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APPLICATION OF EUTECTIC FREEZE CRYSTALLIZATION FOR WASTEWATER TREATMENT: A REVIEW

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ABSTRACT
A process known as eutectic freeze crystallization (EFC) has demonstrated considerable promise in treating industrial waste while recovering potentially valuable minerals and reusable water. Numerous research up to this point that have focused on the evolution of EFC has been done in batch operation and without taking into account the impact of small components that may have an impact on the process efficiency and product quality. Large volumes of brines should be treated by means of a nonstop EFC route because it provides for greater product quality control, eliminates waste, and requires less labor overall. Salty waste matter disposal in any industry is regulated by more stringent regulatory regulations. The present review looked into the mechanism of the process of eutectic frozen formation of crystals as a way to split ice and salts concurrently in a typical effluent.
Keywords: Freeze Crystallization, Types, Industrial Wastewater, Salt Removal, Water Treatment.
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INTRODUCTION

The world now has a lack of potable water due to rising population and industrialization. Consequently, major efforts have been made to develop desalination techniques in addition to the conventional methods for producing water from brine.[1,2,3,4] The method by which crystals form, including techniques for desalination that use petrol hydrates and freezing, is solitary of the emerging technologies researched in modern times. The benefits of using the freezing approach have been discussed as an alternative to the desalination of salt water, mixture purification[5,] treatment of wastewater, and liquid concentration in food by various researchers.[,7,8,9,10] The separation method known as eutectic freeze crystallization (EFC) is capable of recuperating salts from hypersaline brine solutions while also generating relatively pure water. Under sub-eutectic conditions, fluids with salt content concurrently crystallize from the electrolytic solutions that are aqueous, and ice and crystalline ions are created.EFC has a number of benefits over traditional separation techniques like evaporative crystallization (EC). The freezing process is less expensive than its equivalent in evaporative crystallization since the enthalpy from ice fusion is around 6 times smaller than the enthalpy of water vaporization. The power needed to remove copper sulfate and sodium nitrate from aqueous solutions was reduced by 30 and 65 percent, respectively, while utilizing EFC as opposed to the traditional multi-step EC procedure. Additionally, EFC uses less land than evaporative ponds, which are frequently used to store brines and reduce their volume through natural evaporation.[11] EFC can be applied for complex brines to recover water and salts, as crystallization is a more energy-efficient method. In order to maximize water regaining and shield the potential threat to the environment from dangerous chemical species, it can therefore be used with reverse osmosis. However, antiscalants, which are designed to inhibit salts from scaling the membranes, are frequently present in the brines produced by reverse osmosis (RO).

Background of EFC

Nelson and Thompson's attempts to ascertain the sequence of salt crystallization led to the development of eutectic freeze crystallization (EFC) in the 1950.[12] Direct cooling was employed in the nonstop EFC route described to treat brines, and it was found that Ice and salt could both be extracted from dual solutions.[13]

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When cooling directly, a solution is injected with an inert cooling fluid, which vaporizes at the desired temperature by removing the solution's heat of vaporization. This design resulted in impurity crystals and separation equipment contamination from the refrigerant. These factors led to the idea's abandonment. Despite not having achieved commercial scale, the Frozen Crystallization of sodium chloride (NaCl) solution by means of direct cooling showed that the technique is cheaply viable.[14] EFC has the potential to be a viable substitute for traditional evaporative procedures in the conduct of wastewater generated by the mining and manufacturing industries. Further, it also demonstrated to consume less energy.

Freeze Crystallization System Overview

The usual phase diagram of a dual solution that displays symmetry lines among liquid and solid phases of materials, can be used to explain the principle of desalination via frozen crystallization. Figure-1 shows the phase graph of saline water (Nacl-H_2O).

