Fenton Process-A Pre Treatment Option for Hospital Waste water

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Abstract - Advanced oxidation Process such as Fenton, Photo Fenton and Photo Oxidation like processes constitute a promising technology for the treatment of waste water containing non bio degradable organic compounds. In Fenton's process iron and hydrogen peroxide are the two chemicals used as reagents. Oxidation using Fenton's reagent causes the dissociation of the oxidant and the formation of reactive hydroxyl radicals that destroy organic pollutants to harmless compounds. The Fenton reaction has a short reaction time among all advanced oxidation processes. The reagents are cheap and non toxic as well s there is no energy involved as catalyst and the process is easy to run and control.

In this work efforts are made to investigate the potential application of Fenton's reaction as a pre treatment technique for hospital waste water. The prime objective of this study is to evaluate the improvement in biodegradability of pollutants in hospital wastewater using the Fenton process. The physical and chemical characteristics of the waste water have been analysed. Experiments were conducted with varying doses for optimization of process variables for the process. The effect of operating conditions on the efficiency of the process has been investigated. The appropriate conditions for the Fenton process for application to hospital wastewater are reported for the design of the treatment process.

Keywords – Advanced Oxidation Process, Fenton Process, Hydroxyl radical

I. INTRODUCTION

Improvement of the hospital waste management has received increasing attention throughout the world since hospitals generate a considerable amount of medical waste each year. The generation of waste in hospitals has been increasing due to disinfectants. Besides the active substances, formulation adjutants, pigments and dyes are also waste generating components. Disinfectants, in particular, are often complex products or mixtures of active development in medical services and products. In hospitals, a variety of substances besides pharmaceuticals are used for medical purposes as diagnostics and substances. After application, many drugs are excreted non-metabolized by the patients and enter into wastewater. Diagnostics agents and disinfectants also reach the wastewater after as residual quantities. First findings of pharmaceuticals in the aquatic environment were reported in the 1970s. Some investigations represented the existence of drugs in public owned treatment works effluents. Hospital wastewater has similar quality to municipal wastewater, but may also contain various potentially hazardous components including, mainly, microbiological pathogens, hazardous chemical compounds, disinfectants, pharmaceuticals and radioactive isotopes. Indeed hospital wastewater may have an adverse impact on environmental and human health; therefore, the proper management of hospital wastewater is needed.

Hospitals consume an important volume of water a day. Indeed the consumption of domestic water is on average 100 litres/person/day, while the value generally admitted for hospitals varies from 400 to 1200 litres/day/bed. In hospitals water consumed by various parts such as hospitalization, surgery rooms, laboratories, administrative units, laundry, health services, kitchen and etc, physical chemical and biological quality decreased and converted to wastewater. This important consumption in water of hospitals gives significant volumes of wastewater. [7]

Hospital wastewater contains antibiotics, pharmaceuticals, heavy metals, x-ray contrast and some organic substances that are resistant to biological degradation. The contact of hospital pollutants with aquatic ecosystems leads to a risk directly related to the existence of hazardous substances, which could have potential negative effects on the biological balance of natural environments. There is a need for efficient pre-treatment options which can effectively reduce/alter/modify the recalcitrance/toxicity profile of the wastewater. Advanced oxidation processes (AOPs) such as Fenton, Photo-Fenton and Photo Oxidation like processes constitute a promising technology for the treatment of wastewaters containing non-biodegradable organic compound. However, the development of oxidation processes is showing higher removal rates, oxidation reactions have primarily been used to supplement rather than replace conventional systems and to enhance the treatment of refractory organic pollutant.

The present research work was carried out to evaluate the efficiency criteria of advanced oxidation processes (Fenton and Photo-Fenton-like) for the removal of hazardous pollutants from hospital wastewater.

II. METHODOLOGY

A. Fenton Process

In Fenton process, iron and hydrogen peroxide are two major chemicals determining operation costs as well as efficiency. The Fenton reaction has a short reaction time among all advanced oxidation processes and it has other important advantages. Iron and H_2O_2 are cheap and non-toxic, there is no mass transfer limitation due to its homogenous catalytic nature, there is no energy involved as catalyst and the process is easily to run and control.
Fenton's oxidation, an advanced oxidation method, appeared to be the most promising method, in terms of cost-effectiveness and ease of operation. Fenton's oxidation is very effective method in the removal of many hazardous organic pollutants from wastewaters. Fenton's oxidation can also be an effective pre treatment step by transforming constituents to by-products that are more readily biodegradable and reducing overall toxicity to microorganisms in the downstream biological treatment processes [2].

