

COD reduction of Phenolic Effluent Using Freeze Crystallization

Patel Parth V.¹, Prof. Suchen B. Thakore², Samidha Banka³

¹ Chemical Engg. Dept., L.D. College of Engg., University Area, Ahmedabad – 380015

² Chemical Engg. Dept., L.D. College of Engg., University Area, Ahmedabad - 380015

ABSTRACT

The paper presented here is regarding the experimental determination of Chemical Oxygen Demand and its declination using an advanced novel technique namely, Eutectic Freeze Crystallization. Here, a phenolic effluent from a dye industry has been taken for the test. The presence of Phenol in the waste water is extremely toxic and it cannot be released in any source of water. Commercially, number of different techniques is used for reduction of COD from such effluent, whereas here experiments show a steep decline in same by using multistage freeze crystallization only.

Keywords: Freeze Crystallization, Waste Water Treatment, COD Reduction, Phenol Separation, Azeotropic Separation

1. INTRODUCTION

Freeze crystallization has all the characteristics of a revolutionary breakthrough in sustainability in the chemical industry. In this case, it is not a minor incremental improvement, but an innovative leap forward.

The principle of the process is as follows: when a solution containing dissolved contaminants is slowly frozen, water ice crystals form on the surface, and the contaminants are concentrated in the remaining solution (the mother liquor). The ice crystals can be separated from the mother liquor, washed and melted to yield a nearly pure water stream. The mother liquor will contain a pure salt, which crystallizes at the eutectic temperature. Theoretically, a 100% yield can be obtained in a binary system, which is one of the advantages of EFC technology. The level of accumulation of impurities can be controlled by means of purge streams.

1.1 Freeze Separation Technology

A general process schematic of the freeze crystallization separation process is shown in Figure. The major components of the process include:

- **A Freezer**, or crystallizer, where a portion of the liquid is changed to the solid phase by removing heat.
- **A Separator** where the crystal phase is separated from the remaining liquid, and the crystals are washed to remove adhering brine from the surface. Leaching of the crystal pack can also occur here if there is a solid solution in the crystals.
- **Refrigeration Cycle** that acts like a heat pump, removing heat from the freezer and compressing it to a sufficient pressure that it will condense to provide the heat needed to melt the crystal after it has been separated. A Heat Rejection portion of this cycle 'pumps' the ambient heat leaking into the system and inefficiencies in the process from the operating temperature up to ambient conditions, where this heat is rejected from the system.
- In the process are **Heat Exchangers** to recover the 'cold energy' from the process streams, for cooling the fresh feed material.

A general operating mode is as follows. Feed enters the process through heat exchangers where the cold is recovered from the product and concentrate streams exiting the system. This feed then enters the freezer or crystallizer where a portion of it is converted to a solid, in discrete, relatively small (100 to 500 microns) crystals. The crystals are pumped as slurry from the freezer to a separator which removes the liquid from the slurry, and usually washes the crystals with a small portion of either melted product or some suitable wash material that will not dissolve the crystal. Most of the liquid is recycled to the freezer where more of the desired constituent is recovered. Excess concentrate is bled from the system, through the feed exchanger, to prevent excessive build-up of impurities. The washed crystal is then melted, either directly in contact with the refrigerant (which condenses on the crystal giving

up its latent heat to melt the crystal), or through a heat exchange surface. Part of the melted product can be recycled to re slurry the washed crystal, as necessary. The net product flow is pumped through the feed exchanger and out of the system. The refrigeration equipment removes heat from the freezer and transfers it to the melter, with any excess heat being removed from the system through the heat rejection compressor.

