



# COD REMOVAL THROUGH FENTON CATALYTIC REACTOR IN DYES AND DYES INTERMEDIATE INDUSTRY

## ABSTRACT

The present study focuses on the performance of FENTON CATALYTIC REACTOR for the removal of COD from wastewater generated during manufacturing process of dyes and dyes intermediate industry.

A real time case study of CETP Vatva is also conducted to illustrate impact of FENTON CATALYTIC REACTOR on to the performance of overall treatment scheme.

Case study illustrates that the Fenton Catalytic Reactor does not remain mere theoretical concept of treating refractory COD and rather proves to be an effective solution for removing refractory COD in actual practice.

The comparative study of COD value reflects that after commissioning Fenton Catalytic Reactor at CETP-Vatva , COD values reduced by approx. 60%.

Therefore, it is not out of context to state that Fenton Catalytic Reactor can be proven effective tool for reducing refractory COD of effluent generated from dyes and dyes intermediate industries. However, further research has to be carried out for optimization of its operation.

Moreover, The present study does not only limit itself to provide alternative approach to reduce COD and thereby organic load present in wastewater generated from dyes and dyes intermediate industry, but it also covers the probability of further scope of fenton treatment in terms of felicitating new horizon of wastewater treatment of different sector of industries such as textile, complex chemical compounds etc.

### ❖ Background :

Around the world, the water problem is one of mankind's greatest issues, along with manners to avoid the contamination of this vital resource's cycle.

Through its wastes and effluents, the industry can be pointed out as one of the main sources of pollution. Yet, on the other hand, the operation of this sector is imperative for all human beings' known needs after centuries of technological development. Therefore, these unwanted rejects must not reach watercourses untreated and, to do so, satisfying legislation limits is mandatory.

More than 70 % of our planet's surface is covered by water. Yet, when we look closely to the actual situation, less than 3 % of the total water volume is freshwater and most of it is frozen in ice caps and glaciers. Only 1 % of the total water resources on earth are available for human use.

Biological treatments are the most used due to attractive costs and proper organic matter removal, but not all kinds of effluents can be remediated by them.

The presence of toxic compounds or the seasonal character of some effluents may disable their application. This way, it is necessary to appeal to other degradation techniques, such as chemical treatments. In this matter, advanced oxidation processes (AOPs) have been widely used by the industry for several years.

One of them is the Fenton catalytic reaction, highlighted by the low costs associated and non-selectivity of the oxidative species generated along chain reactions.

A scientist called Henry John Horstman Fenton discovered this process in the end of the 19th century with the oxidation of tartaric acid into dihydroxymaleic acid by hydrogen peroxide in the presence of ferrous ions (Fenton, 1894).

Mechanisms for this reaction were suggested more than thirty years later, in 1932, in two lines: formation of hydroxyl radicals ( $\bullet\text{OH}$ ) followed by autocatalysis by Haber and Weiss (1932), while Bray and Gorin (1932) proposed the formation of the ferryl ion ( $\text{FeO}_2^+$ ) combined with additional equilibrium to explain the presence of  $\text{Fe}^{3+}$ .

### ❖ Objective of Study :

The present study focuses on the performance of FENTON CATALYTIC REACTOR for the removal of COD from wastewater generated during manufacturing process of dyes and dyes intermediate industry.

A real time case study is also conducted to illustrate impact of FENTON CATALYTIC REACTOR on to the performance of overall treatment scheme.

The present study does not only limit itself to provide alternative approach to reduce COD and thereby organic load present in wastewater generated from dyes and dyes intermediate industry, but it also covers the probability of further scope of fenton treatment in terms of felicitating new horizon of wastewater treatment of different sector of industries such as textile, complex chemical compounds etc

## ❖ Need of Study :

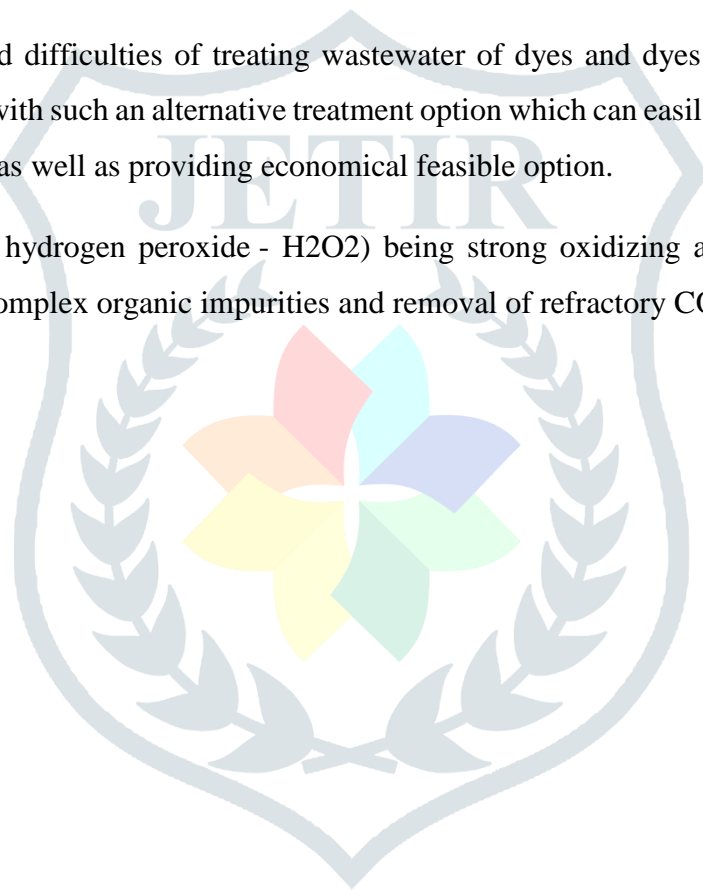
The effluent discharged from dyes and dyes intermediate industries is highly acidic and contains toxic compounds; many of them are carcinogenic and highly hazardous to human health and the environment.

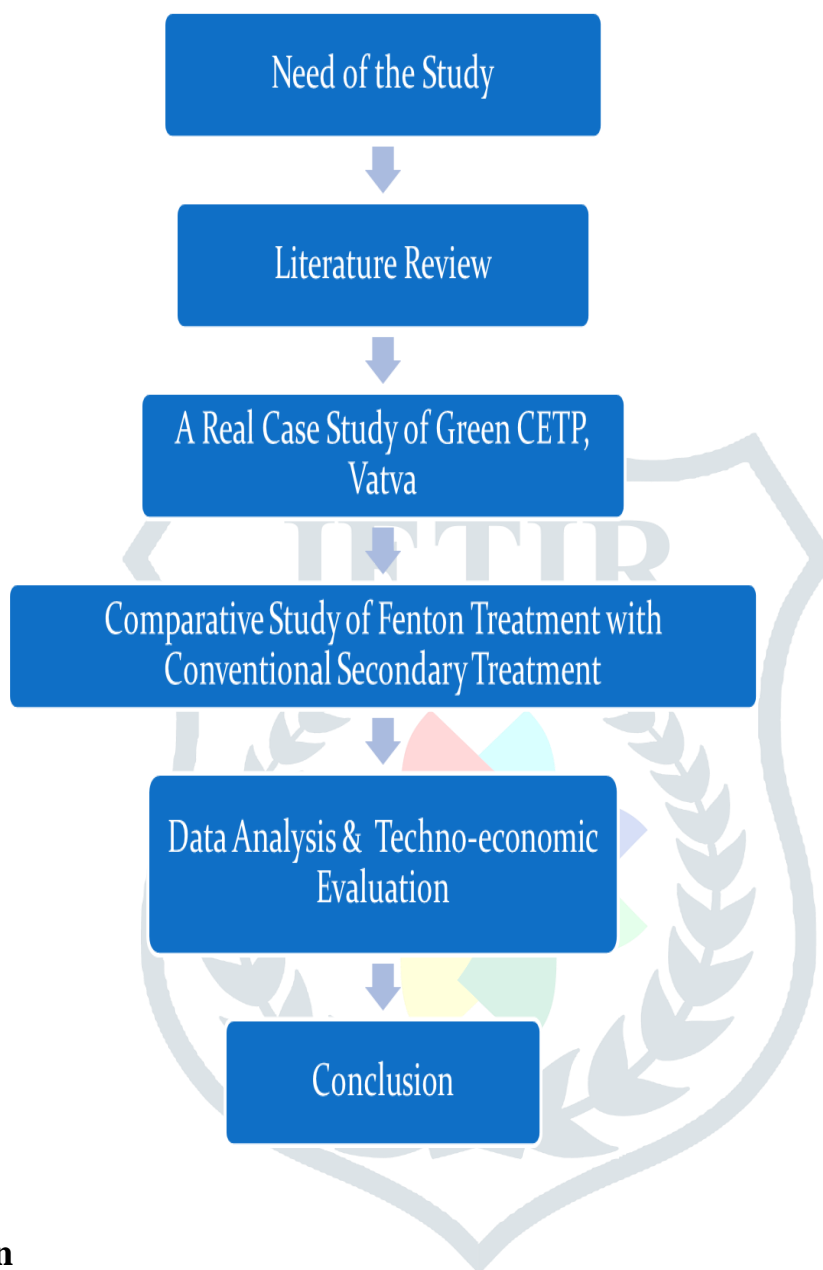
Due to the excess use of acid and alkali quantity, the wastewater contains high concentration of inorganic salts that results in the high concentration of TDS. Due to this, treatment of effluent is very difficult and highly expensive.

Moreover, COD present in this wastewater is Refractory COD which are non-biodegradable organic compounds.

Due to aforementioned difficulties of treating wastewater of dyes and dyes intermediate industries, it is necessary to come up with such an alternative treatment option which can easily treat the complex impurities present in wastewater as well as providing economical feasible option.

Fenton (a solution of hydrogen peroxide -  $H_2O_2$ ) being strong oxidizing agent, helps to overcome the difficulty of treating complex organic impurities and removal of refractory COD.



