Reduction Of Cod And Bod By Oxidation: A Cetp Case Study

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ABSTRACT

The present study is focused on a Common Effluent Treatment Plant (CETP) located at Umaraya, District Baroda. Waste water from about thirty five small and medium scale industries majorly comprising of chemical manufacturing and pharmaceutical industries are treated in this CETP. The incoming wastewater was collected and segregated into three groups as per their BOD/COD ratio. They were then oxidized independently by two oxidants Fenton's reagent (Fe^{2+}/H_2O_2) and Sodium Hypochlorite (NaOCl) and reduction in COD and BOD were observed at different chlorine, H_2O_2, $FeSO_4$ doses, different pH values and contact time for determining the optimum values. COD and BOD values at optimized conditions for the two oxidants were compared and observed that maximum reduction of 64.35% and 68.57% respectively was achieved by Fenton's reagent. The results clearly indicate that conventional system should be replaced by advanced oxidation process and Fenton's reagent is a suitable choice.

Keywords - CETP, COD and BOD reduction, Fenton's Reagent, Optimum Conditions, Oxidation

I. INTRODUCTION

During the last few years the concept of CETP for the different small and medium scale industrial estates in the Gujarat state has developed with a great speed. One of these CETP has been established for the cluster of industries in western side of Baroda district particularly between Padra Taluka and Jambusar Taluka. M/s Enviro Infrastructure Co. Ltd. (EICL), village Umaraya, Taluka Padra has set up a Common Effluent Treatment Plant (CETP). The plant is located on Effluent Channel Road. The CETP was commissioned on 1st May 2000. CETP was set up to cater Small and Medium scale industries situated in and around Padra & Jambusar Districts.

These small scale industries go on expanding and as per the market demand they change their processes also. Therefore the composite wastewater strength on which a CETP is designed is also getting changed in every couple of years. Because of these changes in the parameters of the composite wastewater it is observed that the present CETP is not able to treat the composite effluent in an efficient manner. It may happen that the entire biological treatment along with the primary treatment also gets totally and /or partially disturbed. The study here is aimed for some modifications in the CETP, for maintaining two of the important parameter COD and BOD of the treated waste water from CETP as they do not meet the required GPCB (Gujarat Pollution Control Board) disposal standards to discharge into ECP (Effluent Channel Pipe) which is a closed effluent channel that carries the effluent to Bay of Cambay.

This is achieved by oxidizing the wastewater independently by two oxidants viz. Fenton reagent (Fe^{2+}/H_2O_2) and Sodium Hypochlorite (NaOCl) and comparing the results of COD and BOD reduction between them. Such advanced physico-chemical processes, can take much higher fluctuating load and characteristics of inlet effluent as compared to conventional biological treatment methods.

1.1 Field Study

At present, there are 52 member units, out of which only 35 member industries are discharging their waste water at CETP. As only 35 industries are working the study is carried out only for composite waste water of these industries, discharged into equalization tank of CETP. The following Table 1 shows the type of industries and their effluent contributions.

Table 1 - Category of Industries and their contribution to the CETP

Sr. No	Category	No of Industries	Effluent flow (m^3/d)
1	Chemical manufacturing industries	25	144
2	Pharmaceutical industries	8	446
3	Glass manufacturing industries	1	10
4	Others	1	0.4
Total flow			600.4

1.2 Present Condition of the CETP

CETP at Umaraya is provided for treatment of about 52 member industries. The present CETP is designed for 2250 m^3/d of flow. The present CETP needs modification because though the quantity of flow is very less (600.4 m^3/d) than the designed capacity, the parameters like COD, BOD, NH_3-N, SS and oil & grease after final treatment comes out to be 450,150, 87.8, 484 and 25mg/L respectively which do not meet the GPCB disposal standard into

ECP which are 250,100, 50, 100 and 20 mg/L respectively.

The effluent is received from different industries through a rubber lined tanker. Before the effluent is loaded in the equalization tank, the effluent parameters are measured and then only effluent is loaded in the equalization tank. From here, the effluent is lifted to Flash Mixer. At this tank, continuous dosing of hydrated lime and Aluminum Sulfate (Alum) slurry is added for flocculation and coagulation. After mixing, the effluent is transferred to Primary Settling Tank. As per original treatment scheme (2250 m^3/day), two stage Aeration followed by Secondary Clarifier treatment process was provided. As the present effluent quantity is very less only one compartment of Aeration Tank is used. At tertiary treatment level, four Dual Media Filter tanks and chlorination unit is provided.

