COD removal from pharmaceutical effluent via Freeze Crystallization

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ABSTRACT

Freeze Crystallization is very efficient operation for removal of chemicals from it's aqueous solution. In this paper COD of effluent stream from pharmaceutical industry is reduced from 200000 ppm to 300 ppm by this operation. As latent heat of vaporization of water is 7 times higher than latent heat of fusion of water. And also this effluent stream is eutectic mixture hence energy consumption by freeze crystallization is 30% less compare to Evaporation operation.

Keyword: *Eutectic Freeze Crystallization, Phase separation diagram, COD removal, Mass balance and energy balance.*

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1. INTRODUCTION:

The world currently facing major problems are firstly: the declining availability of sufficient quantities of water, and secondly: the deterioration of the quality of the available water. However, with the increasing use of water recycling technology such as desalination, ion exchange regeneration, inorganic precipitation, biological processes and membrane treatments, the result has been an increased generation of inorganic brines and concentrates.

Non-soluble compounds and soluble compounds are the two kinds of pollutants encountered in waste-water. The treatment of the ®rst is achieved easily by mechanical separating processes e.g. sedimentation,Cocculation, Fotation, hydrocycloning and Filtration. On the other hand, the treatment of soluble compounds is more difficult. The conventional solutions used at present are: biological processes (but these are not suitable for toxic pollutants); adsorption (but only for low concentrations); oxidation (but this is very expensive for dilute organic compounds); membrane processes (but low cut-off molecular weight is needed for the removal of soluble compounds). The objective of this paper is to present freezing as a new solution for soluble pollutant treatment.

2. PRINCIPLE:

The principle of freezing separation is based on liquid-solid-phase diagrams. Several kinds of diagrams exist to represent a binary mixture but the eutectic form is most often encountered for water and a soluble compound. Because of the small dimensions of the ice crystal lattice, inclusion of compounds in the crystal lattice is impossible except for fluorhydric acid and ammonia and so there is no solid solution with ice. Eutectic diagrams are sought because, theoretically, they require only a single step to remove pollutants.

Freezing of a binary solution of water and a compound X, which is the pollutant, is represented in Fig. 1. The whole diagram and a zoom have been plotted in order to understand what happens generally in a classical eutectic separation and particularly in the case of wastewater where the starting point is very close to the left of the diagram. The path [MN] corresponds to cooling of the solution to its solidi®cation temperature. Freezing of pure water starts at point N and continues until point P, which represents the system at equilibrium for a given temperature. The location of point P gives the proportions and concentrations of the phases according to the inverse segments method:[SP]/ [SQ]=liquid proportion and [PQ]/[SQ]=solid proportion. The solid concentration is always 100% of water and the liquid concentration increases from xM to xQ. The eutectic temperature is the boundary of the freezing technique. Below it, co-precipitation of ice and pollutant X occur at the same time so separation is impossible. The idea is to gradually freeze wastewater and theoretically, pure water ice will be produced while pollutant concentration increases in the remaining liquid.

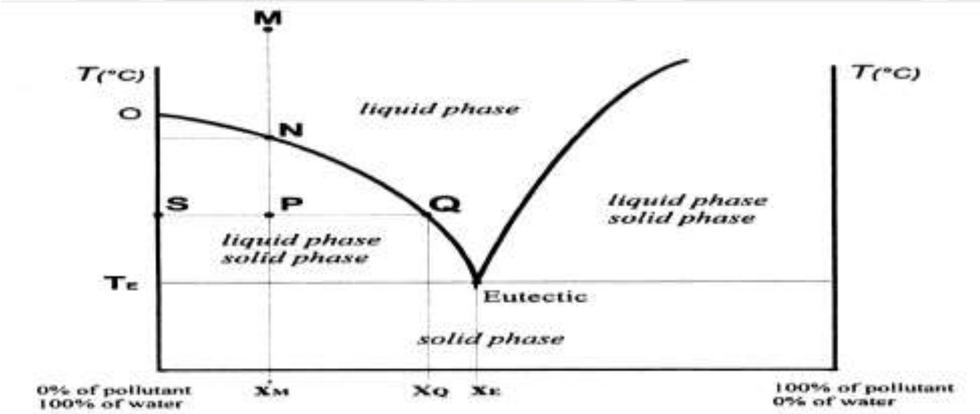

Figure 1 solid-liquid phase diagram

Usual wastewater concentrations are always very low, a few grams per litre. So, the starting point, M, is very close to the Y-axis as shown in the zoom. In this way, even with a working temperature just a few degrees below zero, which means minimum energy costs, high concentration ratios could be reached easily.

