Physico chemical treatment of industrial effluent using Hydrogen Peroxide and Ferrous Sulphate

Sunil Shaha* and Kalyani S. Patake**

* Research guide ** Research Student

Environmental Engineering Department, KIT's College of Engineering (Autonomous),
Kolhapur, Maharashtra, India

Abstract

Industrial effluents with varying characteristics may have very high pollution potential with high COD. Such effluents are difficult to treat using biological treatment only. In this case, use of hydrogen peroxide in c*ombination with ferrous sulphate popularly known as Fenton's* reagent can be used a pre-treatment to reduce the toxicity of effluent to a certain level. This pre-treatment will aid in reducing load on the biological system which will in turn reduce the size of the biological treatment reactor. Operational problems such as disturbance of the biological system, disintegration of the filter media will also be avoided.

*Fenton's reagent give*s an average COD removal efficiency of 35%. It also helps in reduction of BOD, chloride, oil & grease, TSS and phosphate and increases TDS and Sulphate content.

Keywords: Industrial effluent, pollution potential, hydrogen peroxide, ferrous sulphate, pre-treatment.

1. Introduction

The industry process effluent contains high chemical and organic load. This effluent post-treatment is used on land for irrigation purposes. If the effluent is not treated to a desirable level, it may cause harm to flora and fauna as well as contaminate the land. In such cases, conventional treatment may not suffice and an additional pre-treatment may help in lowering the pollutant levels and make it easily treatable in the conventional treatment process.

Here, for the purpose of study, hydrogen peroxide and ferrous sulphate (Fenton's reagent) was used as pre-treatment.

The Fenton's reagent was discovered by Fenton in 1894, (Fenton, 1894). Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals. The ferrous iron (Fe++) initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. Generally Fenton's oxidation process is pH adjustment, oxidation reaction, neutralization and coagulation for precipitation. Hydrogen peroxide being a strong oxidative agent, Fenton's reagent was selected for the study.

Table 1: Characteristics of the primary treated industrial effluent used for trials

Parameter	Average characteristics (in mg/l except pH)
pH	5-7
TDS	4500-6500

TSS	50-150
COD	5000-8000
BOD	1500-3000
Oil & Grease	50-100
Chloride	1000-2000
Sulphate	100-200
Phosphate	200-300

1.1 Effluent Sampling

Grab sample of effluent from the dissolved air floatation (DAF) unit was taken for analysis. Five such samples were collected on consecutive days for the trials.

1.2 Fenton Process

The traditionally accepted Fenton mechanism is represented by following equations and implies the oxidation of ferrous ions to ferric ions as a means to decompose hydrogen peroxide to hydroxyl ions. It is usually considered as the core of the Fenton chemistry. The formation of the hydroxyl radicals by using the photo-Fenton and photo-Fenton processes under application of Fe (II) or Fe (III) occurs according to the following reaction (Arjunan Babuponnusami et al., 2013).

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

The reaction carried out in sun to contribute the UV radiations to the reaction coins its name as photo-Fenton reaction. The photo reduction of various ferric species contributes to the production of ferrous ions and radical species. The reaction time needed for photo Fenton to work is low and is dependent on operating pH.

pH has a decisive effect on the oxidation potential of the radical ions due to the reciprocal relation of the oxidation potential to the pH value. Therefore, the role of pH in the photo-assisted Fenton reaction is crucial. In Photo-Fenton reactions, the maximum catalytic activity is observed at pH of about 2.8–3. The pH value influences the generation of OH_ radicals and thus the oxidation efficiency. When the pH is maintained above 3, the hydrogen peroxide auto decomposes rendering the reaction ineffective.

1.3 Experimental set-up

1 lit beaker was used of experimentation. pH meter was used to check pH as per necessity during the experimentation. The analysis was carried out at ambient temperature (around 25 degrees Celsius) throughout the experiment.

Chemical used were hydrogen peroxide, ferrous sulphate, hydrochloric acid and lime.

1.4 Procedure

- 1 lit effluent from dissolved air floatation unit was taken.
- COD was measured and recorded before experimentation. Other parameters such as pH, BOD, TSS, TDS, O&G, Chlorides, Phosphate and Sulphate were also analysed to correlate outcome of the trial on other parameters.