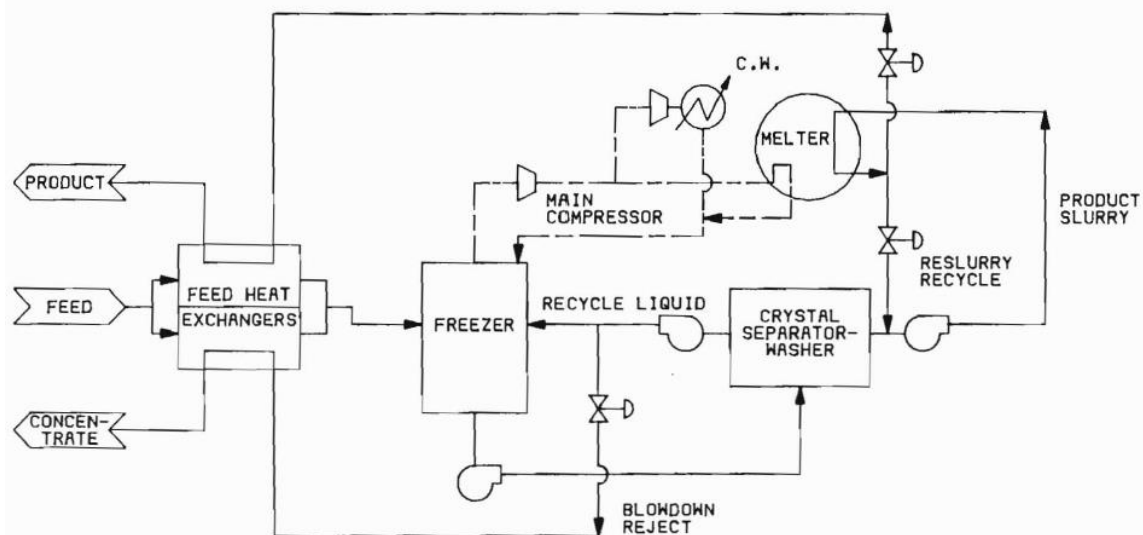


Fig. 1 Freeze Crystallization Process Diagram

2. REDUCTION OF COD FROM INDUSTRIAL EFFLUENT

Chemical Oxygen Demand test is commonly used to indirectly measure the amount of organic compounds in water. The basis for COD test is that nearly all organic compounds can be fully oxidized to carbon dioxide with strong oxidizing agent under acidic conditions. Potassium dichromate is a strong oxidizing agent under acidic conditions. (Acidity is usually achieved by the addition of sulfuric acid). For all organic matter to be completely oxidized an excess amount of potassium dichromate must be present. Once oxidation is complete, the amount of excess potassium dichromate is titrated with ferrous ammonium sulphate (FAS) until the entire oxidizing agent has been reduced to Cr^{+3} . Typically, the oxidation-reduction indicator ferroin is added during the titration step as well. Once all the excess dichromate has been reduced, the ferroin indicator changes from blue-green to reddish brown. This test is widely used to determine:

- Degree of pollution in water bodies and their self-purification capacity,
- Efficiency of treatment plants,
- Pollution loads, and
- Provides rough idea of biochemical oxygen demand (BOD) which can be used to determine sample volume for BOD estimation.

The limitation of the test lies in its inability to differentiate between the biologically oxidizable and biologically inert material.

COD determination has an advantage over BOD test in that the results can be obtained in less than 5 h where as BOD determination requires 3 or 5 days. Further the test is relatively easy and precise. Also there is not much interference as in the case of BOD.

2.1 Principle

Most of the organic matters are destroyed when boiled with a mixture of potassium dichromate and sulphuric acid producing carbon dioxide and water. A sample is refluxed with a known amount of potassium dichromate in sulphuric acid medium and the excess of dichromate is titrated against ferrous ammonium sulphate.

The amount of dichromate consumed is proportional to the oxygen required to oxidize the oxidizable organic matter.

2.2 Apparatus:

Reflux Apparatus — consisting of series of flat bottom, 150 to 250 ml capacity tubes with glass joint and a long condenser.

Hot Plate — A digester block on which a series of refluxing sets are connected to provide uniform heating to all the tubes.

2.3 Reagents:

1. Standard Potassium Dichromate, 0.25 N—Dissolve 12.259 g potassium dichromate to 1 litre of distilled water.

2. Sulphuric Acid

3. Standard ferrous ammonium sulphate approx. 0.25N (0.25M): Dissolve 98g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in about 400mL distilled water. Add 50mL concentrated H_2SO_4 and dilute to 600mL.