❖ **Methodology :***Figure 1: Approach Methodology of Study*❖ **Work Plan***Table- 1.1: Work Plan*

| Sr. No | Stage                          | 1 <sup>st</sup> Quarter |     | 2 <sup>nd</sup> Quarter |     |     | 3 <sup>rd</sup> Quarter |     |     | 4 <sup>th</sup> Quarter |       |     |
|--------|--------------------------------|-------------------------|-----|-------------------------|-----|-----|-------------------------|-----|-----|-------------------------|-------|-----|
|        |                                | July                    | Aug | Sept                    | Oct | Nov | Dec                     | Jan | Feb | March                   | April | May |
| 1      | Study Conceptualization        | ✓                       | ✓   | ✓                       |     |     |                         |     |     |                         |       |     |
| 2      | Literature Review              |                         |     |                         | ✓   | ✓   | ✓                       |     |     |                         |       |     |
| 3      | Development of Lab Scale Model |                         |     |                         |     |     |                         | ✓   |     |                         |       |     |

|   |  |  |  |  |  |  |  |   |   |   |   |   |
|---|--|--|--|--|--|--|--|---|---|---|---|---|
| 4 | Case Study of CETP-Vatva                   |  |  |  |  |  |  | ✓ | ✓ |   |   |   |
| 5 | Sample Collection and Analysis             |  |  |  |  |  |  |   | ✓ | ✓ |   |   |
| 6 | Data Analysis & Techno-economic Evaluation |  |  |  |  |  |  |   |   | ✓ | ✓ |   |
| 7 | Conclusion                                 |  |  |  |  |  |  |   |   |   |   | ✓ |

## LITERATURE REVIEW

### ❖ THE DYES AND DYE INTERMEDIATE INDUSTRY :

The importance of dyes cannot be understated. From textiles to medicines, the industry forms an important constituent to various product lines. The synthetic organic chemical industry began in 1856 when English chemist William Henry Perkin prepared the dye mauve from coal-tar chemicals. Perkin built a factory near London to supply the world's first synthetic dye. Since then, the industry has grown by leaps and bounds, with a large chunk of its base shifting to Asia post World War II. The origin of the dyestuff industry in India can be traced to the fifties when most dyes and intermediaries were totally imported in the country. Gradually the manufacturing of dyestuffs picked up in the country and in the early eighties this industry started export in good quantity.

Today, the Indian State of Gujarat alone is home to a dyes and dye intermediate industry with an estimated worth Rs. 15,000 crores. And yet, with the prosperity, there are problems as well. The environmental problems arose first after industrialization replaced traditional natural dyes by the synthetic dyes used today. Over and above the pollution the industry generates, issues pertaining to poor economies of scale, ban on certain dyes in export markets, ever-increasing prices of raw materials, and competition from other developing countries, have started squeezing profit margins to such an extent that small scale producers (the very backbone of this industry in India) are finding it hard to stay afloat.

Dyestuff is a general industry term covering both dyes and pigments in terms of chemistry, reactions and properties. Dyes are intensely coloured organic compounds or mixtures used for imparting colour to the substrates ranging from cloth, paper, leather to plastics in a permanent fashion. There are about 600 types of dyestuffs produced in the country. A dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fibre. The basic importance of dye lies in its product and resistant to washing. Pigments, on the other hand, are insoluble and are important inputs to products such as paints.

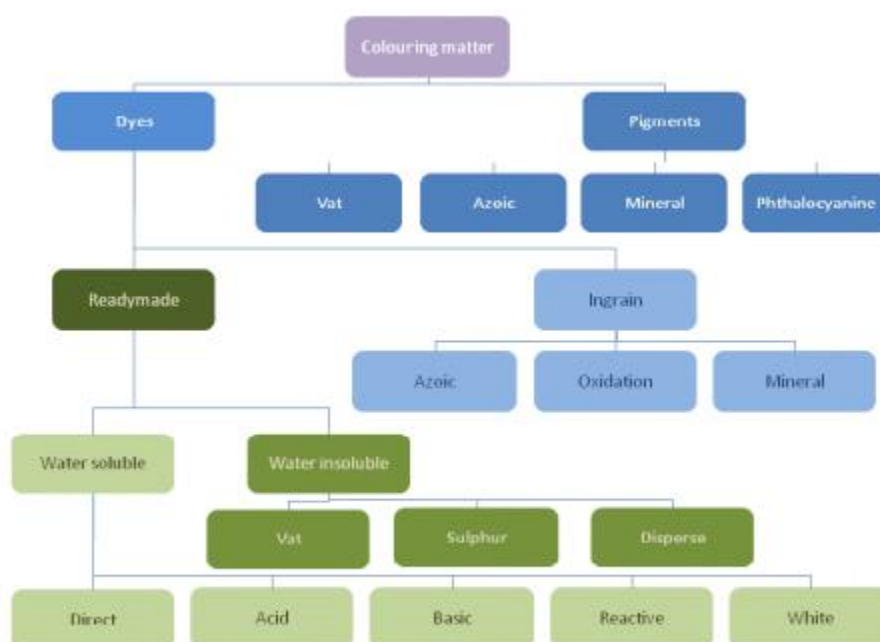
A dye intermediate is the main raw material used for the manufacturing dyestuff. The manufacturing chain of dyes can be traced back to petroleum-based products. Naphtha and natural gas are used for the production of benzene and toluene, which are subsequently used for manufacturing nitro-aromatics. The nitro-aromatics are then used for manufacturing the compounds called dye intermediates. Hence, the third stage of

production i.e., from nitro aromatics to a dye intermediate is a part of the dyes and dye intermediate sector. Examples of major dye intermediates are Vinyl Sulfone, Gamma Acid, H Acid, CPC Blue, J Acid,  $\alpha$ -Naphthyl Amine, etc.

## ❖ CLASSIFICATION OF DYES :

Dyestuffs have been classified in different categories based on the criteria like the colour, origin (natural or synthetic), chemical structure or constitution, applications and method of application. Application-based classification is the most useful and widely accepted classification system by dye manufacturing industries. The various types of colouring matter based on their classification are shown in Figure 1.

*Figure 2: Types of Dyes Based on Classification*



Dyes are also used in high technology applications, such as in the medical, electronics, and especially the reprographics industries. These applications are low volume (tens of kg up to several hundred ton per annum) and high added value (hundreds of dollars to several thousand dollars per kg), with high growth rates (up to 60%).

## ❖ CHARACTERISTICS OF EFFLUENT GENERATED FROM THE DYES AND DYE INTERMEDIATE INDUSTRY :

The environmental problems attributed to this industry arose first after industrialization replaced traditional natural dyes by the synthetic dyes used today. Since synthetic dyes are designed to resist bleaching by ultraviolet light and chemicals to improve the quality of the end product, they are also persistent in the environment and some dyes can be biologically modified into carcinogenic compounds.

The release of untreated wastewater poses a threat to the environment and the most serious problems are ground water and surface water pollution. Further, the discharge of coloured effluents into water bodies affects the sunlight penetration which in turn decreases both the photosynthetic activity and dissolved oxygen levels.

The removal of dyes from wastewater is one of the major environmental challenges. Since the majority of dyes are recalcitrant to conventional biological methods the most common techniques used today are physico-chemical in nature.

However, many of these methods suffer from limitations. They are usually not cost-efficient and most of them lead to generation of hazardous waste that needs to be dealt with separately.

The quantum of wastewater generated per ton of dyestuff production is very low compared to that generated per ton of dye intermediate production. The specific wastewater generation for major dye intermediates is about 15-20 m<sup>3</sup>/ton of product.

The main sources of wastewater generation are:

- Mother liquor or filtrate streams from filtration operations.
- The wastewater streams from the washing of filter cake to remove either salt impurities or residual filtrate adhere from the cake
- Leakage and spillage
- Floor washing of the work area

The typical characteristics of the wastewater from this sector are mentioned in the Table 2.

*Table 2: Typical Characteristics of Wastewater from the Production of Dyes and Dye Intermediates*

| Parameter                    | Value                  |
|------------------------------|------------------------|
| Colour                       | Varying deep colours   |
| pH                           | 4 – 6                  |
| Chemical Oxygen Demand (COD) | 50,000 - 1,00,000 mg/l |
| Total Dissolved Solids (TDS) | 15,000 - 2,00,000 mg/l |

The effluent discharged from this industrial sector is highly acidic and contains toxic compounds; many of them are carcinogenic and highly hazardous to human health and the environment.

This is due to the presence of benzene, naphthalene and other nitro-aromatic based compounds in the wastewater, which are used as raw materials during the production of dye intermediates.

Due to the excess use of acid and alkali quantity, the wastewater contains high concentration of inorganic salts that results in the high concentration of TDS.

Due to this, treatment of effluent is very difficult and highly expensive.



## ❖ ISSUES IN TREATMENT OF EFFLUENT FROM DYES AND DYES INTERMEDIATE INDUSTRIES :

The effluent discharged from this industrial sector is highly acidic and contains toxic compounds; many of them are carcinogenic and highly hazardous to human health and the environment.

This is due to the presence of benzene, naphthalene and other nitro-aromatic based compounds in the wastewater, which are used as raw materials during the production of dye intermediates.

Due to the excess use of acid and alkali quantity, the wastewater contains high concentration of inorganic salts that results in the high concentration of TDS. Due to this, treatment of effluent is very difficult and highly expensive.

### **Treatment of refractory COD and high TDS in waste water:**

Refractory COD is organic compounds that show up in the COD tests as being chemically oxidizable, but are not readily biodegradable.

Examples of refractory organics include: some detergents (alkyl benzene sulfonate), and detergent additives including complexing and sequestering agents like EDTA and NTA, halogenated organics including pesticides, PCBs, dioxins and dibenzofurans, polycyclic aromatic hydrocarbons, nitroaromatics including TNT, certain organic acids, aldehydes, certain pharmaceutical active ingredients (PAI's) as well as naturally occurring cellulosic and lignin compounds.

## ❖ TREATMENT TECHNOLOGIES ADOPTED FOR REMOVAL OF COD FROM WASTEWATER GENERATED FROM THE DYES AND DYE INTERMEDIATE INDUSTRY :

A number of physical, chemical and biological methods are available for the treating wastewaters containing aniline derivatives.

Physical treatment methods consist of floatation, sedimentation, filtration, ion exchange, adsorption, stripping and other processes that remove soluble and insoluble substances without altering their chemical structure.

Chemical methods include chemical precipitation, chemical oxidation or reduction including advanced oxidation processes (AOPs).

Biological treatment processes are mainly used for secondary treatment of wastewater and are based on the microbial action to decompose suspended and dissolved organic compounds in the wastewater. These microbes use the organic compounds as both a source of carbon and as a source of energy.

### ➤ **Biological treatment methods**

Biological processes are a good option for wastewater treatment as they are relatively economical and the end products of complete degradation are harmless.



For better understanding the role of biological treatment method in treatment of effluent generated from dyes and dyes intermediate industries, example of 4-nitroaniline (4-NA) is discussed below.

In a study carried out by Saupe (1999), a municipal wastewater bio sludge was acclimated to the degradation of 4-nitroaniline (4-NA).

This was achieved by using this compound as the sole source of nitrogen during the degradation of succinate as the sole source of carbon and energy. Bacteria were able to eliminate and mineralize 4-NA as the sole source of carbon and energy.