The oxidation using Fenton's reagents (Fenton's process) causes the dissociation of the oxidant and the formation of reactive hydroxyl radicals that destroy organic pollutants to harmless compounds (CO_2, water and inorganic salts). Fenton's reagents are H_2O_2 and ferrous ions. They generate hydroxyl radicals following the chain reaction schematized as follow:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad \text{(chain initiation)} \quad (1)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \quad \text{(chain termination)} \quad (2)$$

As shown in Eqs. (1) and (2), the ferrous iron (Fe^{2+}) starts the reaction and catalyses the decomposition of H_2O_2 in hydroxyl radicals. However, the newly formed ferric ions (Fe^{3+}) may decompose hydrogen peroxide in water and oxygen (forming ferrous ions and radicals)

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{-}OOH^{2+} + H^{+} \quad (3)$$

$$Fe^{-} OOH^{2+} \leftarrow HO_2\bullet + Fe^{2+} \quad (4)$$

The above reactions are referred as Fenton-like reaction.

The organics (RH) are oxidised by hydroxyl radicals proton abstraction ending with the production of organics radicals (R•) (Chia-chi su *et al*., 2013).

In Fenton oxidation, the pH value has to be in the acidic range to generate the maximum amount of hydroxyl radicals to oxidize organic compounds. However, pH value should not be too low since at very low pH values (<2.0) the reaction is slowed down due to the formation of complex iron species and formation of oxonium ion [H_3O_2] On the other hand, at high pH (pH > 4), the generation of hydroxyl radicals gets slower because of the formation of the ferric-hydroxo complexes. Therefore, the initial pH value has to be between 2 and 4 to generate the maximum amount of hydroxyl radicals to oxidize organic compounds.

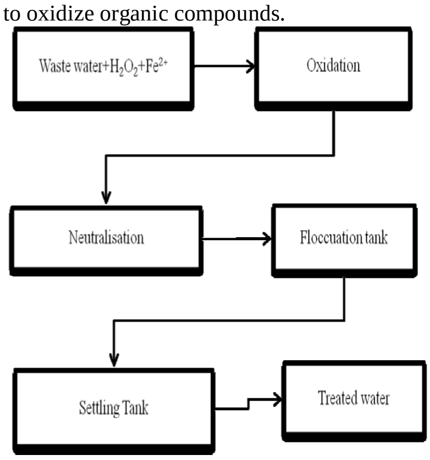

Figure 1. Fenton Process

B Biodegradability Index (BOD: COD)

BOD: COD ratio is generally expressed as biodegradability index. A significant proportion of soluble COD is not removed by the physico-chemical treatment. To achieve maximum treatment biological treatment is needed. So biodegradability index (BOD: COD) was taken in order to achieve high quality of treated waste water. Waste water can be considered biodegradable if it has a ratio between 0.4 and 0.8 [16]

The biodegradability of organic substances is a measure of speed and completeness of its biodegradability by micro organisms and the BOD_5/COD ratio is usually determined to analyze the difficulty of organic substances to be degraded. The biodegradability of the raw wastewater was estimated and the initial value of the BOD_5/COD ratio was equal to 0.30. As reported by Fresenius et al. the biodegradation starts immediately and runs rapidly with a ratio of BOD_5/COD in the range over or equal to 0.5. However, with a $BOD_5/COD < 0.5$, there is a possibility for chemical substances which have low biodegradability to slacken or delay the biological process. The studied hospital wastewater represented relatively low biodegradability, which is in good agreement with previous work. In addition, raw hospital wastewater exhibited high toxicity to micro-organisms with the inhibition of 100%.