4. Ferroin indicator

5. Mercuric Sulphates: HgSO_4 , crystals, analytical grade.

2.4 Procedure

- a) In one reflux, take 10 ml H_2SO_4 , 10 ml $\text{K}_2\text{Cr}_2\text{O}_7$ (0.25), 10 ml effluent and 0.4g of HgSO_4 in 250 ml reflux sample. Mix well.
- b) If the color turns green, either take fresh sample with lesser aliquot or add more potassium dichromate and acid.
- c) In an another reflux , take , take 10 ml H_2SO_4 , 10 ml $\text{K}_2\text{Cr}_2\text{O}_7$ (0.25), 10 ml distilled water and 0.4g of HgSO_4 in 250 ml reflux sample. Mix well.
- d) Connect the flask to condenser. Mix the contents before heating. Improper mixing will result in bumping.
- e) Reflux for a minimum of 2 hours. Cool and then wash down condenser with distilled water.
- f) Disconnect reflux condenser.
- g) Cool to room temperature and titrate excess $\text{K}_2\text{Cr}_2\text{O}_7$ with 0.1M FAS using 2-3 drops of ferroin indicator. The sharp color change from blue green to reddish brown indicates endpoint or completion of the titration. After a small time gap, the blue-green color may reappear. Use the same quantity of ferroin indicator for all titrations.
- h) Reflux blank in the same manner using distilled water instead of sample.

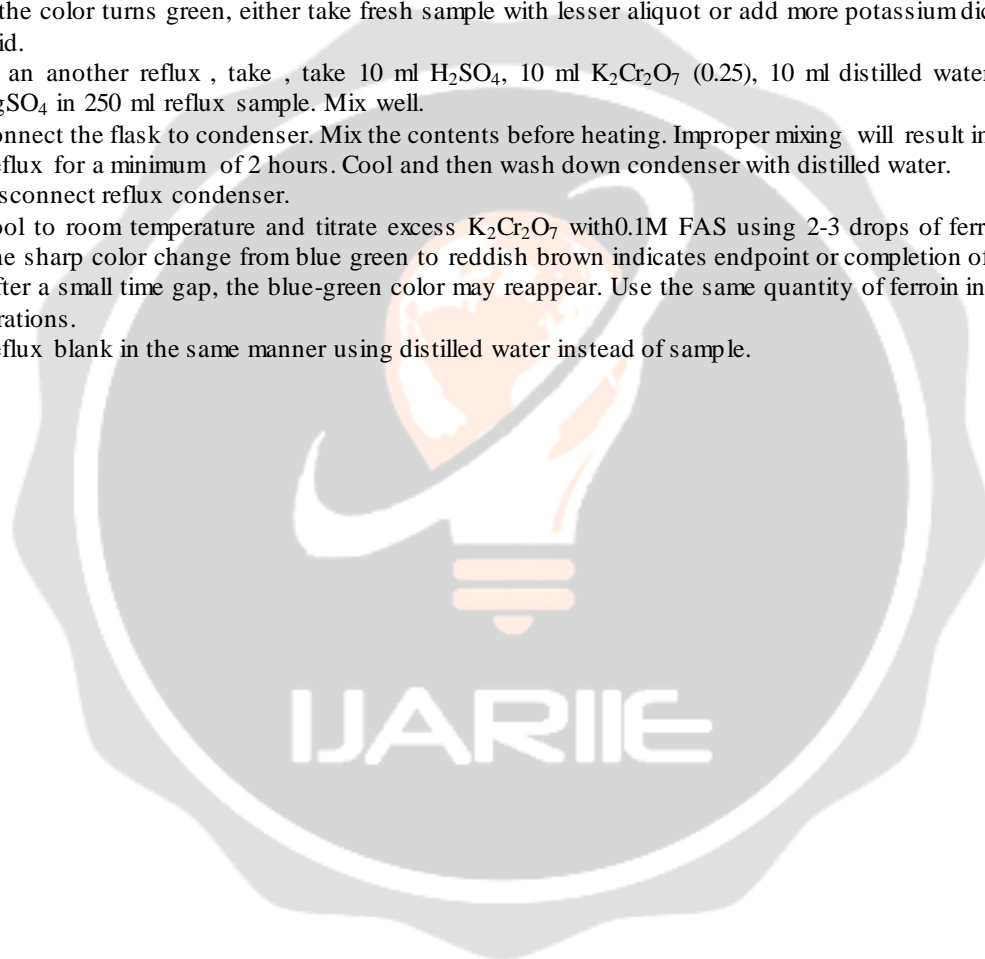




Fig. 2: COD Apparatus

2.5 Standardization of Ferrous Ammonium Sulphate

Dilute 10.00 ml standard $K_2Cr_2O_7$ solution to about 100 ml. Add 30 ml concentrated H_2SO_4 , and cool. Add 3-4 drops of ferroin indicator and titrate with ferrous ammonium sulphate till the colour changes to wine red.

$$\text{Normality of ferrous ammonium sulphate} = \frac{10 \times 0.25}{V}$$

Here,

V= volume of $Fe(NH_4)_2(SO_4)_2$ required for titration, in ml.