The degradation process was found to be unstable and occurred at comparatively low rates in the batch studies. To overcome these drawbacks, a continuously operated miniaturized fixed-bed bioreactor was inoculated with the acclimated bacteria and fed with 4-NA as the sole substrate.

After gradual adaptation, the bacteria also degraded 3-NA and 4-NA simultaneously in this system. Additional batch tests showed, that 3-NA can serve as the sole source of carbon, nitrogen and energy.

### ➤ Chemical treatment methods

Treatment using chemical process can be used as an alternative when biological treatments do not completely remove the impurities from water and wastewater.

Among the various chemical treatment methods, advanced oxidation processes (AOPs) are reported to be most effective in the removal of non-biodegradable substances.

Advanced oxidation processes have been studied as a promising kind of wastewater treatment system to treat the organic wastewater. Under advanced oxidation process, the complex organic molecules are either oxidized to smaller molecules or to the carbon dioxide and water (Wang et al., 2016).

The AOPs are defined as the near ambient temperature and pressure water and wastewater treatment processes, which involve the generation of highly reactive hydroxyl radicals.

These hydroxyl radicals are extremely reactive species that attack most of the organic molecules. AOPs can be classified as homogenous or heterogeneous processes. AOPs include Fenton type oxidation, ozonation, photocatalysis, UV-H<sub>2</sub>O<sub>2</sub>, UV-H<sub>2</sub>O<sub>2</sub>-Fe (II, III), electro coagulation and electron decomposition that oxidizes the non-biodegradable organic compounds with the OH radical which are produced during reactions.

AOPs are the promising alternatives for destroying toxic and bio refractory organic compounds.

Here again, example of 4-nitroaniline (4-NA) is discussed below to understand the chemical treatment methods to understand the role of chemical treatment method.

4-Nitroaniline, a non-biodegradable contaminant is usually manufactured or used as an intermediate during the synthesis of pharmaceuticals, azo dyes and corrosion inhibitors.

The chemical stability and toxicity of 4NA makes it hazardous once it enters the natural water bodies and it is considered toxic for human health and aquatic microorganisms even at significantly low concentrations. 4NA has been listed by the National Environmental Protection Agency (NEPA) of the People's Republic of China as one of the priority pollutants for removal from water (Zhao et al., 2015).

Many attempts have been made for the treatment of 4NA wastewater, including physical, chemical & biological methods. 4NA is resistant to biological degradation due to the presence of a nitro group in the aromatic ring which enhances its stability. Hence the rate of degradation is quite low.

The physical methods manage to transfer the contaminants from one medium to another such as activated carbon, in which the degradation or mineralization could be achieved. However, further treatment is required using chemical methods for decomposition of nitroaniline. Photo catalytic degradation has a few drawbacks like high capital and operating cost.

Hence, new cost-effective technologies have to be developed to treat 4NA-contaminated wastewater. In the conventional AOPs, FeSO<sub>4</sub> & similar compounds are used as a catalyst to release the hydroxyl radical from peroxide and present research focus is towards finding low cost material containing iron to substitute the ferrous compound.

Ferric iron (III) can be extracted from laterite soil using sulphuric acid or HCl as leaching agents. Laterite often contains secondary oxides of iron, Aluminium or both, minor amounts of Nickel, Cobalt, Chromium, Quartz and Kaolinite, and is nearly devoid of basis and primary silicate. The high proportion of Iron (III) oxide in laterite represents a residual accumulation brought about by the removal of silica and alkali.

### ➤ Fenton oxidation process (also known as Fenton Catalytic Reaction)

The Fenton reagent is a mixture of H<sub>2</sub>O<sub>2</sub> and ferrous ion, which dissociates the oxidant (H<sub>2</sub>O<sub>2</sub>) and forms highly reactive hydroxyl radicals. The hydroxyl radical (OH•) is a powerful, non-selective chemical oxidant, which rapidly oxidizes most organic compounds. Once generated, the hydroxyl radicals aggressively attack virtually all organic compounds. After addition of the iron and the hydrogen peroxide, they are going to react together to generate some hydroxyl radicals as it shown in the following equations:



It is a chain reaction with step (1) serving as chain initiation, steps (4) and (5) as termination and the cycle (1)-(2)-(3) forms the chain which is the site of O<sub>2</sub> evolution. In the free radical mechanism, reaction (2) becomes insignificant at low [H<sub>2</sub>O<sub>2</sub>] as a mode of reaction of OH•. Hydroxyl radical could then react with Fe<sup>2+</sup> and produce Fe<sup>3+</sup> (reaction (5)). As an alternative, OH• could react with Fe<sup>3+</sup> (reaction (6)). If this reaction occurred it would be even more plausible to assume that the pair Fe<sup>3+</sup> + OH• (as products of reaction 1) would not become separated at all and the species FeOH<sup>3+</sup> would appear instead. It can be stated that the species FeOH<sup>3+</sup> is merely the protonated form of FeO<sub>2</sub><sup>+</sup>.

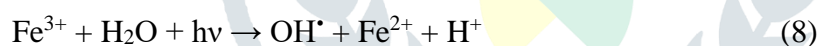
Some of the advantages of Fenton oxidation process over the conventional treatment methods include:

- Highly effective at removing organic compounds that are resistant to conventional treatment methods
- Capable of complete mineralization of organic compound into carbon dioxide
- Less susceptible to the presence of toxic chemicals
- Produce less harmful by-products
- Low maintenance
- Rapid process
- Low production of residual sludge
- Excess H<sub>2</sub>O<sub>2</sub> degrades to oxygen in the solution

One of the advantages of the Fenton process with respect to other advanced oxidation processes is that it does not require any energy input to activate hydrogen peroxide because the reaction takes place at atmospheric pressure and at room temperature. The main disadvantages are the high cost of chemicals (hydrogen 17 peroxide and iron) in addition to the cost of removal of homogeneous catalyst (iron salt) to prevent further pollution of water.

#### ➤ Photo Fenton process

Photo-Fenton oxidation is a promising and attractive treatment method to overcome the drawbacks of Fenton's oxidation process. The rate of Fenton reaction is strongly enhanced by irradiation with UV or visible light. The photo-Fenton reactions involve irradiation with UV light or solar rays which significantly increase the rate of contaminant degradation by photo reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>. Fenton reaction generates hydroxyl radicals and photo Fenton reactions reduce the Fe<sup>3+</sup> to Fe<sup>2+</sup> thus leading to the production of additional OH• radicals and continuous regeneration of Fe<sup>2+</sup> in a catalytic way.



UV light has a dual advantage of generating additional hydroxyl radicals and also recycling of ferrous ions by reduction of ferric ions. This leads to an increase in the Fe<sup>2+</sup> concentration, thus accelerating the overall reaction. The high efficiency of the photo-Fenton process to oxidize a variety of organic compounds, the simplicity of operation and the possibility of using solar light are advantages which can make the implementation easier of in situ and small scale treatment processes.

The photo-Fenton oxidation has many advantages compared to the classic Fenton reaction

- Higher rate of degradation
- Lower operational costs due to lower consumption of chemicals
- Minimal quantity of sludge formation, hence further reducing the operational cost which would occur during sludge removal and treatment.

➤ **Factors affecting Fenton and photo Fenton processes**

There are several parameters and operational conditions which can substantially affect reaction rates and stoichiometry. These parameters have to be duly considered during the conduction of experiments, so as to achieve optimum conditions to ensure highest degradation rate.

➤ **Effect of pH**

Fenton's oxidation process has been reported to have high efficiency in acidic medium. At pH 3, the observed removal is maximum, which may be due to the formation of  $\text{Fe}(\text{OH})^+$  which has higher activity than  $\text{Fe}^{2+}$  in Fenton oxidation. When the pH is greater than 3, oxidation efficiency rapidly decreases due to auto-decomposition of  $\text{H}_2\text{O}_2$  affecting the production of OH radical and deactivation of the ferrous catalyst with the formation of ferric hydroxide precipitates. Also, there is a decrease in the oxidation potential hydroxyl radical with an increase in pH value. When the pH is less than 3, the reaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$  is affected that leads to a reduction in the hydroxyl radical generation and water is formed by the reaction of hydroxyl radical with  $\text{H}^+$  ion.

➤ **Effect of  $\text{H}_2\text{O}_2$**

The concentration of hydrogen peroxide plays an important role in the Fenton's oxidation reactions since it is the source of OH radicals that cause the degradation of organic compounds. The hydroxyl radicals either oxidize the pollutant and other intermediates or react with the oxidant itself to cause a reduction in the pollutant efficiency. The reaction rate increases with increase in the hydrogen peroxide concentration (Sun et al., 2007). The addition of  $\text{H}_2\text{O}_2$  exceeding the optimum limit decreases the degradation efficiency. This may be attributed to the auto decomposition of  $\text{H}_2\text{O}_2$  to oxygen and water, and the recombination of OH radicals. In addition, higher concentrations of hydrogen peroxide act as free-radical scavenger itself, which decreases the concentration of hydroxyl radicals and thereby reduces compound degradation efficiency (Mahamood 2013).

➤ **Effect of catalyst concentration ( $\text{Fe}^{2+}$ )**

Catalyst plays an important role in a reaction by providing a route that requires low activation energy, thereby increasing the rate of reaction. In Fenton's oxidation process, the degradation rate tends to increase with increasing Fe (II) concentration, up to the optimal dosage (Sun et al., 2007). The addition of iron salt above the optimal dosage does not affect the rate of degradation. When the Fe (II) concentration is higher than the optimum, the rate of hydroxyl radicals originated from the decomposition of  $\text{H}_2\text{O}_2$  is so high that much of hydroxyl radicals are consumed by the side reactions before they are utilized for the removal of the pollutant. Moreover, it would result in the formation of a large compound sludge resulting in brown turbidity that hinders the absorption of the UV light required for photolysis and also would cause the recombination of OH radicals (Masomboon et al., 2011).

➤ **Effect of initial concentration of contaminant.**

The initial concentration of contaminant on the degradation is also an important parameter in Fenton's reaction. When the initial concentration of contaminant increases, the generation of  $\text{OH}^\bullet$  is not increased correspondingly, so a relative lower  $\text{OH}^\bullet$  concentration resulted in a decrease in the degradation efficiency.

# **EXPERIMENTAL SETUP AND CASE STUDY OF CETP**

## **VATVA:**

### **❖ CONCEPT OF CETP:**

Common Effluent Treatment Plant (CETP) is the process of collecting, conveying, treating, and disposing of the effluents from industrial estates. The effluent includes industrial wastewaters and domestic sewage generated from industrial plant. This concept of CETP helps small as well as medium scale industries to discard/dispose of their effluents. Common effluent treatment plants had been mounted and are in operation at several business clusters in India. They serve to lower effluent treatment expenses, offer higher collective treatment, and decrease land expenses for small-scale business centers that can't have enough money for a man or woman treatment plants. However, the pollution that we see in today's world will be increasing day by day.