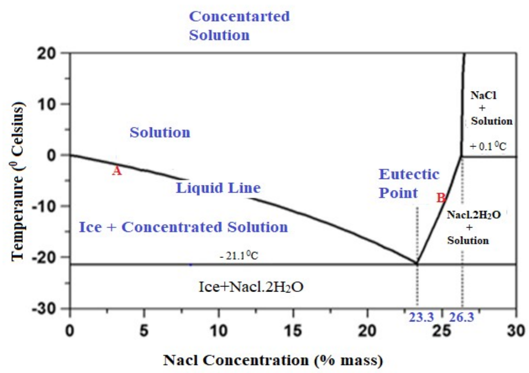

Fig.-1: Phase diagram of the Water- Sodium Chloride System

Line A shows the Water's freezing point at various sodium chloride mass concentrations, while Line B shows the NaCl solubility curve in water. The starting point is where ice crystallizes first, at the eutectic point's left side. When the unsaturated saline solution reaches supercoiling temperature, ice crystals begin to form in binary solutions and are mostly reduced linearly at greater solute weight percentages. The solution will continue to cool down the arc given by string 1 until it reaches the eutectic point at -21.2^{0}C. The mixture's unfrozen portion is now saturated with NaCl; any more cooling will result in the creation of solid salt, and there is no longer any brine. For example, saltwater with a typical salinity of 35 ppt (3.5%) freezes at -2^0 C, and ice crystals made of pure water begin to form at this temperature and they persist to expand as the temperature is reduced. As seen in Fig.-1, ice crystal nucleation occurs at lower freezing points for highly concentrated brine solutions. In order to ensure subsequent recovery of pure water and convenience of managing, it is important to understand how to make the crystals form and how to encourage their growth to proper dimensions and size ranges. There are several ways to freeze substances, but the four most common are Vacuum, eutectic freeze, and direct and indirect contact crystallization.[15,16] However, two new ice crystal formation techniques that fall under the category of indirect contact crystallization were recently developed in the field of freeze crystallization: crystallization on a cold surface and crystallization by suspension surface.[17,18] The crystallization methods are divided into evaporation and freezing methods. There are four subtypes of freezing methods such as direct FC, indirect FC, vacuum FC, and eutectic FC. There is a newly developed indirect method namely, suspension FC and cold surface FC.

Direct Contact FC

The solution that is to be frozen is in close proximity to a refrigerant. This way primarily possesses an operating temperature of –5°C, making it a small energy utilization procedure.[16] The principal advantages of this technique include its high output pace with little effort, small size, and efficient construction. The freezing procedure, however, needs a specific refrigerant.

Crystallization by Indirect Contact Freezing

It employs refrigerant devoid of coming into connection with the crystallizing suspension directly; rather, the refrigerant's energy passes through the heat exchanger's walls.[19] In general, not direct refrigeration can be divided into two categories: freezing in liquid and sub-zero on a cold plate.[15] In the process of suspension crystallization, many little frost particles are created in the mother liquid suspension in two phases: at first, crystals are formed in ice nucleate later, they are relocated to recrystallize, where they grow larger using the Ostwald mature method. However, suspension crystallization is frequently employed in the food concentration sector,[34] It has a number of problems, including expense, complexity, difficulty in nucleation, and controllability of crystal development.[20,21] The chief benefit of sub-zero on a cold plate is that layer-by-layer crystallization results from ice crystal formation, which occurs in a one-dimensional orientation.

Vacuum Freezing Crystallization

This technique uses a high vacuum to evaporate some water, which subsequently causes the solution's temperature to drop, producing the process of ice crystal growth.[16]

Eutectic Freezing Crystallization

This method functions at the binary solution's eutectic temperature/point (NaCl-H_2O), as depicted in Fig.-1 phase diagram. This process results in the simultaneous partition of fresh water as frost from brine and salts as solids. Ice and salt both form separate nuclei and expand over time. Because of the dissimilarity in thickness, ice floats and brackish sinks, making separation easier. Eutectic freezing requires more money than other freezing techniques due to its extremely low working temperature (-20 to -25^0 C). The most important details of each of the aforementioned freeze crystallization techniques are represented in Table-1.

Table-1: Comparison of Techniques for Freeze Crystallization[22]

Method	Approach	Advantages	Drawback	References
Direct FC	Direct interaction of a solution with a refrigerant result in crystallization	-High production rate at low driving power and low operating temperatures -compacted plan	-Refrigerant restrictions include (Chemically inert, non-combust, and harmless appropriate hot temp.) -Uneven coolant and mixture mixing results in significant contaminants.	16 19
Suspension indirect FC	Solution crystallization caused by inadvertent contact with a refrigerant	-indirect contact enables a variety of refrigerants to be selected	-expensive -complex, challenging crystal growth, and nucleation	19 15 20 21 23
Progressive indirect FC	-A solution-filled tube is gradually submerged in a frigid refrigerant route.	stirrer reduces the impurity content close to the ice-growing surface, resulting in lesser impurities due to 1-D crystal development.	-Bath size restrictions make scaling up challenging	15 17 24
Falling film indirect FC	-solution flowing dynamically over a freezing vertical surface	growth of a single-dimensional crystal - Impurity transfer from the growing surface is improved by shear caused by flow, which raises the mass transfer coefficient.	-challenging ice separation	18 19 17 15 25