- Considering average COD of DAF outlet to be around 4000 mg/lit, calculation of amount of chemicals was done.
- 1 ml/l of H_2O_2 and 0.75 g/l of FeSO4 (Ebrahiem, 2013)
- As per the abovementioned ratio, 30 mg of $FeSO_4$, $7H_2O$ added to the sample.
- pH was checked and found to be around 6 for each sample it was brought down to 3 using acid.
- 15 ml of H_2O_2 added to the sample.
- After addition of H_2O_2, the sample was stirred vigorously.
- Reaction time of 40 mins was given (Ebrahiem, 2013).
- After 40 mins, pH was adjusted to 7 using lime, to destruct the excess H_2O_2 present in the sample.
- COD was analysed after reaction. Other parameters were also analysed to understand correlation of the experiment output on other parameters.
- This reaction was followed by coagulation and flocculation in the overall treatment process.

1.5 Analytical Methods:

The experimental procedure for all parameters were as per standard methods.

2. Results and discussion

2.1 Effect of Fenton's reagent on COD and BOD removal

The industrial effluent treated under following conditions (pH 3 and ambient temperature) treated with ferrous sulphate and 30% hydrogen peroxide resulted in good COD removal. The BOD: COD ratio of the effluent was 0.38 which indicated good biological degradability. The reaction of photo Fenton results in an average reduction of COD by 35% and average BOD removal by 40% which could be further reduced in a conventional biological system.

It has been noted that with the reagent dose used for trial, maximum COD reduction achieved is around 3000 mg/l. For further COD reduction, an effective tertiary treatment system is required in order to achieve consent conditions in India.

