Color Removal and COD Reduction of Organic Effluent Stream from a Petrochemical Plant

Swati Jain, Priyadarshini Lenka, Pujan Vaishnav, Jinali Shah, Ajay Joshi

Abstract: The best known procedures for effluent treatment from petrochemical industry are to be discussed and systematized. This article briefs the concerns raised due to wastewaters released by petrochemical industry, treatment methods presently used for treating the petrochemical industrial effluents and new innovative processes proposed for the petrochemical industrial effluents. This paper investigates the various effluent treatment methods for the removal of color and COD reduction in caprolactam effluent. The results demonstrated that advanced oxidation processes are found to be effective for the removal of color and COD reduction from caprolactam effluent.

Keywords: Caprolactam, effluent, reduction, treatment.

I. INTRODUCTION

The production of caprolactam has been started in India in 1974 with the commissioning of 20,000 MTPA plant at Vadodara by Gujarat State Fertilizers and Chemicals Ltd. (GSFC). A new plant of caprolactam at GSFC was commissioned after a few years with capacity of 50,000 MTPA caprolactam and 1,20,000 MTPA ammonium sulphate as by-product. During production of caprolactam, crude caprolactam containing traces of ammonium sulphate and other organic impurities is purified by counter current extraction with organic solvent. Concentrated solution containing caprolactam and organic solvent is further concentrated by distillation and organic solvent is recycled. Pure caprolactam is obtained as distillate after removing light impurities. The residue from the bottom is collected and pumped to effluent treatment plant. The residue i.e. caprolactam wastewater (Caprolactam effluent stream) is produced at a volume of 80 m^3/day having a COD value 50,000-70,000 ppm and color value 2800-3000 Pt-Co.

Under a sustainability drive for zero effluent discharge by GSFC, various methods have been researched for this stream. After initial identification of organics in the stream, various methods such as wet air oxidation, adsorption by charcoal, fly ash, membrane studies, freezing followed by de-freezing, incineration, biodegradation, evaporation followed by solvent extraction, coagulation, flocculation, adsorption followed by aerobic biodegradation, chlorination/hydrogen peroxide/UV treatment have been tried. Fig. 1 represents various wastewater treatment technologies used in petrochemicals industry. Around 35% petrochemicals industry in US have biological treatment facilities followed by ion exchange, membrane treatment and physico-chemical treatment [1].

II. TREATMENT PROCESSES/EXPERIMENTS

Presence of long chain organic components (Fig. 2) along with ammonium sulphate and both has high solubility in water makes the treatment of caprolactam effluent stream a very complex process. Fig. 2 shows Gas Chromatography Mass Spectrometer (GCMS) results (Done in SICART Vadodara, 2015) on caprolactam effluent stream. The peaks identified in GCMS graph shows presence of derivatives of cyclohexanol, cyclohexanone and caprolactam in the subject stream.

Revised Manuscript Received on November 15, 2019

Swati Jain, Research & Development, Gujarat State Fertilizers and Chemicals (GSFC) Limited, Vadodara, India. Email: skjain@gsfcltd.com

Priyadarshini Lenka, Research & Development, Gujarat State Fertilizers and Chemicals (GSFC) Limited, Vadodara, India. Email: pplenka@gsfcltd.com

Pujan Vaishnav, Research & Development, Gujarat State Fertilizers and Chemicals (GSFC) Limited, Vadodara, India. Email: pujan.vaishnav@gsfcltd.com

Fig. 2. GCMS results showing long chain derivatives of Cyclohexanone and caprolactam
The typical analysis of caprolactam effluent has been shown in Table 1. Various physicochemical processes and biological treatment such as incineration, wet air oxidation, membrane treatment, adsorption by charcoal, fly ash, freezing followed by de-freezing, other chemical treatment followed by aerobic biodegradation, biodegradation, coagulation, flocculation, evaporation followed by solvent extraction, chlorination, and hydrogen peroxide were employed on caprolactam effluent to see the effect on COD and color reduction.