### **Types of methods used in CETP.**

CETP Plant can be installed as a mixed effluent plant so that it can deal with all of the distinctive forms of wastewater from the industries located in the estate, through the usage of numerous methods/steps withinside the CETP which can be available. These include :

- Sludge Management
- Preliminary Treatment
- Primary Treatment
- Secondary Treatment
- Tertiary Treatment

Having a CETP is a handy choice for all of the industries in an estate. However, it's best to perform a survey of the quality and amount of the wastewater produced so that the maximum appropriate system may be implemented.

### **❖ ABOUT CETP VATVA:**

M/s. Green Environment Services Co-operative Society Ltd., (GESCSL) is located in Vatva industrial estate (22°57'18.8"N, 72°38'21.9"E) in Ahmedabad, Gujarat, formed in 1992 with the main objective to subdue pollution and environmental resources to achieve sustainable growth and development in Vatva. The city is surrounded in the north by Mehsana and Gandhinagar district and on the south by Gulf of Cambey and Bhavnagar district and in the east by Kheda district. The city is one of the industrially developed districts of Gujarat consisting of micro, medium, small and large industries related to textiles, dye and dye intermediates, chemicals, machinery, metal products, pharmaceuticals, engineering plastics, electrical appliances, electronics



and passenger cars. There are about 12 industrial estates in Ahmedabad District and is an industrial hub for textiles and is popularly known as Manchester of India. Vatva Industrial Estate houses has more than 4000 enterprises, comprising 15% of large corporate houses and 85% MSMEs. Vatva has an annual turnover of more than Rs. 15000 crores and exports of more than Rs. 7500 crores. It provides employment to 2 lacs employees directly and indirectly.

### ❖ LOCATION OF CETP:

M/s. Green Environment Services Co-Operative Society Ltd., (GESCSL) is located (22°57'18.8"N, 72°38'21.9"E) at Plot no.:244-251, 242/1, 242/3 Phase: II, GIDC Estate, Vatva, Ahmedabad, Gujarat. The area of existing units and structures of CETP, is 11669 m<sup>2</sup> and MEE and spray dryer is 6288.88 m<sup>2</sup>.

The CETP handles wastewater from 674 industrial units. Majority of the industries produce dye and dye intermediates, pigments etc. The treated effluents from the CETP are pumped to river Sabarmati River through a closed Mega Pipeline. The treated effluent is pumped to Mega Pipeline which carries effluent from Reliance and other CETPs like Naroda, Odhav and Narol Dyestuff and ultimately discharge into River Sabarmati where it is mixed with approximately 1000 MLD sewage.

### ❖ TREATMENT PROCESS OF CETP

#### Primary Treatment

A collection cum screening tank is the first course in effluent treatment which receives preliminary treated effluent as an inlet of CETP. The condensate from MEE and spray dryer are also pumped to collection tank. The treated effluent from Novel is also sent to GESCSL CETP for further treatment. From the collection tank the wastewater is flash mixed where coagulants and flocculants are mixed. The cationic and anionic coagulants are added through dosing pump from the chemical tanks and are thoroughly mixed in the Flash mixer.

After complete mixing of the coagulants like Cationic and Anionic polyelectrolytes with the effluent, the effluent is clarified in clarifloculator with designed detention time of 3.45 hrs. The solids separated during clarification are collected in primary sludge holding tank from where it is pumped to centrifuge decanter for dewatering. The dewatered sludge is then transported to TSDF and the concentrate from decanter is transferred to equalization tank. The supernatant flows to equalization tank for homogenization. The equalization tank provides a detention time of 24.87 hrs under designed flow. In equalization tank the content is thoroughly mixed with the help of coarse bubble diffuser aeration supported by Turbo Aerator.



The equalized flow is sent to flash mixer where cationic polyelectrolyte and anionic polyelectrolyte are added. After complete mixing of the chemicals with effluent, it flows into flocculator tank where coagulation and flocculation of suspended solids, colloids and dissolved pollutants takes place.

The overflow from flocculator goes to settling tank and flocs removed by scrapper in the form of sludge. DAF unit works on the principle of super saturation of the liquid with dissolved air. However, under the present circumstances, the functionality of DAF is in-effective and the unit is used just as a settling tank.

### **Secondary Biological Treatment (Activated Sludge Process)**

The extended aeration model is employed for biological treatment. The effluent received from settling tank where the desired level of DO and MLSS is provided by five numbers of root blowers (each of 175 HP capacity) with medium bubble diffused aeration grid and 23 nos. triton type Jet Aerators (each of 60 HP capacity) with 10 HP air blowers. The treated sewage from STP, Vinzol (Municipal Corporation) is added to aeration tank for bio augmentation. The organic matter and some nutrients in the form of nitrogen and phosphorous present in wastewater are degraded aerobically by the active micro-organisms contained in the activated sludge. Two secondary clarifiers having a total capacity of 3924 m<sup>3</sup> (each of 1962 m<sup>3</sup> capacity) receive an effluent containing MLSS through the flow distribution chamber. Anionic poly-electrolyte & spent aluminium chloride (75 ppm) are added to the effluents from aeration tank before clarification in the secondary clarifier. The spent aluminium chloride which is used as chemical aid for clarification is a by-product of CETP member units. The activated sludge mixed liquor is clarified by gravity in the clarifiers from where it is taken to the Sludge Sump. A portion of this activated sludge (Recycled Activated Sludge) is recycled into the aeration tank to maintain F/M ratio. The excess sludge (Waste Activated Sludge) is taken into sludge holding tank from where it is pumped to Centrifuge/Decanter for dewatering. Again non-anionic polyelectrolytes are added to decanter. The supernatant/treated effluent from the secondary clarifiers is collected in Holding Tank from where it is pumped to river Sabarmati for discharge through a closed Mega pipeline. The treated effluent is pumped to mega line which carries effluent of reliance and other CETP like Naroda, Odhav, Narol Dyestuff for ultimate discharge at downstream of river Sabarmati where it is mixed with 1000 MLD treated Sewage.

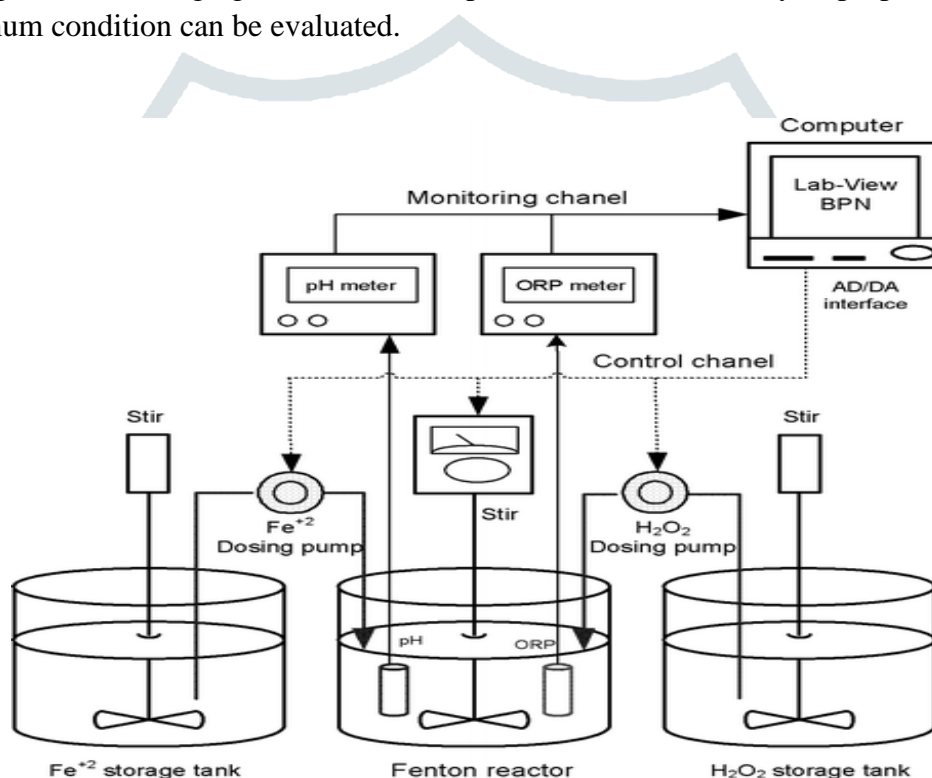
### **❖ PERFORMANCE ASSESSMENT OF FCR TREATMENT**

The evaluation of this pilot plant was conducted at the CETP site. The pilot plant consists of an Intermediate Bulk Container tank (IBC) of 850 litres capacity, Fenton Catalytic Reactor with feed and recirculation pump, a neutralisation and coagulation/precipitation unit. The IBC tank was used as storage tank to collect the final treated effluent from CETP and fed to the pilot plant. The Fenton's Catalytic Reactor is the heart of the pilot plant unit where the advanced oxidation process takes place was operated on continuous mode. Nine batches of

experiments were carried out. The study was conducted under varying pH conditions for major pollutant parameters viz., COD, TOC, TSS and TDS. The use of feed chemicals viz., ferrous sulphate, hydrogen peroxide, lime and polyelectrolyte were optimised to reduce sludge formation and wastage of chemicals. Samples were collected at the following locations for performance assessment of the reaction process.

### ❖ EXPERIMENTAL SETUP :

The Fig.3 shows the layout of experimental set-up at pilot scale. As illustrated in the figure, layout consists of collection cum equalization tank, Fenton Catalytic Reactor with feed and recirculation pump, Hydrogen Peroxide ( $H_2O_2$ ) dosing tank, Ferrous Sulphate ( $FeSO_4$ ) dosing tank, hopper bottom settling tank. During the course of experiment, optimization of FCR process was carried out by providing different proportion of catalysts along with oxidizing agent. Various samples were taken for analysis purpose so that removal of COD in optimum condition can be evaluated.



*Figure 3: Schematic diagram of the experimental set-up*

### ❖ CHARACTERISTICS OF EFFLUENT SAMPLE:

*Table 3: Characteristics of the Effluent sample*

| Parameter      | Range       |
|----------------|-------------|
| COD (mg/L)     | 1300 - 2000 |
| BOD (mg/L)     | 320 - 480   |
| SS (mg/L)      | 400 - 600   |
| Color ( pt-Co) | 1000 - 2000 |
| pH             | 6.5 - 8.5   |

## ❖ ANALYTICAL PROCEDURE :

### ➤ Determination of color

The sample was centrifuged at 10,000 rpm for 30 min to remove all the suspended matter. The pH of the supernatant was adjusted to 7.6 by the addition of 2 M NaOH and absorbance was measured at 465 nm. Color units (CUs) were determined from UV absorbance using the following equation (Bajpai et al. 1993).

$$\text{CU (Pt-Co)} = 500 \times A_2/A_1$$

Where  $A_1$  is the absorbance of 500-CU standard platinum cobalt solution (Pt-Co; 0.1214),  $A_2$  is the absorbance of the effluent samples.