2.6 Calculation

$$COD \text{ mg/l} = \frac{(V_1 - V_2) N \times 8000}{V_0}$$

where

V_1 = volume of $Fe(NH_4)_2(SO_4)_2$ required for titration against the blank, in ml = 24;

V_2 = volume $Fe(NH_4)_2(SO_4)_2$ required for titration against the sample, in ml;

N= Normality of $Fe(NH_4)_2(SO_4)_2$; and

V_0 = volume of sample taken for testing, in ml.(10 ml in this case)

Results are expressed as mg/l of O_2 .

2.7 Procedure for COD Testing

- Take a phenolic effluent of Meghmani Dyes Industry
- Above mixture is then freeze in apparatus upto $-5^{\circ}C$
- As desired temperature is achieved ice (solids) and melt are separated.

- Ice is crushed into fine crystals and washed by melts. Then crystals and melt are analysed
- The Procedure is repeated for -8°C & -10°C temperature.

2.8 Result

Table: Result Summary for COD Reduction

| Sample | Temperature ($^{\circ}\text{C}$) | Vol. of Sample taken (ml) | Burette Reading V_2 | COD(mg/l) |
|-------------|------------------------------------|---------------------------|------------------------------|-----------|
| Feed Sample | 35 | 0.5 | 19.4 | 7669.12 |
| Melt | -5 | 0.4 | 18 | 12504 |
| Crystal | | 1.2 | 15.8 | 5696.2 |
| Melt 1 | -8 | 1.0 | 14.8 | 7669.12 |
| Crystal 1 | | 1.5 | 17.5 | 3612.26 |
| Melt 2 | -10 | 1.3 | 14 | 6412.3 |
| Crystal 2 | | 2.6 | 19.1 | 1571 |

3. ACKNOWLEDGEMENT

I would like to pay my heartfelt thanks to M/s Meghmani Dyes Industry, Vatva, for providing me with their effluent sample, to perform this experiment.

4. CONCLUSION

From the experiment performed it is apparent that Phenolic Effluents can be easily treated with freeze crystallization. Also, the results show that there is approx. 80% reduction in COD in just three stages of freeze crystallization.

5. REFERENCES

- [1]. F. van der Ham, G.J. Witkamp, J. de Graauw, and G.M. van Rosmalen, "Eutectic freeze crystallization: Application to process streams and waste water purification", Chemical Engineering and Processing 37 (1998) 207–213
- [2]. Raymond Vaessen, Marcelo Seckler, and Geert Jan Witkamp, "Eutectic Freeze Crystallization with an Aqueous $\text{KNO}_3\text{-HNO}_3$ Solution in a 100-L Cooled-Disk Column Crystallizer", Ind. Eng. Chem. Res. 2003, 42, 4874-4880
- [3]. Frank van der Ham, Marcelo Martins Seckler and Geert Jan Witkamp, "Eutectic freeze crystallization in a new apparatus: the cooled disk column crystallizer", Chemical Engineering and Processing 43 (2004) 161–167
- [4]. James A. Heist, "Freeze Crystallization: Improving The Energy Efficiency Of a Low-Energy Separation Process", Proceedings from the Third Industrial Energy Technology Conference Houston, TX, April 26-29, 1981
- [5]. JigarMalaviya, "Separation of Azeotropic and Heat Sensitive Material using Freeze Crystallization", Gujarat Technological University, Ahmedabad, 2015
- [6]. S.B.Thakore, B.I. Bhatt, *Introduction to Process Engineering and Design*, 2nd ed., McGraw-Hill, New York, 2010.
- [7]. Robert E. Treybal, *Mass Transfer Operations*, McGraw Hill International Publications, 3rd ed., 1981.
- [8]. Perry R. H., Maloney J. O., *Perry's Chemical Engineers' Handbook*, 8th ed., McGraw-Hill, New York, 2008
- [9]. S. B. Thakore, B. I. Bhatt, "Stoichiometry", 5th ed., Tata McGraw Hill Education Private Ltd., 2010