		-simple to scale up -Lower COD is caused by a higher Reynolds number.		
Vacuum FC	A portion of the water is vaporized under a high vacuum, which lowers the temperature and leads to crystallization.	-When atmospheric operating conditions are adopted, volatile refrigerant recovery can be made simpler and less expensive.	A more effective design of the melting unit is required since the compressor must manage high volume and low pressure of water vapor.	16
Eutectic FC	Works at the eutectic level of the solution, resulting in the crystallization of salts and ice.	-due to ice and solid salts' different densities, separation is simple. -high water recovery creating ZLD	-Additional cost is necessary since a very low working temperature is needed.	19 26

In one study, EFC was used where salty whey, a typical saline effluent, was subjected to the formation of crystals through eutectic freezing research as a potential method for synchronous ice and salt extraction. Brackish whey samples gathered from an industrial dairy were used in experiments. Using differential scanning calorimetry, it was discovered that the salty whey's eutectic point was significantly lower (24°C for salty whey vs. 21°C for NaCl solutions) than that of NaCl liquids. The dairy stream's phase diagram was then built using crystallization experiments under equilibrium conditions.[27] Research has been done on the efficacy of both eutectic and progressive freezing concentrations (PFC and EFC) methods for recovering salt.[28] When using the concentrate is left behind in liquid form after pure water crystallizes into crystals using the PFC process. However, when using the EFC method and the water-salt mixture's initial concentration perfectly matches the eutectic concentration, both the water and salt crystallize simultaneously. Ice hovers at the crest of the crystallizer in the EFC, while salt falls to the bottom, and both are separated by gravity. Calculations are made to assess the efficiency of the recovery of solute (Y) and effective partition constant (K). In their investigation, the PFC approach produced sodium chloride 0.88 g of recoverable solute for every 1 g of starting sodium chloride, while the EFC method produced an optimum partitioning efficiency and solute retention of 0.59 and 0.66, respectively. Largely, the seawater desalination process can use either method. One potential method for dealing with wastewater treatment is crystallization. The usefulness of the progressive freeze concentration (PFC) technology in treating wastewater from the food sector was investigated in this paper. In PFC, pure water is created as ice crystal blocks, leaving behind a solution with a greater concentration. They Investigated the impacts of stirring speed and coolant temperature on Y and K. As a substitute for wastewater, a glucose solution was employed. The optimal circumstances were discovered at a maximum stirring speed of 500 rpm at a moderate coolant temperature of -10°C, which produced the highest Y and lowest K values, as well as the uppermost effectiveness for the dealing of wastewater.[29] In order to recover from used pulping fluid, and inorganic compounds, EFC has the ability to save some of the energy that is used in the process now used in the departure step.[30] A review of the literature indicates that, if lignin has already been eliminated by acidification and precipitation, EFC be able to used to extract reasonably clean sodium sulfate, sodium carbonate, and ice made by reasonably clear water from the waste liquor. Inorganic scale formation problems that arise when an EFC process is used to produce black liquor without lignin will need to be researched. The chemical reactions to regenerate sodium hydroxide and sodium sulfide, the active pulping chemicals, from sodium carbonate and other complex extracted by EFC be able to done separately or via adding the substances back to a recovery boiler's existing feed. Tetrahydrofuran was utilized as a solvent in the Grignard reagent wastewater, which was treated using the freezing techniques of crystallization in suspension and gradual freezing. Performance was scrutinized in relation to freezing temperature, seed ice crystal addition, and stirring speed. The purity was improved by the supplement of ice as seed, at the right temperature. COD elimination effectiveness was greater than 90% and the ideal working conditions for the mixing speed was 300 rpm and the freezing temperature was 60C, respectively. Performance- and energy-wise, suspension crystallization outperforms progressive freezing, requiring an estimated 38.26 kWh per tonne of treated wastewater. Considering the outcomes, a technique for recovering THF from Grignard reagent effluent through freezing and concentration is offered.[31] The possibility of recovering Na2SO4 from its solution was examined. Additionally, the impact of various variables and operational circumstances on the effectiveness of the purification and recovery process was investigated. Before being released into the environment, wastewater must be treated due to strict legal requirements. By using freezing to create a layer of less contaminated ice, wastewater can be cleaned. The residual wastewater becomes more concentrated after freezing. When it comes to salt recovery, reaching the eutectic point by freeze crystallization might affect the instantaneous crystallization of water and soluble salt. Due to the substantial density difference, ice and salt can be easily separated. One of the major elements in wastewater coming from various industrial sources, Na_2SO_4, was regarded as a model compound in their work. It is an energy and money-efficient method to regain Na_2SO_4 from the mother solution by means of eutectic ice-up crystallization.