### ➤ Determination of total suspended solids

The determination of suspended solids has been done by using glass fiber filter discs (Whatman grade 934AH) connected with filtration setup. Initially, the filter disc was washed with distilled water and dried to a constant weight in a desiccator. The filter disc was returned to the filter apparatus, and a known volume of the sample was added through the filter disc. The sample was then washed with 10 ml of distilled water. Then the disc was inserted into the drying oven at 103 – 105°C for one hour. The dried sample was then allowed to cool in a desiccator and weighed. By using the formula, total suspended solid was calculated (Lenore S. Clesceri et al. 1998).

$$\text{Total Suspended Solids in mg/l} = (A-B) \times 1000 / \text{Sample Volume (ml)}$$

where

A - weight of filter + dried residue (mg)

B - the weight of filter (mg)

### ➤ Determination of pH

The pH was measured with a WTW 320 model pH meter (Germany) connected with digital display.

### ➤ Determination of chemical oxygen demand

Chemical Oxygen Demand is a measure of the total quantity of oxidizable compounds present in a liquid solution. 50 ml of the sample is refluxed strongly in an acid solution with a known excess of potassium dichromate (0.00417M). After digestion, the remaining unreduced  $K_2Cr_2O_7$  is estimated by titrating with ferrous ammonium sulphate (0.025M). From the result, the amount of  $K_2Cr_2O_7$  consumed as well as the oxidizable matter present is calculated in terms of oxygen equivalent.

$$\text{COD as mg/l} = (A-B) \times M \times 8000 / (\text{ml of sample})$$

where

A - ml of ferrous ammonium sulphate used for blank

B - ml ferrous ammonium sulphate used for sample

M - molarity of ferrous ammonium sulphate and

8000 = mill equivalent weight of oxygen  $\times$  1000 ml.

### ➤ Determination of biological oxygen demand

BOD measures the amount of oxygen taken up by an acclimatized microbial culture when exposed to the water sample for three days. It is primarily used to determine the level of oxygen depletion that will occur if the effluent stream tested is discharged to a natural water way or biological treatment plant. The sample was diluted in two BOD bottles with the addition of 1 ml each of phosphate buffer,  $\text{MgSO}_4$ ,  $\text{CaCl}_2$  and  $\text{FeCl}_3$  solutions per liter of water. Then two BOD bottles were filled with distilled water, and the above said reagents as blank. The initial dissolved oxygen (DO) was immediately found for one of both sample and blank. The other two BOD bottles were tightly stoppered (to prevent any air entry) and incubated at  $27^\circ\text{C}$  for three days. After three days of incubation, the final dissolved oxygen was measured (Lenore Clesceri et al. 1998).

$$\text{BOD in mg/l} = [(D_o - D_T) - (B_o - B_T)] \times (100 / \text{Percent Sample})$$

where

$D_o$  - DO of diluted sample initially, mg/L

$D_T$  - DO of diluted sample after 3-day incubation at  $27^\circ\text{C}$ , mg/L

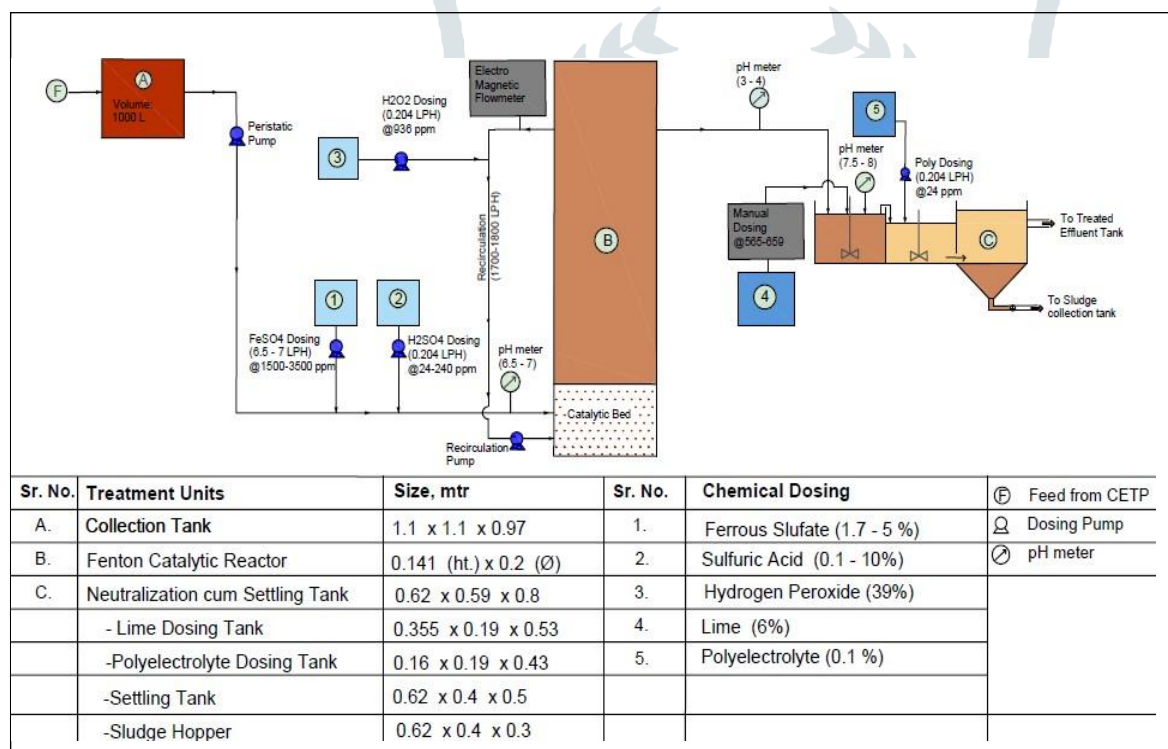
$B_o$  - DO of diluted water initially, mg/L

$B_T$  - DO of diluted water after 3-day incubation at  $27^\circ\text{C}$ , mg/L

# RESULTS AND DISCUSSION :

## ❖ PERFORMANCE ASSESSMENT OF FCR TREATMENT

The evaluation of this pilot plant was conducted at the CETP site. The pilot plant consists of an Intermediate Bulk Container tank (IBC) of 850 litres capacity, Fenton Catalytic Reactor with feed and recirculation pump, a neutralisation and coagulation/precipitation unit. The IBC tank was used as storage tank to collect the final treated effluent from CETP and fed to the pilot plant. The Fenton’s Catalytic Reactor is the heart of the pilot plant unit where the advanced oxidation process takes place was operated on continuous mode. Nine batches of experiments were carried out. The study was conducted under varying pH conditions for major pollutant parameters viz., COD, TOC, TSS and TDS. The use of feed chemicals viz., ferrous sulphate, hydrogen peroxide, lime and polyelectrolyte were optimised to reduce sludge formation and wastage of chemicals. Samples were collected at the following locations for performance assessment of the reaction process.



**Figure 4:** Schematic of Pilot Plant Fenton Catalytic Reactor Run at M/s. Green Environment Services Co. Op. Society Ltd., Vatva

The pH of the feed to the FCR is controlled by addition of sulphuric acid and caustic soda. The optimum pH range for the Fenton’s Catalytic Reaction process suggested by the vendor is between pH-3.3-3.8. The study was extended at laboratory for repeatability of experiments using samples bought from M/s. GESCSL, Vatva CETP. The results of the bench scale studies are presented as Table 4. The experiments validated the pilot scale results with SS, BOD and COD reduction.

**Table 4: Details of Feed Chemicals and Doses used in the Study**

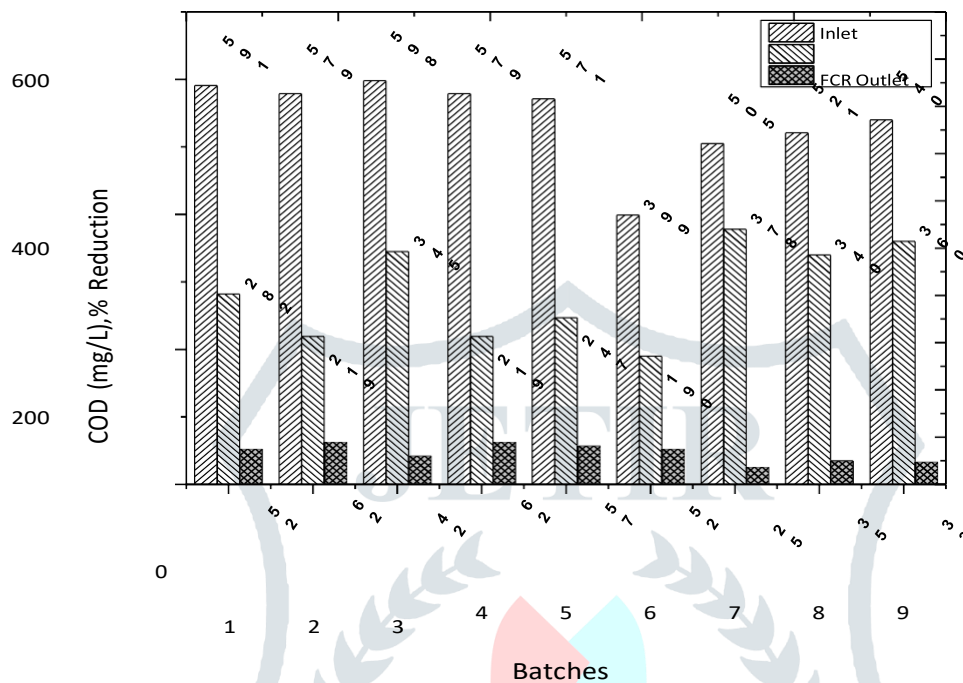
| Chemical   | Batch 1         | Batch 2         | Batch 3        | Batch 4         | Batch 5        | Batch 6        | Batch 7        | Batch 8        | Batch 9        |
|--|-----------------|-----------------|----------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| FeSO <sub>4</sub> <sup>+</sup> , mg/l<br>(kgs)   | 3500<br>(2.975) | 2500<br>(2.975) | 1500<br>(1.2)  | 1500<br>(1.2)   | 1500<br>(1.2)  | 1500<br>(1.2)  | 1500<br>(1.2)  | 1500<br>(1.2)  | 1500<br>(1.2)  |
| H <sub>2</sub> O <sub>2</sub> <sup>+</sup> ,<br>mg/l (litres)  | 1000<br>(2.04)  | 1000<br>(2.04)  | 1000<br>(2.04) | 1000<br>(2.04)  | 1000<br>(2.04) | 1000<br>(2.04) | 1000<br>(2.04) | 1000<br>(2.04) | 1000<br>(2.04) |
| H <sub>2</sub> SO <sub>4</sub> , litres  | 0.0064          | 0.0064          | 0.089          | 0.0468<br>(10%) | 0.059<br>(1%)  | 0.059<br>(1%)  | 0.45<br>(1%)   | 0.45<br>(1%)   | 0.65           |
| Lime, kgs  | 0.56            | 0.50            | 0.48           | 0.5             | 0.50           | 0.5            | 0.55           | 0.50           | 0.50           |
| Poly-<br>electrolyte<br>(anionic),kgs  | 0.002           | 0.002           | 0.002          | 0.002           | 0.002          | 0.002          | 0.002          | 0.002          | 0.002          |
| Feed pH  | 6.5-7.0         |                 |                |                 |                | 5.5            |                | 4.5            | 3.5            |
| * Concentration 5% and flow rate 6 Lph<br>+ Concentration 39% and flow rate 0.204 Lph<br>Values in brackets present quantity consumed per batch. |                 |                 |                |                 |                |                |                |                |                |