3. SOLID-LIQUID EQUILIBRIUM:

All freeze separation processes are based on the difference in component concentrations between solid and liquid phases that are in equilibrium. This can be most easily understood by referring to Figure 1. As the solution (say, at point A) is cooled, there will be some temperature at which a solid crystalline phase begins to appear in liquid phase (Point B).
Usually only one component in the solution is crystallizes, and that crystal is pure. This permits operation in a single theoretical stage. The energy efficiency of the freeze separation process results both from this

single-stage capability and from the lower latent heats associated with the solid-liquid phase change.

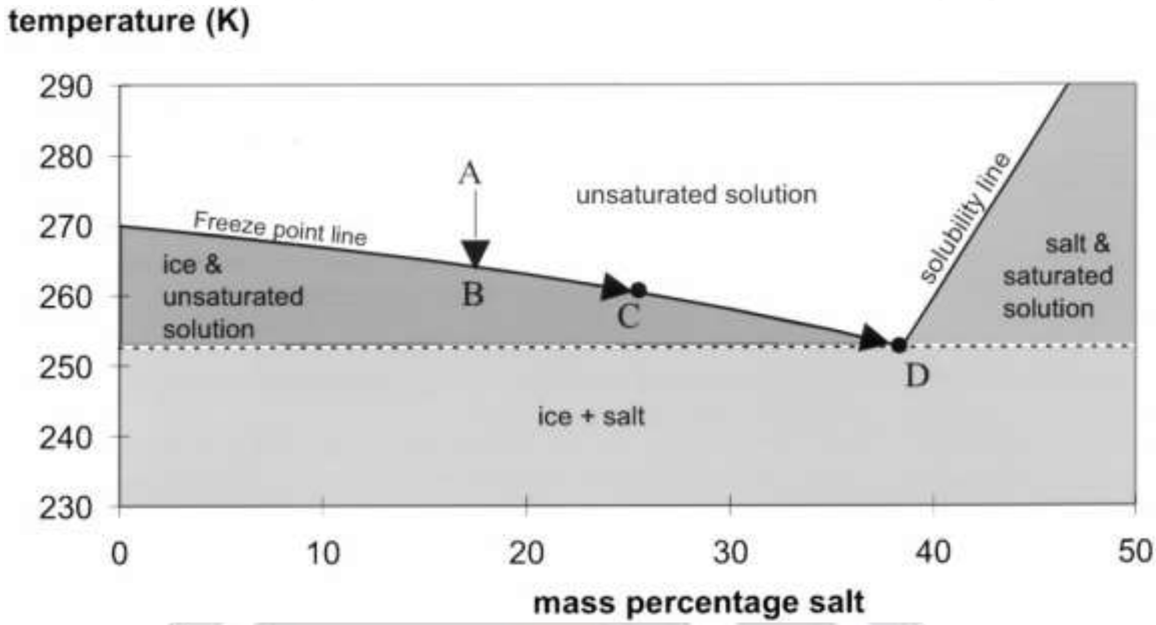

Figure 2 Eutectic point of water-salt system

Crystallization latent heats are one-half to one-tenth those of vaporization.At the initial freezing temperature, only a small amount of crystal will be formed. As crystals of a component are formed, the concentration of that component remaining in the solution isdecreased. This causes the crystallization temperature of the remaining liquid to drop minutely, so that a lower operating temperature is needed to further crystallization. Thus, higher conversions to crystal phase require successively lower temperatures, as shown by the operating line BCD. In a binary mixture, a point is eventually reached where both components crystallize simultaneously: this is called the eutectic and is shown as point D. At the eutectic, the concentrations of solid and liquid phase remain constant..