[32] The process of freeze crystallization is particularly effective at removing compounds from an aqueous solution. This process reduces the COD of the effluent stream from the pharmaceutical sector from 200000 ppm to 300 ppm. Additionally, because this effluent stream is a eutectic mixture, freeze crystallization uses 30% less energy than evaporation.[33] The possibilities of methods for crystallization using the icy technique and the creation of gas hydrates in the desalination of water were examined. Tetrahydrofuran was used as a hydrate forming with hydrate configuration II for this aim. Initially, salts of NaCl, KCl, $CaCl_2$, $MgCl_2$, and Caspian saltwater were used to make salt waters. After crystal production and division from the brine solution, the crystals were melted to generate the distilled water. For freezing and hydrate-based desalination, the removal efficiency of salts is expected to be between 40 and 80 per cent. The outcomes demonstrate that the effectiveness of separation increases further with lowering driving forces and salt concentrations. Removing salt, effectiveness is also influenced by ionic size and electrical charge. By using desalination techniques based on crystallization, Na^+, and K^+ ions can be removed more effectively than Ca^{2+} and Mg^{2+} ions.[34] A novel method for desalinating seawater was devised, in which pure water is created as ice crystal blocks, leaving behind a solution with a higher concentration. This method uses spinning cylindrical crystallizers with anti-supercooling holes. Based on desalination rate, K values, and efficiency of concentration, the effects of coolant temperature and stirring speed were examined, and the effectiveness of the system was appraised. The system performs best at - 8°C, which is the middle coolant temperature.[35] Progressive freeze concentration (PFC) is a method[36] that only produces a sizable single ice crystal that grows on the cooling surface, making it relatively simple to separate the ice crystal from the solution. As a result, the system is relatively straightforward and less expensive. When compared to suspension freeze concentration (SFC), the typical PFC configuration generates ice that is higher in purity but less productive. Ice production often results in a small amount of ice. Therefore, the PFC system's ongoing development includes efforts to increase productivity and efficiency. A variety of designs have been looked into that can produce high-quality products with greater efficiency while also being simple to use and affordable. If a water treatment procedure is to be considered both economically and environmentally sustainable, it must recover both water and other useful products. One such environmentally friendly method of treating water is called eutectic freeze crystallization (EFC), which by operating at a specified temperature may create both pure salt(s) and pure ice (water). The textile sector benefits greatly from the use of EFC for water treatment since frost crystallization removes all contaminants by using the water collected, including colors.[37] EFC can also manufacture other salts with the purpose of using them again later. This study looked into the viability of using EFC to clean wastewater from the textile sector. The outcomes demonstrated that EFC can be utilized to convert 95%. Crystallization tests were carried out using Na_2SO_4 aqueous solution in an EFC crystallizer to examine the impact of residence time and supercooling on the properties of the ice produced in a nonstop way. It was found that the dimension and form of the crystalline substances directly affect how well EFC works in crystallizers, as well as any following cleaning or purification processes.[38] Super saturation and residence duration affect these product properties. Digital image processing was used to examine the shape size distribution of crystals and the crystallization process. Extended stay periods increased a typical crystal dimension, resulting in the arrangement of disk-shaped frost crystals. The mean ice equivalent diameter increased as supercooling increased. A comparison between EFC and Evaporative Crystallization (EC) using LCA: Life Cycle Assessment to see whether an individual has a smaller environmental impact was done. EFC is a fresh, prospective innovation that could challenge EC, however hasn't yet been developed on an industrial scale. EC is a well-established technology.