#### 4.1.1 Pilot Scale Fenton's Catalytic Reactor studies at M/s. GESCSL, vatva

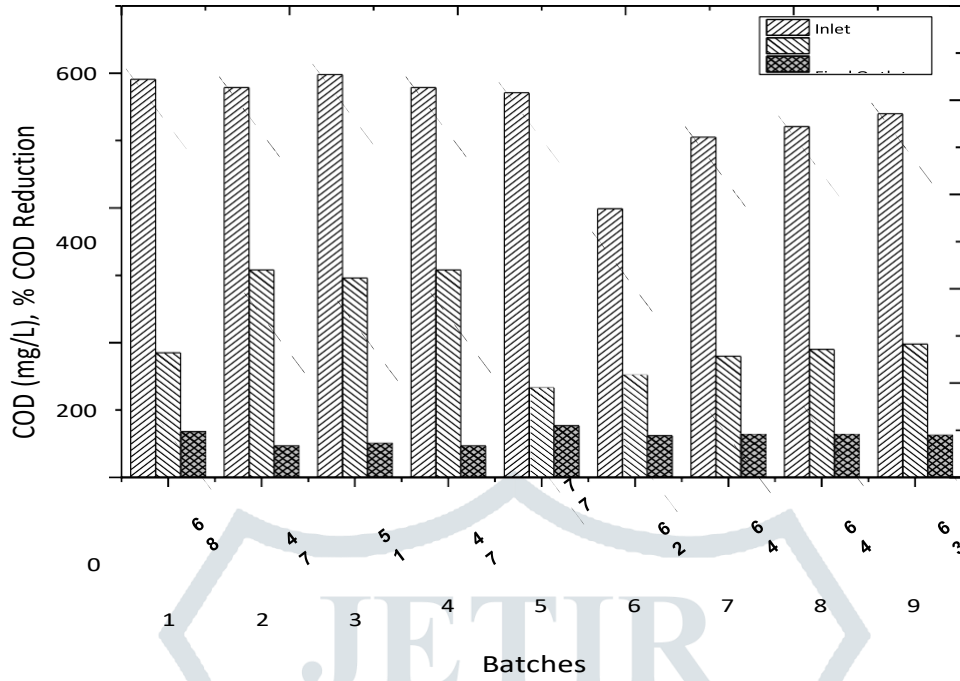
- The studies were conducted at neutral to acidic pH 3.5 using feed wastewater. Ideally the optimal pH required for the Fenton's reaction is pH 3.0.
- In the initial runs, more sludge formation was observed; this could be due to formation of solid precipitates of ferric hydroxide. The feed dose of ferrous sulphate (3500mg/l) was more than the stoichiometric requirement and hence it was readjusted to 1500 mg/l (Table 4- Batch1).
- The overall treatment efficiency of pollutants (TOC and COD) for the entire effluent treatment including Fenton's reaction, neutralisation and precipitation were observed with efficiencies ranging from 47-77% for COD reduction and 34-55% for TOC reduction respectively (Fig 5-10).
- The performance of FCR in the pollution reduction is observed between 25- 62% for COD and 41-65% for TOC respectively. Impact of dissolved solids in the performance of FCR cannot be ruled out. The studies conducted on effluent sample indicate the impact of salts on FCR at lab where as high COD, BOD removes were obtained by FR based on surface response methodology were obtained.
- TSS reduction varied from NIL to 89%. TSS generation was observed higher from the FC Reactor due to precipitation of pollutants in the presence of ferric ion and its hydroxides generated via Fenton's reactions.
- Impact on ammonical nitrogen reduction in FCR is insignificant.



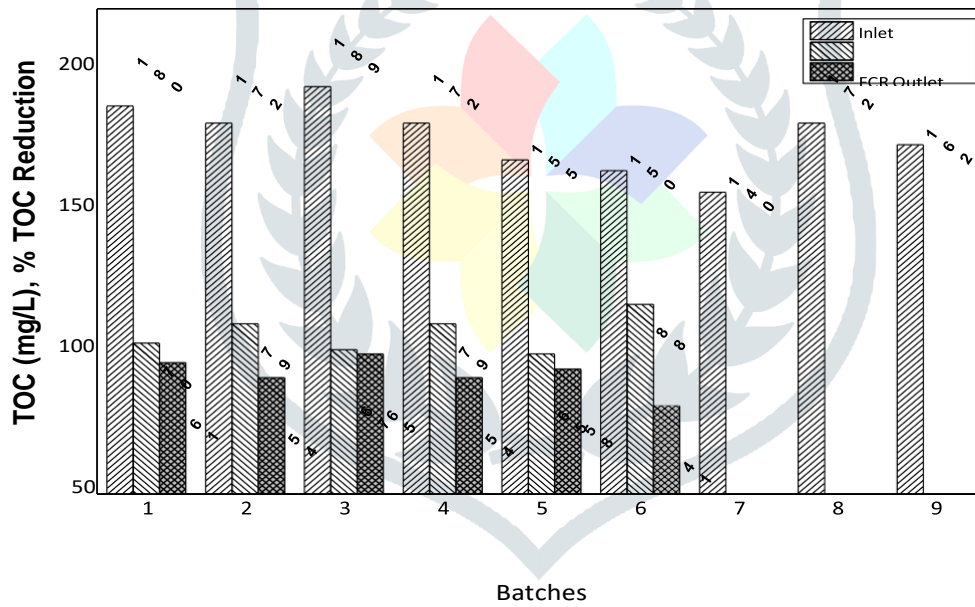
- The 3-D surface plots and contour plots are generated for better understanding of interaction between multiple parameters in Fenton Treatment based on which optimum dose has been selected (Fig. 4.10- 4.15).



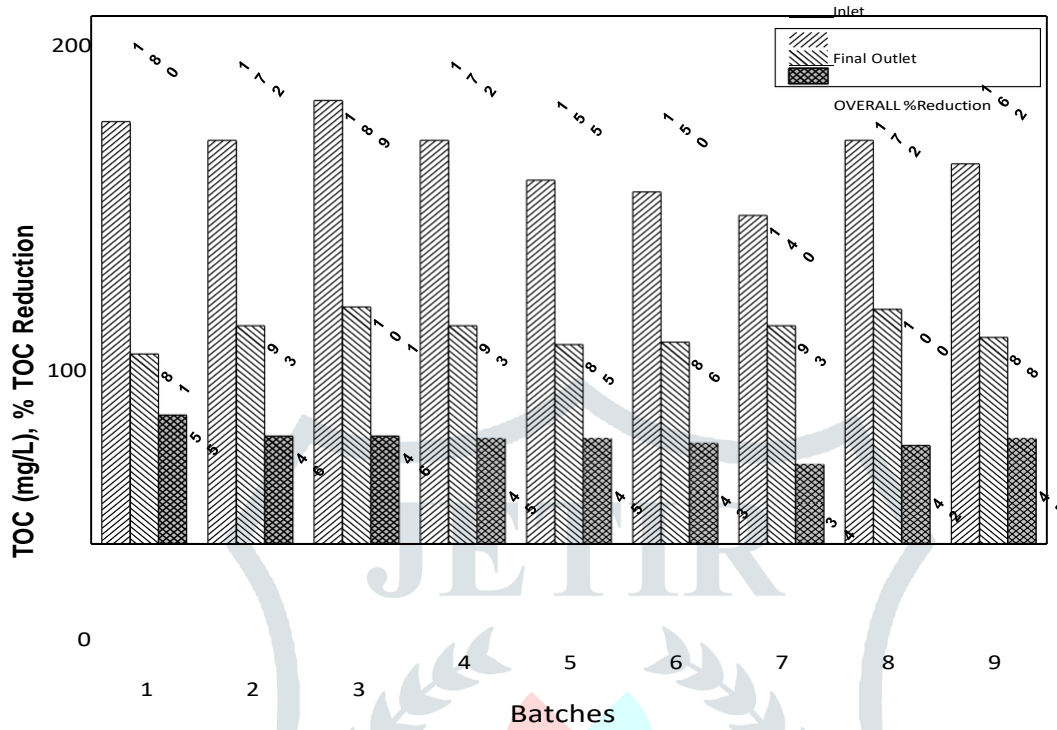
**Figure 5: Percentage COD reduction from FCR Treatment**