4. EXPERIMENT STUDY:

1) Procedure:

- *Feed solution is partially frozen. More than 75% mass of feed is frozen.*
- *Solid or ice is crushed to fine particles.*
- *Crushed solid particles are washed by melt and separated out.*
- *Solid and liquid phases are analyzed separately.*
- *For analysis of liquid solutions instruments available in the laboratories of L.D. College of engineering Ahmedabad.*

2) Pilot Plant:

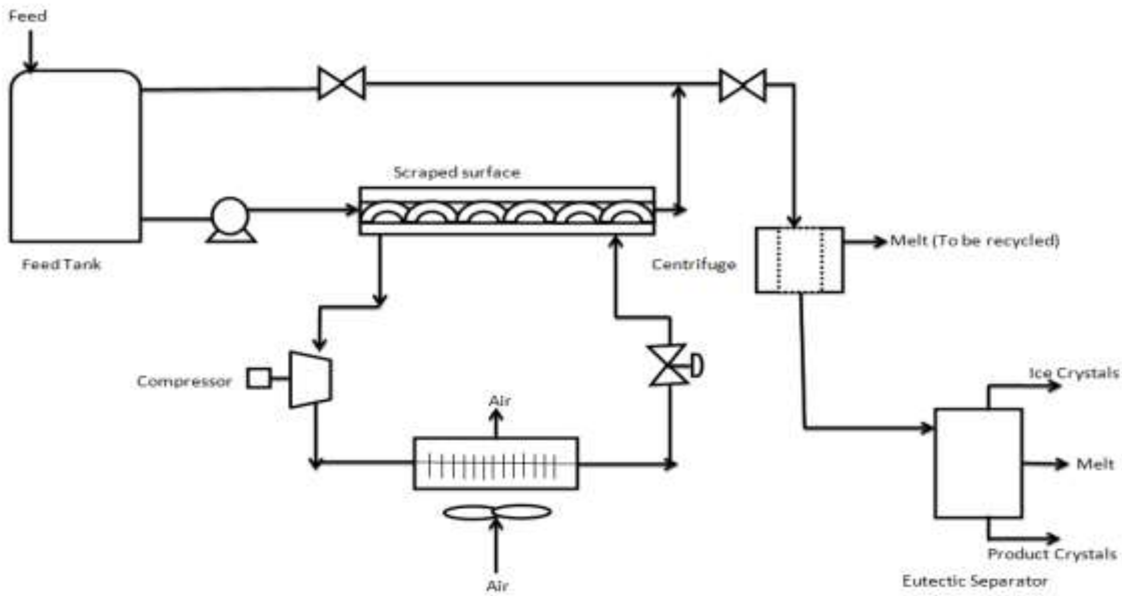

Figure 3 Pilot plant COD removal

3) Analysis Method and Result:

*COD analysis by COD digester equipment. Stage reduction of COD after all recycle stream in **Table 1.***

Table 1 Stagewise COD removal data

Recycle Stream	*COD in ppm(Input)*	*COD in ppm (output)*
Stage-1	*200000*	*72000*
Stage-2	*72000*	*17280*
Stage-3	*17280*	*300*

4) Energy Balance:

10KW = 36000 KJ/h = 2.89 TR

Ice generation capacity = 5 tpd

= 5000/24

=208.33 kg/h

Heat duty required = Ice generation capacity x Heat duty require for freezing

= 208.33 x 334

= 69582 kJ/h

5) Material Balance:

COD of waste water is 200000 ppm (20%)

Ice crystals removed = 89% of water in feed

Waste water can be treated:

(Fx 0.8) x 0.8925 = 208.33(1- 400 x 10-5)

F = 292.67 kg/h

Solid balance:

291.67 x 0.2 = 208.33 x 300 x 10-6 + 83.34 x X

X= 0.6989(69.89%)

5. Conclusion:

For many pharmaceutical, dyes and agrochemical industries 'Zero Discharge' for liquid effluent is imposed by pollution control board. Hence entire water of liquid effluent is to be removed conventionally evaporation followed by drying is used for the removal of water implementation of freeze crystallization for such case is advantageous due to very low energy consumption.

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