Generally, conventional biological treatment such as activated sludge is only able to degrade below 1000 mg/L of COD. Thus, an alternative treatment or pre-treatment of the wastewater is required. There are many treatment options available for the removal of pollutants successfully such as stripping, carbon adsorption and membrane process. However, due to cost effectiveness, stringent regulatory limits and process limitations, advanced oxidation process (AOP) is a flexible technique towards enhancing the existing system. AOP is capable of improving the biodegradability of complex or recalcitrant compounds. This process is based on the chemical oxidation technologies that use hydroxyl radical (•OH) generated in situ. The radical oxidizes the organic and/or inorganic contaminants to produce environmentally friendly fragments and eventually to CO_2 and H_2O if sufficient reagents and time are allowed. There are various ways of generating hydroxyl radical and one such method is using Fenton's reagent. Fenton's reaction is based on the catalyzed decomposition of hydrogen peroxide by Ferrous ions (Fe^{2+}) to produce very reactive hydroxyl radicals [1]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet$$

II. MATERIALS AND METHODS

2.1 Materials

All chemicals employed in this study were analytical grade. All solutions were prepared in distilled-deionized water made on each experimental day. Glassware used in this work was soaked with HNO_3 (~10%) for 24 h, and rinsed with distilled-deionized water prior to drying. A chlorine stock was made from 12% (100ml=12mg) sodium hypochlorite (NaOCl). Hydrogen peroxide was prepared by using the analytical grade (30% by wt.) H_2O_2 as purchased. The ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) was used as the source of Fe^{2+} in the Fenton process. Solutions of NaOH and HCl were used for pH adjustments.

2.2 Sample Preparation

Sampling and analysis of the raw waste water coming from different industries was done by taking grab sample. The waste water sample was collected directly from tanker on approximately weekly basis for segregation purposes. The raw waste water sample was first collected and analyzed for different parameters to determine the quality of the incoming raw waste water and then was segregated into three groups as per BOD/COD ratio as shown in Table 2. Segregation of effluent means separation as per effluent characteristics. It is a new concept for wastewater minimization and optimizes the operation cost [2].

Table 2 **-** Various Industries Categorized in Groups

Group	BOD/COD	Flow rate
A	< 0.30	480.00 m^3/day
B	0.30-0.40	90.00 m^3/day
C	>0.40	70.00 m^3/day

2.3 Experimental Procedure

2.3.1Oxidation by Sodium Hypochlorite

Batches of 100 ml volume of wastewater sample of the three groups A, B and C were prepared. Chlorine solutions of known strength were prepared in de-ionized water in the range of concentration 2, 4, 6, 8, 10 ml. The residual chlorine was found for the different chlorine concentrations by iodometric method. Then by using the optimum chlorine dose obtained for the three group's residual chlorine for varying pH from 4-7 was found. Residual chlorine graph for varying chlorine doses and pH was plotted as shown in Fig.1. Using the optimum chlorine dose and pH range found for the three groups, COD and BOD of the wastewater after chlorination was determined by standard methods and graph was plotted as shown in Fig.6. All the samples were kept in the dark during chlorination to prevent photolysis.

2.3.2 Oxidation by Fenton's Reagent

For various batches of 100 ml volume samples of wastewater for three groups A, B, C, COD and BOD was determined by standard methods for varying doses of H_2O_2 (1,3,5,10ml) to obtain optimum dose. 1mg fixed amount of solid ferrous sulfate was added to the solution and mixed until complete dissolution. The contact time, pH and temperature was kept constant to 40 minutes, 7.5 and 30°C respectively. Similarly the process was repeated for obtaining optimum pH and contact time by using optimized H_2O_2 dose, pH, and contact time as experiments proceed and keeping all other quantities constant. The graphs of COD and BOD were plotted as shown in Fig. 2,3, 4 & 5.Then by using all the optimized parameters obtained above

COD and BOD was again determined and graph was plotted (Fig.6).

Similarly, 100 ml volume sample was prepared by mixing A, B and C group wastewaters. There initial COD and BOD was measured and then treated with different H_2O_2 dose (3, 4,5ml) to obtain optimum dose using 1mg $FeSO_4$, 4 pH, 60 min contact time and 32°C temperature. This process was repeated using optimum H_2O_2 dose for varying $FeSO_4$ dose (0.5, 1, 1.5, 2mg) and graph was plotted (Fig.7). The sludge formation was 3ml.