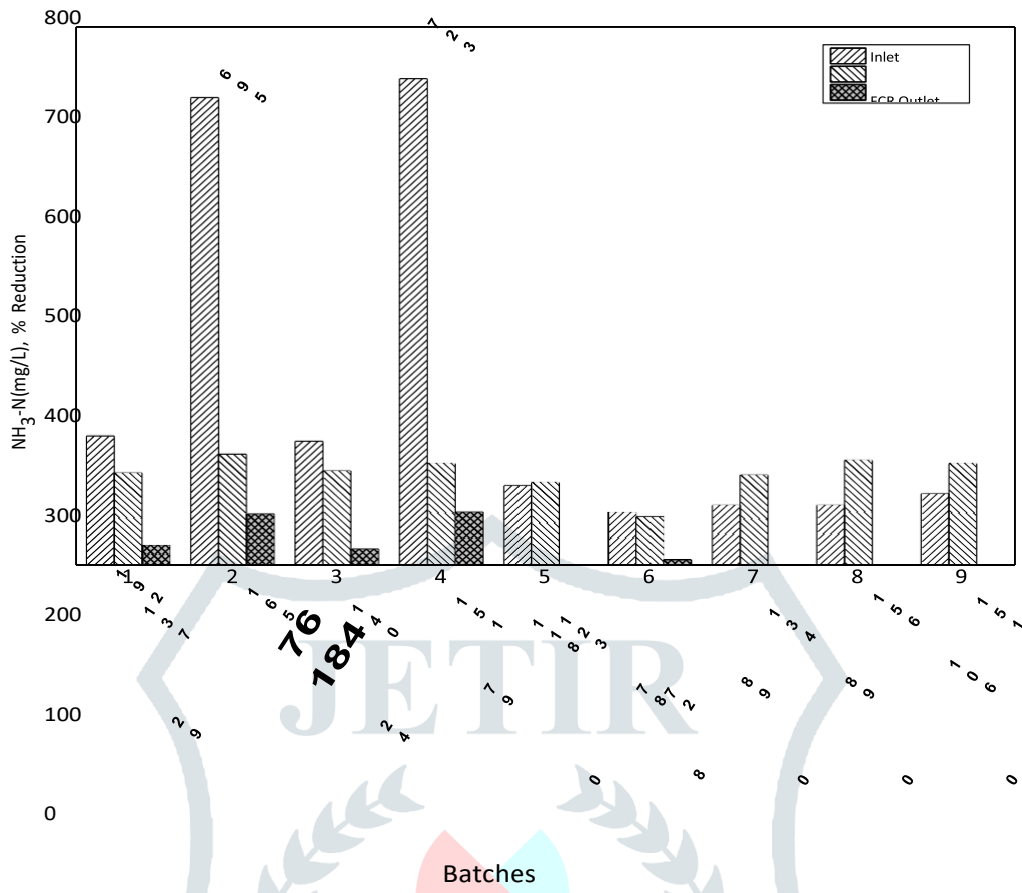
**Figure 6: Overall COD Percentage Reductions after Neutralisation**



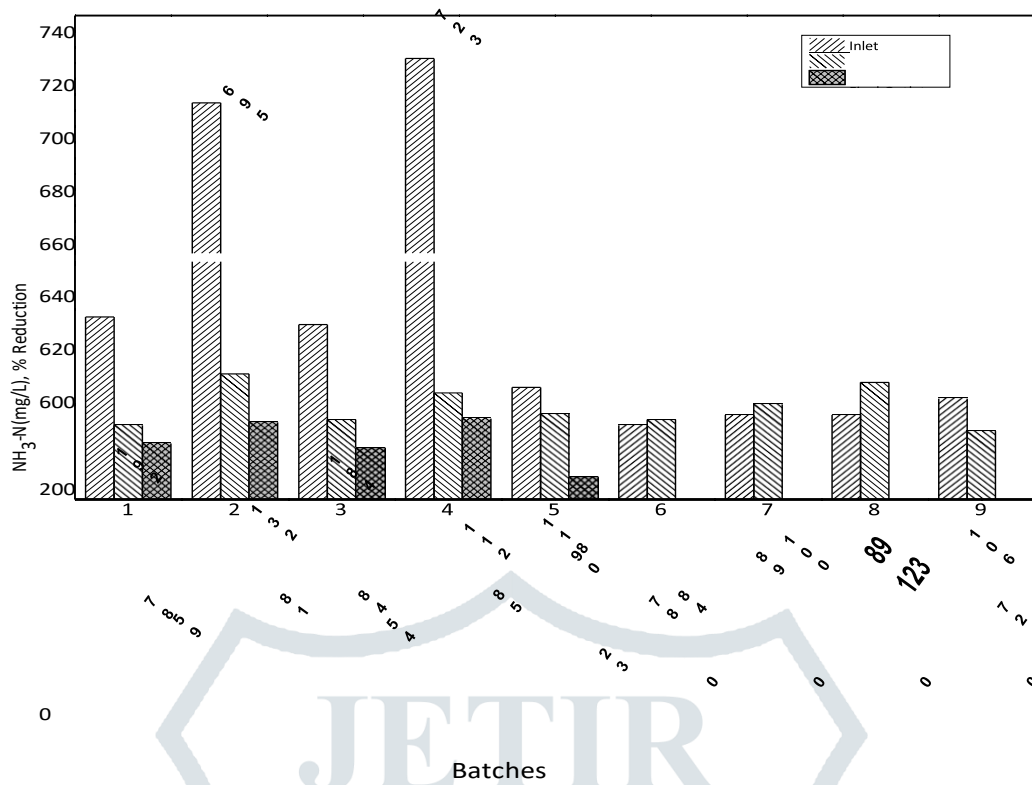
**Figure 7: TOC Reduction by FCR Treatment**



**Figure 8: Overall TOC Reductions after Neutralisation**



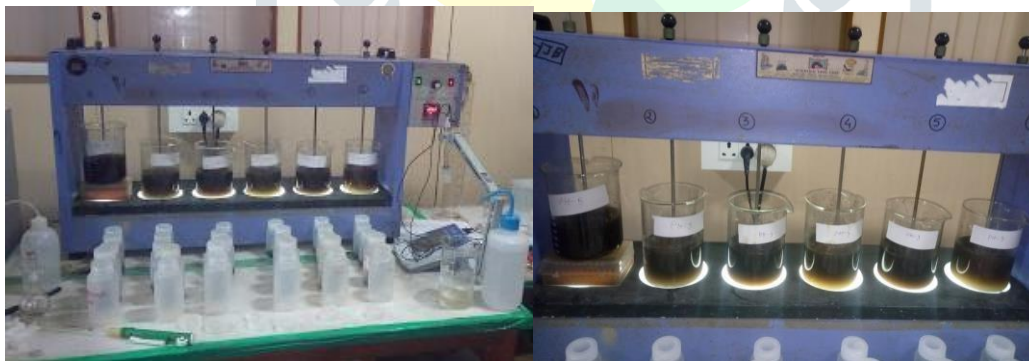
**Figure 9: NH3-N Reduction from FCR Treatment**



**Figure 10:** Overall NH<sub>3</sub>-N Reduction after Neutralisation

### ❖ CONVENTIONAL FENTON STUDIES AT PILOT SCALE

The experiments were conducted under various pH's (3, 4 & 5), ratios of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> (1:3 to 1:5) with minimum Fe<sup>2+</sup> dosage of 500 mg/l as shown in the Fig. 11.

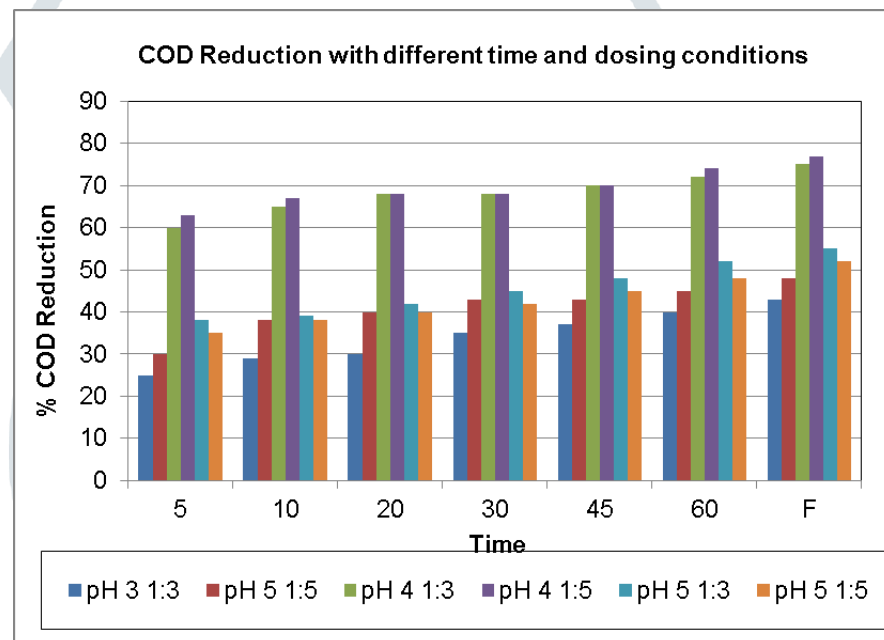


**Figure 11:** Fenton Studies carried at CSIR-NEERI lab

- Experimental runs indicated that there is a successive enhancement in COD reduction as the pH was varied from 3-5. The COD reduction (Fig. 12) increased from 48 to 77% as the pH increased from 3.0 to 4.0. However a decrease (77 to 55%) was observed when pH was further increased from to 5.0.
- This is because at higher pH, stable compounds  $\{Fe(OH)_2(H_2O)_4\}^+$  are formed and precipitation of Fe<sup>3+</sup> to Fe(OH)<sub>3</sub> takes place; hence the oxidation reaction will not proceed as Fe<sup>2+</sup> will not be produced. It can be concluded that optimal pH for Fenton reaction observed at

lab for this CETP effluent was pH 4 as maximum COD reduction was obtained. These results followed similar trend during the pilot scale FCR studies.

- Increasing  $\text{Fe}^{2+} / \text{H}_2\text{O}_2$  ratio from 1:3 to 1:5 enhanced COD reduction as  $\text{H}_2\text{O}_2$  is an oxidising agent (pH 4 and  $\text{Fe}^{2+} / \text{H}_2\text{O}_2$  ratio of 1/5, 77% of COD reduction). Our target was to minimal constituents of ferrous sulphate and hydrogen peroxide.
- Hydroxyl radicals produced during Fenton reaction is highly reactive resulting in completion of 90% reaction within 10 min and after that there was not much reduction in COD. Ideally, the time for Fenton reaction can be fixed to 10 min.
- After Fenton reaction, neutralisation by 1M  $\text{Ca}(\text{OH})_2$  solution aided COD reduction marginally by 20%.