### Table-1: Caprolactam effluent stream analysis

| S. No. | Parameter          | Concentration  |
|--------|--------------------|----------------|
| 1.     | Organic impurities | 4-5% wt.      |
| 2.     | Ammonium sulphate  | 2-4% wt.      |
| 3.     | Water              | Approx. 94%    |
| 4.     | Temperature        | 40°C           |
| 5.     | Density            | 0.994 g/cc     |
| 6.     | Viscosity          | 0.94 cp        |
| 7.     | Molecular Weight   | 100            |

**A. Incineration**

Incineration is a waste treatment method involving the combustion of organic substances present in waste substances. Incineration and other high-temperature waste treatment systems are known as “thermal treatment processes.” Incineration of waste substances converts the waste into flue gas, ash and heat. It can achieve more than 90% volume reduction in waste. Advantages of incineration include high reduction degree and no further decomposition required. In addition to this, the ashes can be used as soil coverage. During incineration, the pathogens are all burned to death, and the perishable organics generating harmful gases are also fully oxidized [2]. The operation of burning is efficient, reliable, stable and clean. In the caprolactam effluent stream, incineration was tried.

**B. Wet Air Oxidation method**

Wet air oxidation (WAO) is one of the existing technologies for the treatment of wastewaters and comes under the category of advanced oxidation processes. In this process, wastewater is oxidized in the liquid phase at temperature ranges from 125-300°C and pressures ranges from 0.5-20 MPa respectively in the presence of an oxygen-containing gas usually air [3]. The major limitations of WAO are the high capital costs and safety factors associated with a system operating at such high operating conditions.

**C. Treatment using Membrane Technology**

Membranes have an important place in chemical industries and are used in wide range of applications. Fig. 3 [4] represents cut off of various membrane separation technologies. The key role of using the membrane in chemical applications is the ability of a membrane to control the permeation rate of a chemical species [5]. The advantages of membrane technology are primarily used for saline and seawater upgrading [6].

**D. Adsorption by charcoal & fly ash**

Among all the available treatment processes, adsorption has been one of the most effective and comparatively low cost methods for the decolorization of colored effluents. Variety of adsorbents such as activated carbon, perlite, bentonite, silica gels, fly ash, lignite, peat, silica has been used for the removal of impurities from waste aqueous solutions. The ability of charcoal to bind chemicals has been recognized for ages [7]. Activated carbon/charcoal has high surface area, microporous structure and radiation stability. It is therefore finds application in various industrial processes as adsorbent, catalyst or catalyst support. The adsorption properties of activated carbon mainly depend on its particle size, ash content, porosity, degree of carbonization and method of activation [8]. The regeneration of activated charcoal is difficult and costly process due to energy intensive nature [9]. Fig. 4 represents basic mechanism of adsorption using activated charcoal.

**E. Freezing followed by de-freezing**

Freezing possesses great potential for concentrating industrial wastewater and recovering valuable products. This approach provides a possibility to feed a waste stream directly into the system without the use of chemical and filters. The advantages of a low temperature process over other treatment systems for industrial waste treatment includes immunity to fouling, negligible corrosion and lack of any pre-treatment requirements [10]. Fig. 5 represents caprolactam effluent stream in frozen condition.
F. Chemical treatment followed by aerobic biodegradation

Aerobic biodegradation is the breaking of organic compounds by microorganisms in presence of oxygen/air. It converts the complex organic matter into simpler compounds like carbon dioxide and new biomass. Oxygen is continuously required during aerobic treatment, so forced air from an air blower or compressor is mixed with the wastewater and biodegradation takes place. Aerobic, in comparison with anaerobic digestion, does not produce foul gases. The aerobic treatment also makes the environment of the workers and the animals congenial and helps to keep pathogens in check. After chemical treatment such as activated charcoal adsorption, freezing followed by defreezing, aerobic biodegradation was tried on caprolactam effluent stream.

G. Biodegradation

Biodegradation is the treatment process in which complex organic matter is broken down into smaller compounds by the enzymes produced by living microorganisms. The microorganisms transform the substance through metabolic or enzymatic processes. Organic material can be degraded aerobically or anaerobically, with oxygen or without oxygen respectively. Fig. 6 represents the process of biodegradation [11].