[39] The network was expanded to create a reasonable judgment because the processes produce water as a byproduct in various phases. Regardless of the nation's energy mix, the LCA results show that the simulation greatly favors the EFC process over the EC for 4-weight percent sodium sulfate solution, needing fewer power supplies. However, cooler energy efficiency and process energy integration can drastically reduce its environmental effects further. A case study in which, liquid effluent from a reverse osmosis facility was treated using EFC. A cutting-edge facility using the HiPRO method, which currently turns 99 per cent into potable water from a waste stream, provided the salt water. Currently, an evaporation pond is used to dispose of the plant's liquid waste (brine). In this investigation, clean sodium sulfate, clean water, and pure calcium sulfate (98.0 percent purity) were recovered from the fluid waste from the RO plant at a conversion rate of 97 percent (96.4 percent purity). A 99.9 percent overall estimate of the excess watercourse produced by the RO plant's conversion to commercially workable goods was made.[26] Complex, hypersaline brines from the mining and extractive metallurgical industries may be treated using EFC. Despite the fact that EFC has proven to be successful in separating a single salt from water, it, yet, has not yet been used for the separation of complex hypersaline brines, which are retentates typical of reverse osmosis (RO) in South Africa. This study focuses on using EFC to purify classic brine with high concentrations of ammonia, chlorine, sodium, sulfate, and chloride, which cannot be done using existing severance methods.[40] Since membrane technology cannot be used to treat the brine because of ammonia, the only remaining options are cooling or evaporation. A mixed salt is produced by evaporation, which needs additional processing. Under various process settings, modeling techniques were used to characterize the phase behavior of complicated saline systems and were then experimentally confirmed. The outcomes show that sodium may be selectively recovered as sodium sulfate salt using EFC. A scaled-up scraped chilled wall crystallizer was used to test eutectic freeze crystallization on an industrial waste stream of bicarbonate and carbonate of sodium that contained amounts of molybdenum.[41] The crystallizer kept its heat transfer rate at 5 kWm^2. By working inside the bicarbonate metastable zone width, molybdenum and decahydrate sodium carbonate concentration less than 1 ppm and clean ice take place by nonstop crystallization at 3.8^0C. Bicarbonate began to co-crystallize around 4.0°C. Due to the mixture's bimodal size distribution, the salt product's filtering and purity were low. An EFC brine technique was developed to treat multi-component, high-saline brine. For Brine 1 and Brine 2, utilizing EFC instead of EC resulted in operating cost savings of 80% and 85%, respectively. By taking into account the money earned from selling the pure salts that were created by EFC, and considering the cost of additional mixed salt disposal EC savings of adopting EFC may be further increased.[42] Ice and magnesium sulfate were recovered from the effluent of a flue gas desulphurization plant using EFC technology.[43] The population balance model was used by the author to construct an outline for estimating the kinetics of crystallization in an EFC process. A comprehensive pilot-size continuous EFC process based on the design and testing of a cooled disc column crystallizer for simple integration into industrial units. An industrial aqueous $MgSO_4$ solution was used in the procedure, which was intended to produce 130 tonnes of $MgSO_4.7H_2O$ per year. The transportable skid also has additional belt filters and washing columns separating the yield from the main liquor.[44] Two case studies of a 7.8 tonne per day, 35 weight percent aqueous sodium nitrate stream, and a 24 tonne per date, 12 weight percent copper sulfate flow that used EFC as a choice for heating crystallization. The heat transfer method used by the suggested crystallizer, a chilled disc column crystallizer, is not direct cooling. The produced frost crystals are employed to cool the supply stream in advance in a single-stage process. The refrigerant condensation in a two-stage refrigeration system makes use of the ice crystals that have formed. EFC requires 1037 kJ /kg $CuSO_4.5H_2O$ and 1282 kJ /kg $NaNO_3$, expressed as a thermal equivalent energy consumption.[45] In comparison to traditional multi-step evaporation, there are energy savings of 30% and 65% for copper sulfate and sodium nitrate, respectively.

CONCLUSION

This review demonstrates the potential of wastewater-derived salts. The mechanism of eutectic freeze crystallization (EFC), which separates salts and ice simultaneously in a typical effluent, was examined in this review. Numerous important criteria, such as the operating cost, beginning concentration, effects on the environment, pH readings, chemicals added, effectiveness of removal, and economic viability, influence the choice of the most effective technology for removing salt from wastewater. The situation presented in the current evaluation addresses a significant section of possible novelty for the industrial sector. According to how the given technology might be implemented in current sectors, as was given in the introduction, it is possible for both lower costs and higher production rates. Here, scientific part and technological experiences have been chronicled, ideally giving readers an idea of how a system might be put together to accomplish some of the numerous concurrent goals in an industry.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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