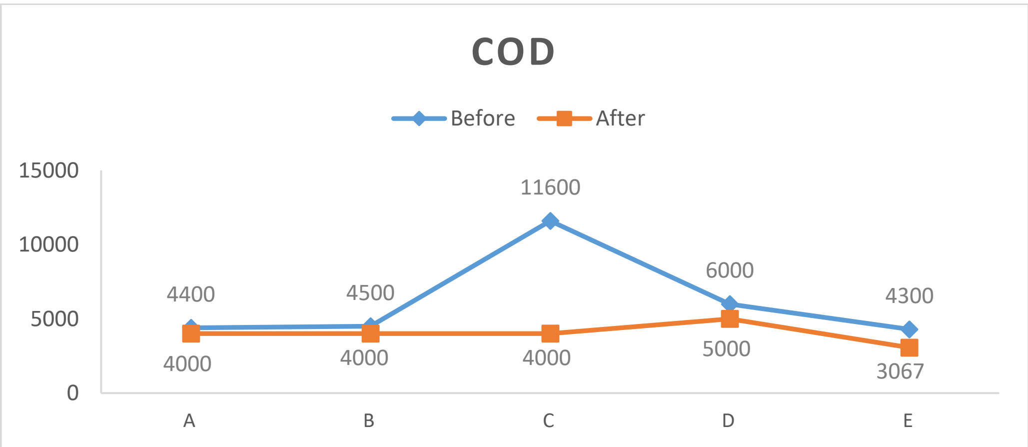

Fig 1: Graph depicting COD removal

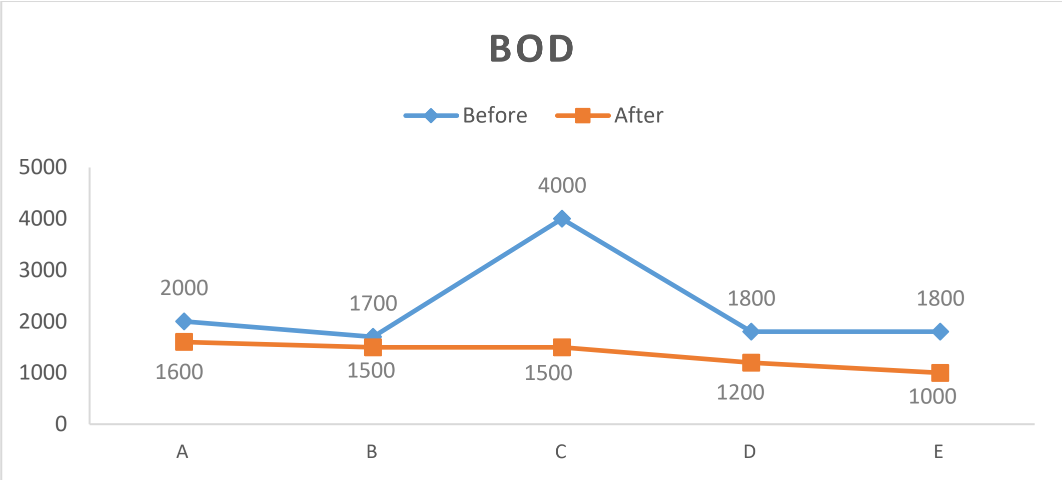

Fig 2: Graph depicting BOD removal

2.2 Effect of Fenton's reagent on other parameters

Fenton's reagent show an average positive impact on TSS, Oil & grease, Chloride and Phosphate reduction and on the other hand, the TDS and Sulphate levels show a negative impact post reaction. The increase in TDS is due to addition of chemicals like hydrochloric acid, hydrogen peroxide and ferrous sulphate. The addition of H_2O_2 also increases sulphate concentration as the sulphides and sulphites in water get converted to sulphates post oxidation.

Table 2: Photo-Fenton's Reagent trials- Analysis results

Fenton Reagent Trials - Analysis results										
Sr. No.	Parameters	Units	Activity	A	B	C	D	E	Average	Increase / Decrease (After - Before)
2	PH	NA	Before	6.7	6.5	6.7	6.5	6.9	6.7	NA
			After	7.1	8.2	7.8	7.7	8.1	7.8	
3	TDS	mg/l	Before	6093.0	4241.0	5534.0	4482.0	3823.0	4834.6	1458
			After	7021.0	7699.0	6788.0	5220.0	4733.0	6292.2	
4	TSS	mg/l	Before	325.0	47.5	232.0	177.0	38.0	163.9	-8
			After	152.0	304.0	57.0	187.0	81.0	156.2	
5	COD	mg/l	Before	4400.0	4500.0	11600.0	6000.0	4300.0	6160.0	-2147
			After	4000.0	4000.0	4000.0	5000.0	3066.7	4013.3	
6	BOD	mg/l	Before	2000.0	1700.0	4000.0	1800.0	1800.0	2100.0	-900
			After	1600.0	1500.0	1500.0	1200.0	1000.0	1640.0	
7	Oil & Grease	mg/l	Before	137.0	57.0	105.0	78.0	72.0	89.8	-5
			After	31.0	275.0	40.0	53.0	26.0	85.0	

8	Chloride	mg/l	Before	2446.0	2543.9	2089.3	1517.7	1507.8	2020.9	-76
			After	2309.0	2465.6	2093.2	1527.5	1330.4	1945.2	
9	Sulphate	mg/l	Before	359.0	139.1	145.6	134.7	349.8	225.6	635
			After	499.0	599.2	1362.9	836.0	1005.0	860.4	
10	Phosphate	mg/l	Before	42.0	115.7	125.5	17.8	0.1	60.2	-7
			After	4.6	6.7	56.3	103.4	97.3	53.7	

*Negative sign indicates decrease in pollutant levels.

3. Conclusion

Photo-Fenton reagent is an environmentally friendly technology for degradation of organic compounds. This advance oxidation process gives positive results for degradation of organic content but the photo-Fenton system does not give viable result to adopt it as a primary means of effluent treatment. This system can hence be effectively used as a pre-treatment to reduce the toxicity to a certain level beyond which biological treatment can be employed. Such combinations will help in obtaining best possible results. It is also to be noted that post the reaction, the excess H_2O_2 should be destructed by addition of lime as presence of H_2O_2 in the biological system will act as inhibitor for the micro-organisms and may disturb the biological system.

Similar studies may also be conducted for other oxidizing agents like Ferric chloride.

4. References

Arjunan Babuponnusami, Karuppan Muthukumar, "A review on Fenton and improvements to the Fenton process for wastewater treatment", Journal of Environmental Chemical Engineering, JECE-186 (2013)

Ebrahiem E. Ebrahiem, Mohammednoor N. Al-*Maghrabi, Ahmed R. Mobarki, "Removal of* organic pollutants from industrial wastewater by applying photo-Fenton oxidation *technology", Arabian Journal of Chemistry 10, S1674*–S1679, (2017)

Mohamed Ksibi, "Chemical oxidation with hydrogen peroxide for domestic wastewater treatment", Laboratoire de l'Eau, de l'Energie et de l'Environnement (LEEE), Ecole Nationale d'Ing´enieursde Sfax (ENIS) Universit´e de Sfax, B.P. W 3038, Sfax, Tunisia (2006)