III. RESULTS AND DISCUSSION

After optimization of chlorination and Fenton's reaction, COD and BOD reduced for three segregated groups of wastewater by both processes can be compared. Figures 3 and 10 shows the initial COD and BOD level and reduced levels after treatment. The COD reduction during chlorination was 23.2%, 19.16%, 45.14% while BOD reduction was 38.91%, 24.27%, 44.67% [3]. Whereas the COD and BOD reduction during Fenton treatment was 50.86%, 49.47%, 60% and 34.55%, 49.33%, 56.67% respectively. Furthermore COD and BOD reduction during Fenton treatment of mixed wastewater at optimized pH, H_2O_2 and $FeSO_4$ dosing was found to be 64.35% and 68.57% respectively [4, 5]. The results obtained clearly indicates that there is no significant difference between the COD and BOD reductions for segregated and mixed wastewater but rather the Fenton's reagent was more effective for combined wastewater. Thus in this case segregation concept cannot be applied. The reduction in other parameters like NH_3-N, SS and oil & grease after treatment with Fenton's reagent of mixed wastewater came out to be 45.76%, 75.43% and 17.32% respectively.

It is obvious from the above data that COD and BOD reduction was achieved maximum during Fenton's treatment. The optimum pH, contact time, H_2O_2 and $FeSO_4$ dosing was found to be 4, 60 min, 4ml and 1mg respectively at temperature 32°C for the mixed wastewater [6]. The reduction achieved by oxidation process was more than that achieved by conventional biological treatment at CETP. It shows that the organic loading coming from the chemical and pharmaceutical industries is majorly of non-biodegradable type. In any case 100 per cent oxidation could not be achieved because all the added oxidant molecules may not be available for the oxidation of organic matter contributing to COD. A portion of oxidant might have also been used in the oxidation of some other metals (in low concentrations) in the sample [7].

IV. CONCLUSION

From the above experiments we can conclude that conventional biological treatment of the CETP should be replaced with physico-chemical process like advanced oxidation process as incoming COD value is more than 1000mg/L majorly consisting of non-biodegradable load. The study showed that among the two oxidants Sodium Hypochlorite and Fenton's reagent, the latter is the most efficient as the maximum COD and BOD reduction was observed for this oxidant.