H. Coagulation and Flocculation

Coagulation-flocculation is another treatment method involving the cationic inorganic metal salts are used as coagulants and long chains non-ionic or anionic polymers are used as flocculants. Though, the coagulation process alone is not always feasible as it may result in small flocs or when coagulation takes place at low temperature resulting in producing fragile flocs which breakup due to physical forces. To prevent this, anionic/non-ionic polymeric flocculants are used to bring the smaller flocs together and agglomerate the slow-settling micro-flocs formed by the coagulant to form larger and denser flocs, thereby allowing their removal in further sedimentation, flotation and filtration steps [12]. The use of flocculants is to increase the density and the solidity of the flocs formed and it also can reduce the consumption of coagulants and helps in the ease of operation and the throughput capacity of the treatment plant. The effectiveness of coagulation depends on the coagulating agent used, the solution pH, the dosage, the nature of the organic compound present in water, and the concentration [13]. Fig. 7 represents the basic mechanism of coagulation and flocculation process [14].

I. Evaporation followed by solvent extraction

From aqueous waste streams, evaporation is done to remove water and other low volatile organics. Solvent extraction is done to recover valuable by product from remaining organic compound containing high value product based on solubility.

J. Treatment by Chlorination

Chlorination is the most widely used disinfection technique for municipal wastewater because it destroys target organisms by oxidizing cellular materials [15]. Chlorine can be supplied in various forms, including chlorine gas, hypochlorite solutions, and other chlorine compounds in solid or liquid form. Some of the main advantages of this process are as follows:

- It is an established technology.
- Presently, chlorine is more cost effective disinfection process than UV or ozone disinfection.
- It is effective and reliable against a wide spectrum of compounds.
- It has flexible dosing control.

K. Treatment using Hydrogen Peroxide

Hydrogen peroxide ("H₂O₂") is a potent oxidizing agent more powerful than chlorinate or potassium permanganate. Hydrogen peroxide liquid is a compound of hydrogen and oxygen (H₂O₂). It is prepared by electrolytic oxidation of sulphuric acid, and by methods involving reduction of oxygen. It is used as a disinfectant, and an oxidizer for submarine propellant and rocket fuel.
The applications of hydrogen peroxide are in the bleaching of pulp for paper manufacturing, household disinfectant and as a bleaching agent for hair. It is becoming more widely used than chlorine in industries because the products of its decomposition are water and oxygen while the decomposition of chlorine bleaches produces poisonous chlorine gas and sometimes salts of chloride (like calcium chloride)/sludge generation. Hydrogen peroxide decomposes into oxygen and water leaving no trace of chemical residues. Thus, the treated water becomes colorless, odorless and non turbid [16]. When peroxide is added to water a large amount of dissolved oxygen is released and a powerful oxidizing effect occurs.

\[ 2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \]

A proposed mechanism for the decomposition of hydrogen peroxide consists of three elementary stages:

\[ \text{H}_2\text{O}_2 \text{ (g)} \rightarrow 2 \text{OH} \text{ (g)} \]
\[ \text{H}_2\text{O}_2 \text{ (g)} + \text{OH} \text{ (g)} \rightarrow \text{H}_2\text{O} \text{ (g)} + \text{HO}_2 \text{ (g)} \]
\[ \text{HO}_2 \text{ (g)} + \text{OH} \text{ (g)} \rightarrow \text{H}_2\text{O} \text{ (g)} + \text{O}_2 \text{ (g)} \]

The basic mechanism states those two molecules of hydrogen peroxide break down to form two molecules of water and one molecule of oxygen gas, along with heat energy.

### III. RESULTS AND DISCUSSION

**A. Incineration**

Incineration is the most advanced level of the waste disposal/treatment hierarchy. However, the disposal cost of ash and the operating cost are found to be high. Incineration was tried on subject stream; however, estimated operating cost of the process was very high.

**B. Wet Air Oxidation (WAO) method**

WAO reduced 90% COD in caprolactam effluent stream for 1 hour at high temperature and high pressure. The advantages of the process are low operating costs and minimal air pollution discharges. The main limitations are the high capital costs and safety factors associated with a system operating at such high operating conditions of temperature and pressure.

**C. Treatment using Membrane Technology**

Membrane studies (filtration through 5µ cartridge filter) were also carried out on caprolactam effluent stream. 60% removal was achieved, and later charcoal/biological treatment can be used as post treatment options for more reduction. The membrane technology is feasible only when extra high quality of water is to be produced for later use. The major disadvantages are membrane fouling, limited membrane life, operating cost, huge capital investment.

