

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 m³/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].

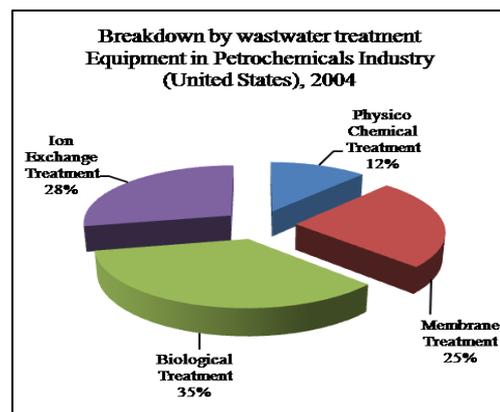


Fig. 1. Various wastewater treatment technologies used in petrochemicals industry [1]

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.

Manuscript published on November 30, 2019.

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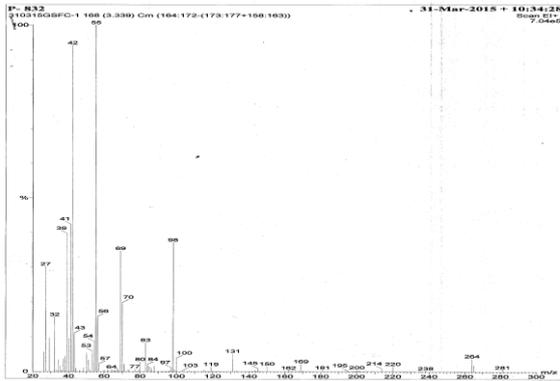


Fig. 2. GCMS results showing long chain derivatives of Cyclohexanone and caprolactam

The typical analysis of caprolactam effluent has been shown in Table I. 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- I: 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].

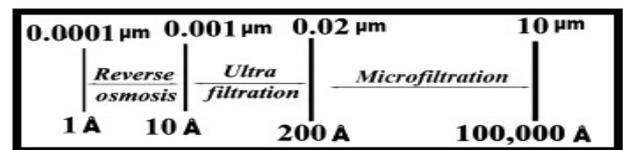


Fig. 3. Cut off of various membrane separation technologies [4].

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.

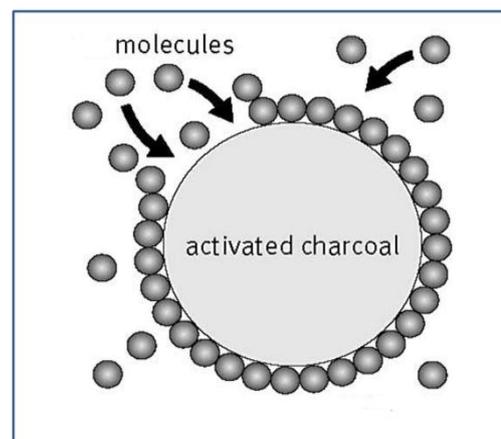


Fig. 4. Mechanism of adsorption using activated charcoal.

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.



Fig. 5. 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 de freezing, 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].

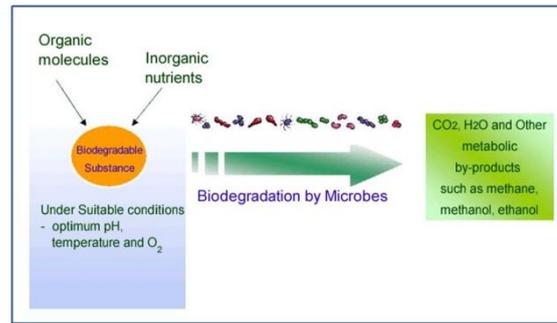


Fig. 6. Process of biodegradation [11].

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].

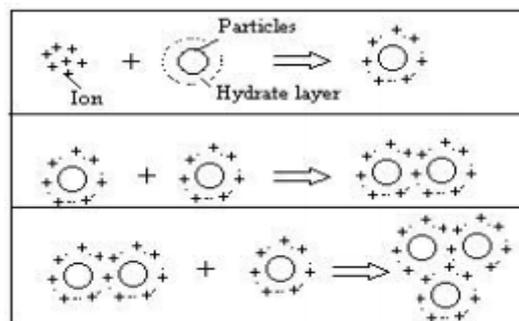


Fig. 7. Mechanism of coagulation and flocculation [14]

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:

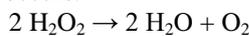
- It is an established technology.
- Presently, chlorine is more cost effective disinfection process than UV or ozone disinfection.
- It is effective and reliable against a wide spectrum of compounds.
- It has flexible dosing control.

K. Treatment using Hydrogen Peroxide

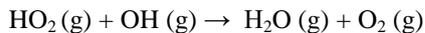
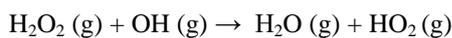
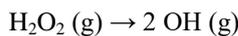
Hydrogen peroxide (“H₂O₂”) is a potent oxidizing agent more powerful than chlorinate or potassium permanganate. Hydrogen peroxide liquid is a compound of hydrogen and oxygen (H₂O₂). It is prepared by electrolytic oxidation of sulphuric acid, and by methods involving reduction of oxygen. It is used as 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.



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



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.

Table-II: COD, pH, Density of three layers

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

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

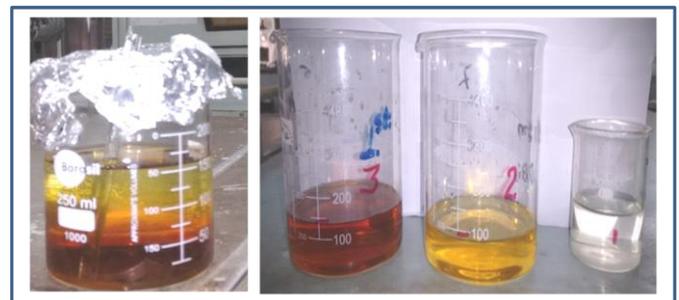


Fig. 8. Separation of layers of caprolactam effluent stream after de-freezing

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 (FeCl ₃ + H ₂ O ₂ , 24 hour)	40	-	-
FeSO ₄ + H ₂ O ₂	50	-	-
Fenton's reagent + lime	60	-	14-27
Fenton's reagent + lime + activated carbon	75	Cultures from Cooling Tower	27
Electrochemical oxidation	10	-	-
TiO ₂ +Sunlight+Air (11 hr)	5	-	-
TiO ₂ +Sunlight+H ₂ O ₂ (2 days)	43	-	-
TiO ₂ +UV (365nm), 3 hr	NIL	-	-
H ₂ O ₂ +UV (365nm)	10	-	-
TiO ₂ + H ₂ O ₂ +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.



Fig. 9. Initial Caprolactam Effluent and after H₂O₂ 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
H ₂ O ₂ (25 kg addition, 0 min) Sample took after 5 min	0.325	43932	2200
H ₂ O ₂ (50 kg addition, 30 min) Sample took after 30 min	0.322	40,187	1400
H ₂ O ₂ (75 kg addition, 90 min) Sample took after 90 min	0.316	39,254	1000
H ₂ O ₂ (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.

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 Layer 1 (topmost): Highest reduction (80-90%) Layer 2 (Intermediate) : 70% Layer 3 (Bottom): COD value increased	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.

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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 (PGDNBT) from LSFII 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 KRIBHCO, 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, Council 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.