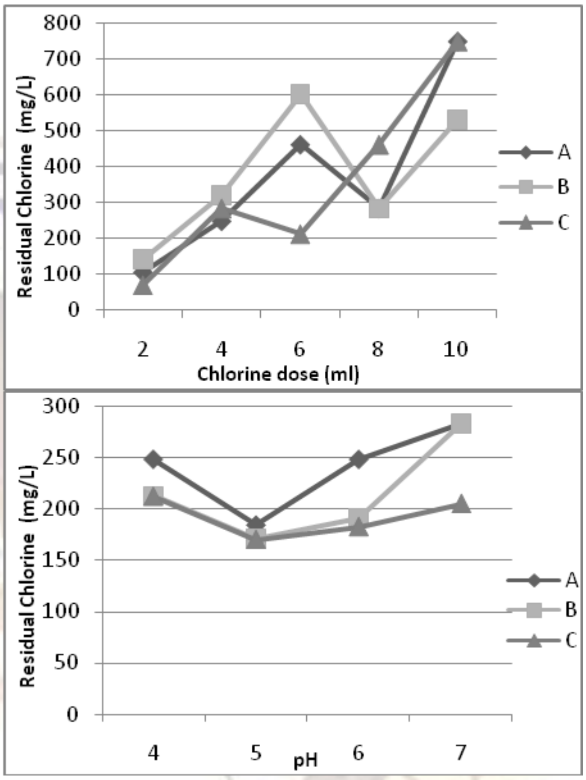

Figure 1: Residual Chlorine for varying Chlorine doses and pH values

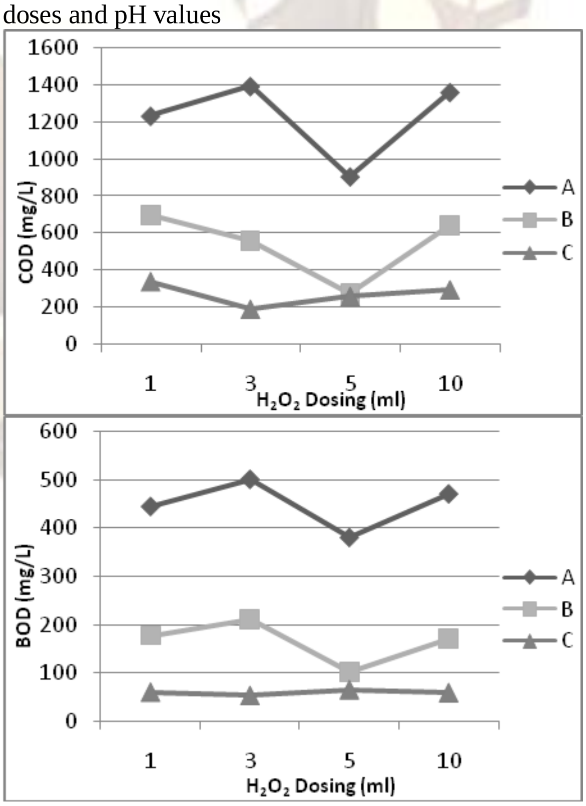

Figure 2: Optimization of H2O2 dosing

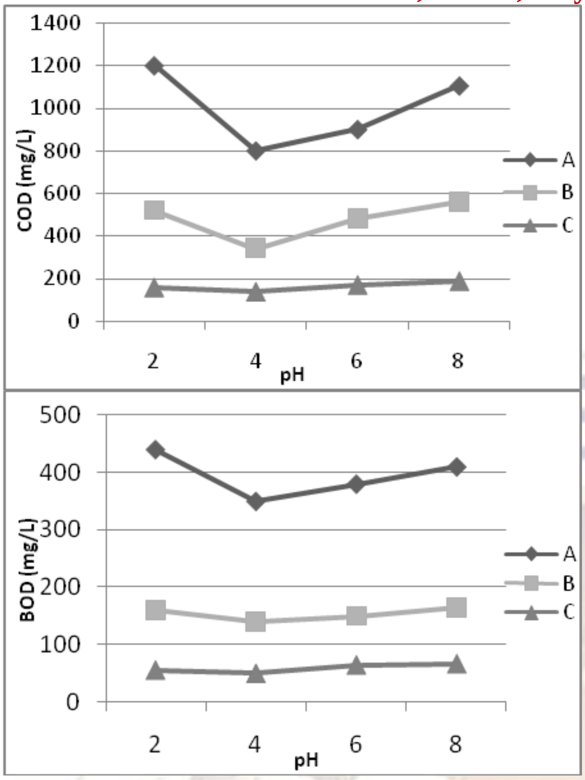

Figure 3: Optimization of pH

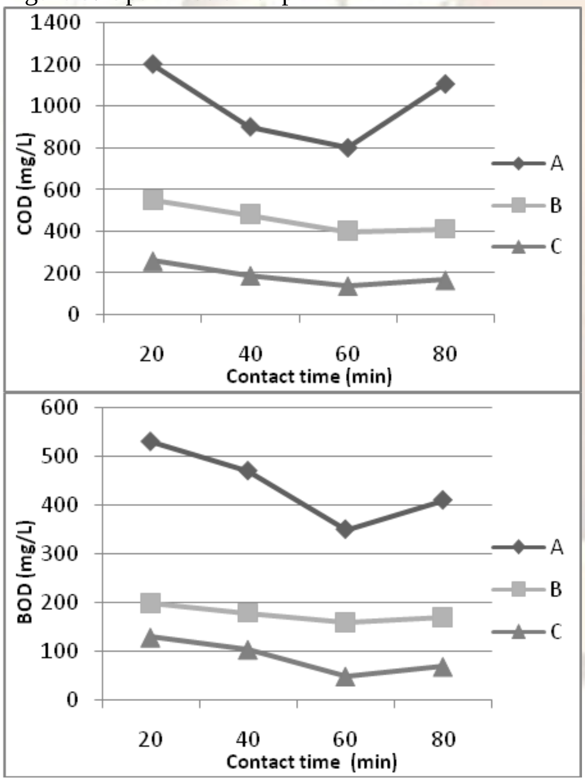

Figure 4: Optimization of Contact Time