**D. Adsorption by charcoal & fly ash**

Activated carbon adsorption (0.5% loading) resulted in 5% COD reduction. Fly ash was used for color removal of caprolactam effluent stream. No significant color reduction was observed in the process.

**E. Freezing followed by De-freezing**

The process of freezing and de freezing resulted in separation of stream into three layers. Table II represents the results of COD, pH and density of three layers.

| Sample         | COD (ppm) | pH  | Density (g/cc) |
|----------------|-----------|-----|----------------|
| Initial P-832  | 63,638    | 3.2 | 1.023          |
| Layer 1        | 1,647     | 3.8 | 0.9979         |
| Layer 2        | 26,965    | 3.3 | 1.003          |
| Layer 3        | 1,13,528  | 3.2 | 1.089          |

Fig. 8 represents separation of layers after de freezing. However, freezing is an energy intensive process.

**F. Chemical treatment followed by aerobic biodegradation**

The results of chemical treatments were employed as pretreatment followed by aerobic biodegradation are listed in Table III. From the table, almost 40-75% reduction in COD was observed through different processes.

**G. Biodegradation**

Biodegradation studies of ammonia stripped caprolactam effluent stream using BOD plant sludge were also carried out, sewage sludge, pure *pseudomonas* culture and other cultures were isolated from various industrial areas. It was found that they were acclimatized for caprolactam effluent stream for extended intervals (11-20 days), initial COD reduction was 10-20% but was not maintained after 11 days. Denitrification chamber and supplement Carbon source were also added, but results were the same.

**H. Coagulation and Flocculation**

Polymeric flocculants along with/without coagulants were also tried in caprolactam effluent stream using 0.1% flocculants and it resulted in only less than 10% COD reduction. Though, the synthetic polymeric flocculants used in this process have the main problems of non-biodegradability, while the natural flocculants are concerned with moderate efficiency and short shelf life [10].
Table III: Results of Chemical treatment followed by aerobic biodegradation of Caprolactam effluent stream

| Chemical Treatment | % COD reduction | Aerobic biodegradation | Further % COD reduction |
|--------------------|----------------|------------------------|-------------------------|
| Lime 1% (2 hr) Mixing and filtration | 40 | Old BOD sludge | 20 |
| Fenton’s reagent (FeCl₃ + H₂O₂, 24 hour) | 40 | - | - |
| FeSO₄ + H₂O₂ | 50 | - | - |
| Fenton’s reagent + lime | 60 | - | 14-27 |
| Fenton’s reagent + lime + activated carbon | 75 | Cultures from Cooling Tower | 27 |
| Electrochemical oxidation | 10 | - | - |
| TiO₂+Sunlight+Air (11 hr) | 5 | - | - |
| TiO₂+Sunlight+H₂O₂ (2 days) | 43 | - | - |
| TiO₂+UV (365nm), 3 hr | NIL | - | - |
| H₂O₂+UV (365nm) | 10 | - | - |
| TiO₂+H₂O₂+UV (3 hr) | 66 | - | - |

I. Evaporation followed by solvent extraction
The initial evaporation of raw effluent is performed in two steps to generate a concentrated mixture of organics and ammonium sulphate (AS). The solvent required to extract the organics from the concentrated mixture is optimized after trials. The solvent was recovered by distillation and residue was incinerated yielding 0.6% ash.

J. Chlorination
Chlorination was used in caprolactam effluent to remove color and to reduce COD at room temperature under stirring conditions. 40% reduction in color and 30% reduction in COD were observed. In addition to this, sludge generation in the form of calcium chloride was obtained.

K. Hydrogen Peroxide Treatment
Hydrogen peroxide was used in caprolactam effluent to remove color and to reduce COD at room temperature under stirring conditions. An appreciable reduction in color was obtained accounting 76% reduction in color as seen in Fig. 9. Out of various treatment processes done on caprolactam effluent stream, this process was found to be the most effective, clean, fast and generates zero residue after treatment.

Table IV illustrates reduction in color and COD value on caprolactam effluent using different concentration of hydrogen peroxide at regular intervals.

