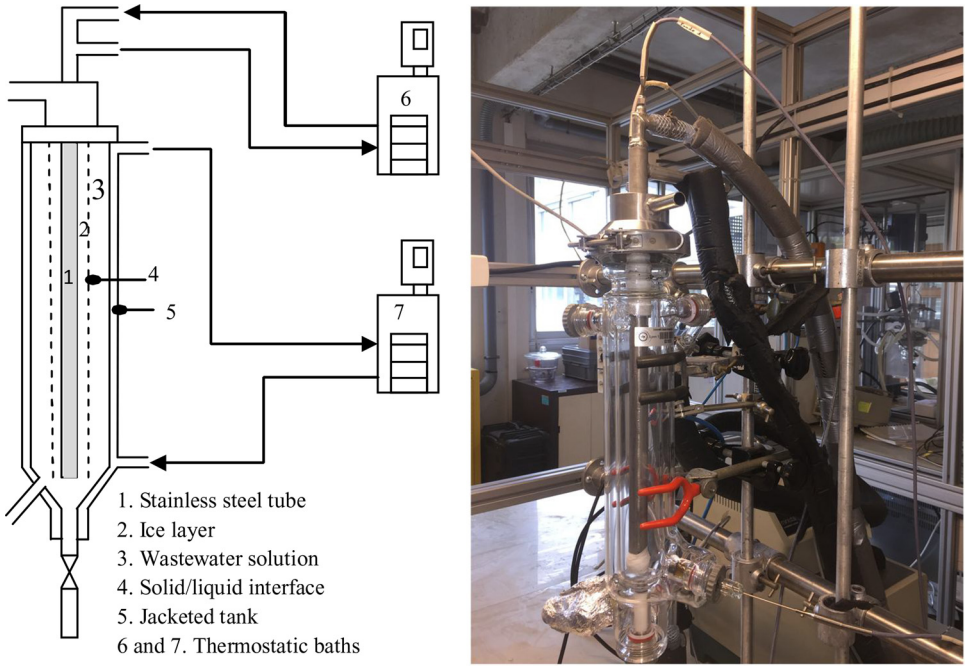

Fig. 1. Experimental setup.