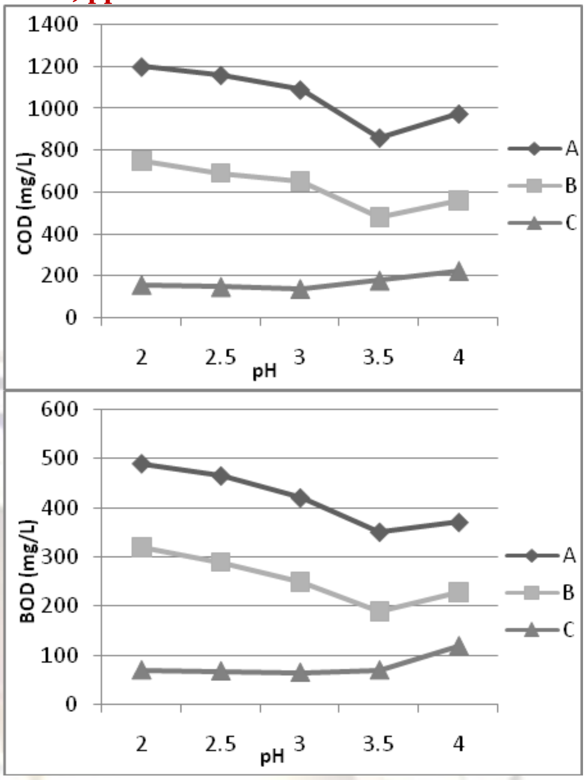

Figure 5: Optimization of pH

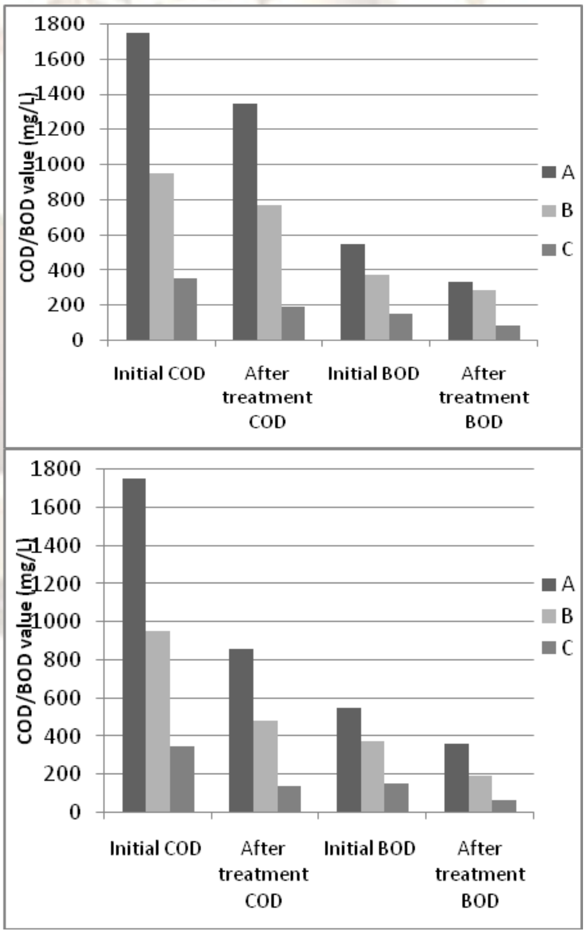

Figure 6: Comparison of Chlorination and Fenton's treatment process at optimized conditions

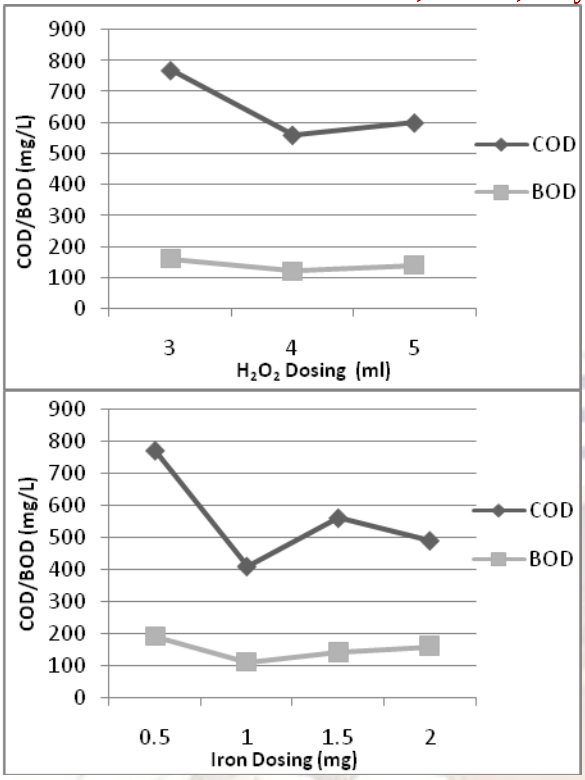

Figure 7: Optimum H2O2 and Iron dosing for mixed wastewater

V. ACKNOWLEDGEMENTS

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