C Materials and Method

The wastewater samples were collected from each source before entering into the entire hospital sewer network, which discharged the effluents into the biological wastewater treatment plant without pre treatment as well as effluent wastewater samples were collected. Effect of ferrous dosage and H_2O_2 and Contact time has been investigated. To determine the optimum dosage experiments were conducted by varying Fe concentrations from 0 to 2000 mg/l, H_2O_2 concentrations from 0 to 1200 g/l and obtained the optimum dosage for ferrous and hydrogen peroxide. In order to study the effect of irradiation time the analysis has carried out under optimized ferrous and hydrogen peroxide concentration and varying the contact time from 30 minutes, 60 minutes, etc up to 160 minutes and obtained the maximum %efficiency. The appropriate conditions for the photo-Fenton process for application to hospital wastewater are reported for the design of the treatment process.

Collection and preservation of sample

Grab wastewater samples are collected from the different disposal sites of hospital. Samples were collected in either glass or plastic (usually polythene) bottles. During sampling the bottles are tightly caped and sealed. After collection of samples bottles are taken to the laboratory for necessary analysis. All the water samples were kept at 4º C until analysis or experiments.

Physico-chemical characterization of hospital wastewater

The parameters such as pH, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solid (TSS) were analysed in the laboratory.

Fenton Oxidation Set Up

The studies were carried out to optimize the pH, dose of H_2O_2 and Fe^{2+} ions for the Pre treatment of Hospitals wastewater. The studies were conducted in a 300 ml stoppered flasks.

Chemicals and Glass wares

The chemicals used in the COD analysis viz. potassium dichromate, mercuric sulphate, ferrous ammonium sulphate, silver sulphate, concentrated sulphuric acid and ferroin indicator. COD test was conducted using Erlenmeyer flasks .The chemicals used for BOD analysis were Sodium thiosulphate, alkali iodide azide, manganous sulphate, starch, potassium dihydrogen phosphate, dipotassium hydrogen orthophosphate, disodium hydrogen phosphate, ammonium chloride, calcium chloride, magnesium sulfate and ferric chloride. BOD bottles of 300 ml capacity made of borosil were used for conducting the BOD test. BOD incubator set at 27^0C was used for incubating the BOD samples. Fenton oxidation was carried out by using ferrous sulphate (FeSo4.7H2O) and Hydrogen peroxide (30%v/v).The pH of the wastewater during Fenton oxidation was adjusted by using 0.5N H2SO4/1N NaOH. Borosilicate glass ware of 300ml capacity was used for Fenton oxidation. Whatsman filter paper no. 42 was used throughout the study for general sample filtration purposes.

Analytical methods

The COD analysis was done as per the standard methods. The BOD analysis was carried out using incubator set at 27^0C for incubating the samples as per standard procedures pH meter (Orion 420 A+) was used for pH measurements.

It was done to assess the BOD, COD, pH value of the influent and effluent grey water obtained from the different disposal sites of hospital. Lab test are performing as per IS 3025 (PART44):1993.

III. EXPERIMENT AND RESULT

Grab wastewater samples are collected from the different disposal sites of hospital. Samples were collected in either glass or plastic (usually polythene) bottles. During sampling the bottles are tightly caped and sealed. The collected samples were analysed in the laboratory by standard methods. The results are tabulated below.

Table 1. Characteristics of studied waste water

Sl No	Parameter	Influent Mean values (mg/l)
1	pH	8.35
2	BOD	158
3	COD	770
4	TSS	172

The BOD_5/COD ratio is 0.2051, which can be classified as non bio degradable waste water. The physico chemical characteristics of the effluent indicate that there is a need for efficient pre-treatment options which can effectively reduce/alter/modify the recalcitrance/toxicity profile of the wastewater.

Fenton Treatment Procedure

Fenton treatment procedure of waste water was carried out at ambient temperature in the following sequential steps.

1) Waste water sample was put in a beaker and stirred by mixing machine.
2) The scheduled Fe^{2+} dosage was achieved by adding the necessary amount of solid $FeSO_4.7H_2O$.
3) A known volume of 35% (w/w) H_2O_2 solution was added in a single step.
4) After fixed reaction time, before carrying out COD tests, pH was adjusted to 8 to remove residual Fe^{2+}
5) Settlement was achieved for 30 minutes, and then examination of COD should be done.

Effect of pH value

The experiments was conducted under the conditions of reaction time 60 minutes, $H_2O_2/FeSO_4$=1:1, and different pH values.