*Figure 12: COD reduction with different time and dosing conditions*

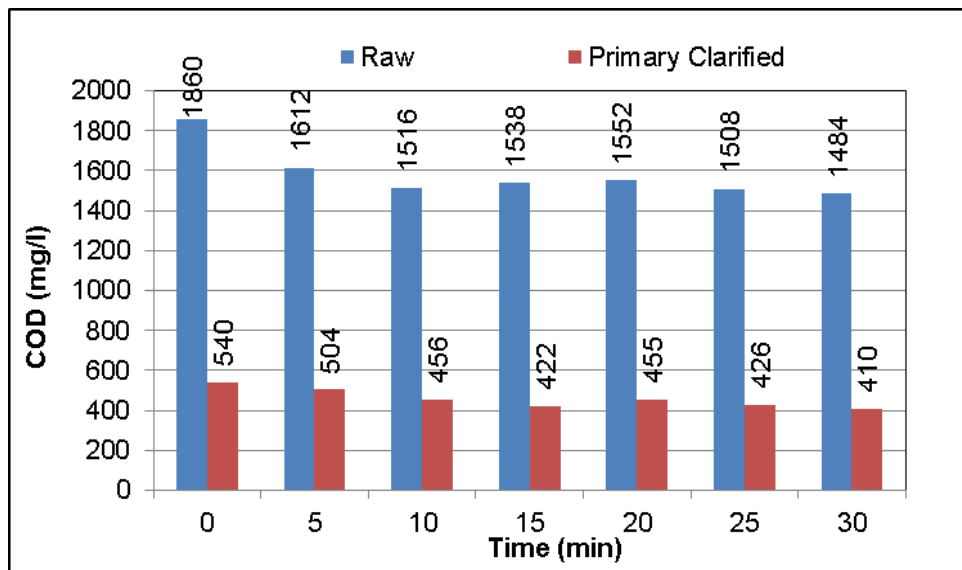
## ❖ EFFECT ON OZONATION ON CETP EFFLUENTS

Experiments were carried to assess efficiency of ozone for possible role in treatment of CETP effluents. Ozone is a powerful oxidant and can be easily installed in water and wastewater treatment systems as plug and play systems. Since the effluents have been observed to have very low BOD to COD ratios and the presence of dye compounds, ozone was thought to be useful to break the compounds prior to biodegradation. The experiments were conducted in a bubble column reactor on raw and primary clarified effluents (Fig. 18). Ozone efficiency was assessed under different contact times and ozone doses.

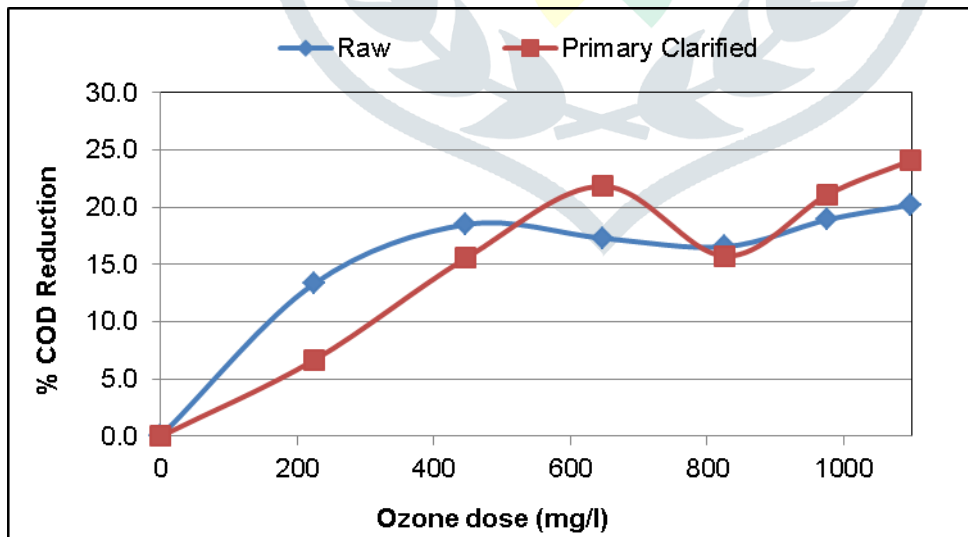




**Figure 18: Ozonation studies at lab scale**



**Figure 19: Percentage Reduction of COD on Ozonation**



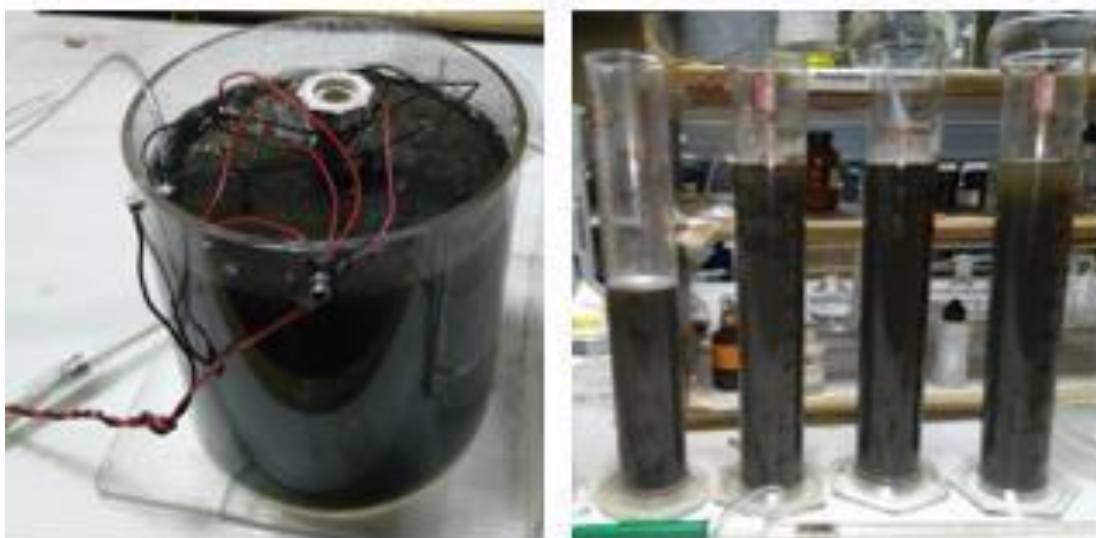
**Figure 20: Effect of Ozonation on COD**

A maximum COD reduction of 20.2% was obtained on raw effluent. This is lower than COD reduction on primary clarified effluent where 24% COD reduction was obtained. A contact time of 30 minutes was required for this treatment. The ozone dose ranged between 447-646 ppm to achieve COD

reduction above 15%. The low efficiency of ozonation is due to presence of high salt concentration (TDS: 11000-15000 mg/l) and recalcitrant in the sample. The results were not significant for consideration of ozonation as option now.

### ❖ ELECTROCOAGULATION STUDIES AT LAB SCALE

Electrocoagulation as an alternative method was also assessed for improving the existing primary treatment with the objective of reducing chemicals and sludge while improving efficiency. The inputs and controlling parameters for treatment of effluents include wastewater type, pH, current density, type of metal electrodes (aluminum/iron) and area. These variables would affect the overall treatment time, kinetics, and also the removal efficiency of the pollutants. The Fig 21 represents the electrocoagulation conducted in lab.



*Figure 21: Experiment of electrocoagulation carried out at NEERI lab*

The experimental studies were carried out using raw effluents from the CETP. The following were the conditions: Current: 2 amp, Voltage: 2V, Current Density: 1.19 mA/cm<sup>2</sup>. The studies were carried out to a maximum of 1 hour. A peak reduction was obtained after 15 min at COD reduction of 22%. Further increasing the time do not reduce COD concentration. It was concluded that the COD reduction was not impacted by electrocoagulation and only aided in reducing of suspended solids. The summary and recommendation of experimental work based on tertiary treatment is represented in Table 5

*Table 5: Summary and recommendation for tertiary treatment*

| S. No. | Process             | Conditions   | Pollutant Reduction  |
|--------|---------------------|--|----------------------|
| 1      | FCR pilot plant     | pH 3.5,<br>FeSO <sub>4</sub> : 1500mg/L<br>and H <sub>2</sub> O <sub>2</sub> : 1000mg/L. | COD: 60%<br>TSS: 89% |
| 2      | Lab scale Fenton    | pH 4,<br>Fe <sup>2+</sup> : H <sub>2</sub> O <sub>2</sub> - 1:3                          | COD: 77%             |
| 3      | Lab scale ozonation | Ozone Dosage: 646mg/L at<br>30 minutes of contact time                                   | COD: 24%             |

|   |                                 |  |           |
|---|---------------------------------|--|-----------|
| 4 | Lab scale<br>Electrocoagulation | Current: 2-amp, Voltage: 2 V,<br>Current Density: 1.19<br>mA/cm <sup>2</sup> | COD: 22%. |
|---|---------------------------------|--|-----------|

## **CONCLUSION :**

Case study of CETP Vatva illustrates that the Fenton Catalytic Reactor does not remain mere theoretical concept of treating refractory COD and rather proves to be an effective solution for removing refractory COD in actual practice. The comparative study of COD value reflects that after commissioning Fenton Catalytic Reactor at CETP-Vatva, COD values reduced by approx. 60%. Therefore, it is not out of context to state that Fenton Catalytic Reactor can be proven effective tool for reducing refractory COD of effluent generated from dyes and dyes intermediate industries. However, further research has to be carried out for optimization of its operation.

## **REFERENCES :**

- [1] Joao Peres Ribeiro, Maria Isabel Nunes: *Recent trends and developments in Fenton processes for industrial wastewater treatment – A critical review*
- [2] Poornima Menon, T.S.Anantha Singh, Nibedita Pani, P.V.Nidheesh: *Electro-Fenton assisted sonication for removal of ammoniacal nitrogen and organic matter from dye intermediate industrial wastewater*
- [3] Andre Fernandis Rossy: *Fenton's process applied to Wastewater Treatment: Heterogeneous & Homogeneous Catalytic Operation Modes*
- [4] Meng hui Zhang, Hui dong, Liang Zhao, De-xi Wang, Di Meng: *A review on Fenton process for organic wastewater treatment based on optimization perspective*
- [5] Aggarwal, S. C. and Kumar S. (2011). "Industrial Water Demand in India: Challenges and Implications for Water Pricing" India Infrastructure Report 2011:
- [6] Water: Policy and Performance for Sustainable Development, IDFC and Oxford University Press.
- [7] Ahluwalia, V. K. (2010). Organic Reaction mechanism, Narosa Publishing House Pvt Ltd, New Delhi, India
- [8] Badawy, M. I. and Ali, M. E. M. (2006). "Fenton's peroxidation and coagulation processes for the treatment of combined industrial and domestic wastewater." J of Haz mat., B136, 961-966.
- [9] Barbusinski, K. (2009). "Fenton reaction - controversy concerning the chemistry." Ecolo chem and engg, 16, 347-358.
- [10] Bautista, P., Mohedano, A. F., Casas, J. A., Zazo, J. A., Rodriguez J. J. (2008). "An overview of the application of Fenton oxidation to industrial wastewaters treatment." Journal of Chemical Technology and Biotechnology, 83, 1323-1338.
- [11] Brillas, E., Mura, E., Sauleda, R. I., Sanchez, L., Peral, J., Domenech, X. and Casado, J. (1998). "Aniline mineralization by AOP's: anodic oxidation,