Table IV: Hydrogen Peroxide treatment on caprolactam effluent stream

| Sample | AN (%w/w) | COD (ppm) | Color (Pt-Co) |
|--------|-----------|-----------|--------------|
| Caprolactam Effluent | 0.397 | 47279 | 2900 |
| Caprolactam Effluent (Caustic Lye addition) | 0.336 | 46860 | 3600 |
| H₂O₂ (25 kg addition, 0 min) Sample took after 5 min | 0.325 | 43932 | 2200 |
| H₂O₂ (50 kg addition, 30 min) Sample took after 30 min | 0.322 | 40,187 | 1400 |
| H₂O₂ (75 kg addition, 90 min) Sample took after 90 min | 0.316 | 39,254 | 1000 |
| H₂O₂ (100 kg addition, 120 min) Sample took after 8 h | 0.272 | 38,074 | 700 |

Table V represents a summary on various treatment methods employed on caprolactam effluent stream with COD reduction and remarks.
Color Removal and COD Reduction of Organic Effluent Stream from a Petrochemical Plant

Table-V: A brief summary on various treatment methods

| Chemical Treatment          | COD reduction | Remarks                      |
|----------------------------|---------------|------------------------------|
| Incineration                | -             | High operating cost          |
| Wet air oxidation           | 90%           | High operating cost          |
| Membrane studies            | 60%           | High cost and membrane fouling |
| Activated Carbon adsorption| 10-12%        | Not effective                |
| Solvent extraction          | -             | Not effective                |
| Biodegradation studies      | 10-20%        | -                            |
| Polymeric flocculants       | 10%           | -                            |
| Coagulation followed by polymeric flocculation | 20% | Not effective |
| Concentration               | -             | Not effective                |
| Adsorption using fly ash    | -             | Not effective                |
| Activated Carbon adsorption followed by biological treatment | 30-35% | Not effective |
| Evaporation followed by solvent extraction | AS recovered/Zero Effluent Discharge | High operating cost |
| Freezing followed by defreezing | Three layers obtained (topmost): | Requires post treatment (biological treatment/adsorption) of all three layers. As bottom layer is having COD more than 1 lac ppm having calorific value 1273 Cal/g, so incineration can be employed. |
| Chlorination                | 50% reduction in COD and color | Sludge generation (Calcium chloride) & high chloride content |
| Hydrogen peroxide           | 20% reduction in COD and color | Clean process and zero residue generation |

IV. CONCLUSIONS

The conventional treatment methods used in current scenario have certain short comings like health hazards, operational costs and risks associated with the effluents released by the petrochemical industries. An effort was made to document identification and formulation of presently available/new technologies for the safe and economic treatment of the caprolactam effluent stream. Among all these methods, particularly advanced oxidation processes such as wet air oxidation and hydrogen peroxide treatment were found to be efficient, effective and convenient for caprolactam effluent stream in terms of COD and color reduction respectively.

REFERENCES:

1. A Report on Wastewater Management in the Petrochemicals Industry published on 1st May, 2005 in US.
2. Li, Y., Zhao, X., Li, Y. and Li, X., 2015. Waste incineration industry and development policies in China. Waste Management, 46, pp.234-241.
3. Kolaczkowski, S. T., Plucinski, P., Beltran, F. J., Rivas, F. J., & McLurch, D. B. (1999). Wet air oxidation: a review of process technologies and aspects in reactor design. Chemical Engineering Journal, 73(2), 143-160.
4. Mukherjee, S. (2019). Isolation and Purification of Industrial Enzymes: Advances in Enzyme Technology. In Advances in Enzyme Technology, Elsevier, pp. 41-70.
5. Baker, R. W. (2012). Membrane technology and applications. John Wiley & Sons.
6. Bick, A., Gillerman, L., Manor, Y., & Oron, G. (2012). Economic assessment of an integrated membrane system for secondary effluent polishing for unrestricted reuse. Water, 4(1), 219-236.
7. Neuvonen, P. J., & Ollikka, K. T. (1988). Oral activated charcoal in the treatment of intoxications. Medical toxicology and adverse drug experience, 3(1), 33-58.
8. Iqbal, M. J., & Ashiq, M. N. (2007). Adsorption of dyes from aqueous solutions on activated charcoal. Journal of Hazardous Materials, 139(1), 57-66.
9. Tiruneh, A. T., Fadiran, A. O., Ndela, W. N., & Heikkila, J. (2016). Assessment of technical and economic feasibility of activated charcoal removal of organic matter from different streams of grey water through study of adsorption isotherms. American Journal of Environmental Protection, 5(3), 56-64.
10. Partyka, V. (1986). Freezing for wastewater recovery. Met. Finishing, 84(11), 55-57.
11. http://www.tikp.co.uk/knowledge/material-functionality/biodegradable/fibre-degradation/.
12. Lee, C. S., Robinson, J., & Chong, M. F. (2014). A review on application of flocculants in wastewater treatment. Process Safety and Environmental Protection, 92(6), 489-508.
13. Sher, F., Malik, A., & Liu, H. (2013). Industrial polymer effluent treatment by chemical coagulation and flocculation. Journal of Environmental Chemical Engineering, 1(4), 684-689.
14. Hanhui, Z., Xiaooi, Z., & Xuehui, Z. (2004). Coag-flocculation mechanism of flocculant and its physical model. Separations Technology VI: New Perspectives on Very Large-Scale Operations, Art, 8, 1-9.
15. Tree, J. A., Adams, M.R. and Lees, D.N. 2003. Chlorination of indicator bacteria and viruses in primary sewage effluent. Appl. Environ. Microbiol., 69(4), pp.2038-2043.
16. Adeyinka J. S., Rim-Rukeh A. (1998). Effect of hydrogen peroxide on industrial waste water effluents: a case study of warri refining and petrochemical industry. Environmental Monitoring and Assessment, 1999 – Springer.

AUTHORS PROFILE

Dr Swati Jain is Ph.D. from Department of Chemical Engineering, MNIT Jaipur and joined GSFC R&D in year 2014. Presently she is serving as Additional Manager (Research) and engaged in new product development, quality improvement projects as well as utilization and treatment of various process waste streams. During her academic career, she was awarded with Graduate Student Exchange Programme (GSEP) Fellowship in University of Saskatchewan, Canada. She also holds Post Graduate Diploma in Nanobiotechnology (PGDNT) from LSFI India and a certificate course on Export Import Management from MSU, Vadodara. Her major contributions were published in the area of Environment & Chemical Engineering Journals as well as she was awarded with Young Scientist Award in 2016 by Venus International Research Association. Recently she was listed in Super 100 Power Women of Udaipur by Rotary Club Panna.

Priyadarshini Lenka is B. Tech in Chemical Engineering from Institute of Technology, Nirma University, Ahmedabad. She is currently working as Research Officer at Gujarat State Fertilizers & Chemicals Limited (GSFC), R & D wherein she is engaged in looking after product scale up and optimization activity from lab to pilot to commercial scale in coordination with R & D scientists, projection and design execution teams. During her academic career she has gone through plant training at Oil and Natural Gas Corporation (ONGC) Ltd, Hazira Surat and KRBHICO, Hazira Surat.
Also her team was awarded 1st position in paper presentation at International Conference on Chemical Industry (ICCI-2014) under the topic “Recent trends in Bio-diesel Blends” held at PDPU-Gandhinagar. At GSFC, she has gained experience in production from Caprolactam and Nylon-6 plants.

Dr. Pujan Vaishnav (Ph.D.) is presently serving as Chief (R&D, QC) at Gujarat State Fertilizers & Chemicals Limited (GSFC), R & D. More than 18+ years of experience in chemical sector with various strategic positions in Research & Development, Quality & Manufacturing Operations. His major areas of expertise includes new product development, technology development & evaluation, technology transfer, process development, improvement of existing product range, scaling up new products, financial planning & control, etc. Executed various projects sponsored by Department of Ocean Development, Counsel of Scientific & Industrial Research. Contributed in six Research Patents, 50+ Research paper publications and scientific Presentation on articles in various conferences and symposium. Currently working towards development of new products in synergy with GSFC’s product profile, value additions from waste streams, providing innovative solutions for continuous improvements in product quality and plants functioning, support operations in the fields of Metallurgy, Corrosion & Microbial Monitoring, quality control of raw materials, intermediates and finished products in GSFC. He is certified ‘Six Sigma Green Belt’ in process improvement & effectiveness.