Low pH has found effective for Fenton's reagent, and the best removal efficiency is obtained at a pH =3.The lower pH is better to remove inorganic carbons from waste water as they can scavenge hydroxyl radicals. At higher pH COD is increasing, the decomposition rate decreases. At high pH formation of Fe(II)complexes with the buffer occurs inhibiting the formation of free radicals Precipitation of ferric oxy hydroxides inhibits the generation of ferrous ions and the oxidation potential of hydroxyl radical is known to decrease with increase in pH.

Effect of Reaction Time:

The optimum reaction time is 90 minute as in fig, demonstrated that the COD decreased gradually to 90 minutes reaction time and then increased. The reaction between ferrous iron and hydrogen peroxide with the production of hydroxyl radical was almost complete in 90 minutes.

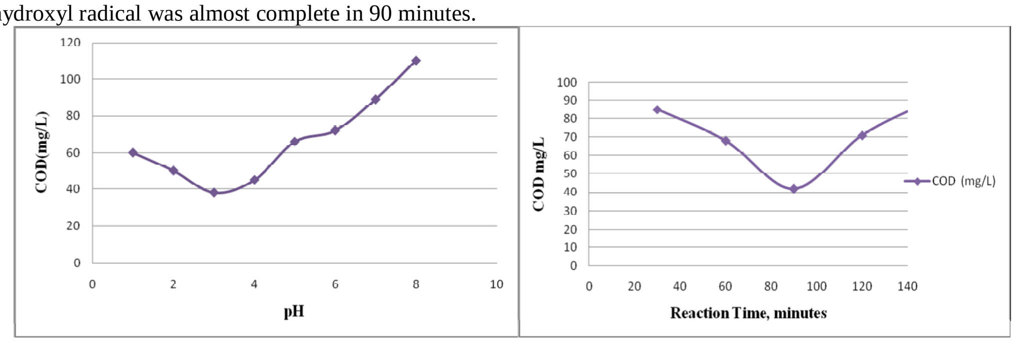

Figure 2 a) Effect of pH on removal of COD by Fenton b) Effect of reaction time on COD removal

Effect of Fe^{2+} and H_2O_2 addition:

Fenton Process, iron and hydrogen peroxide are two major chemicals determining operation costs as well as efficiency.H_2O_2 dosage depends on initial COD.A high initial COD requires more H_2O_2.The optimum amount of

H_2O_2 obtained is 600 mg/l. Increasing the amount of H_2O_2 contributes to residual H_2O_2 leading to increase in COD. The presence of excess hydrogen peroxide is harmful to many microorganisms and will affect the overall efficiency. The hydrogen peroxide present in large quantities acts as a scavenger for the generated hydroxyl radicals. The loading of hydrogen peroxide is to be adjusted so that the entire amount is utilized.

Effect of Fe^{2+} on COD removal:

Usually the rate of degradation increases with an increase in the concentration of ferrous iron but an enormous increase of ferrous iron leads to an increase in the unutilized quantity of ferrous irons, which will contribute to an increase in the TDS content of the effluent stream.

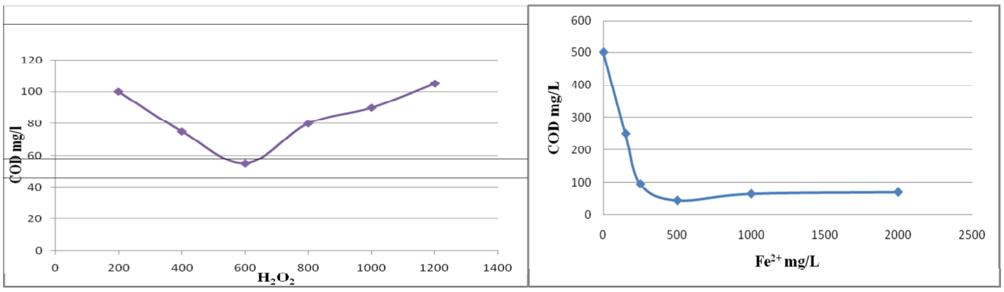

Figure 3a) Effect of H_2O_2 dosage on COD removal b) Effect of Fe^{2+}dosage on COD removal

Improvement of biodegradability of waste water by Fenton Process:

The biodegradability of waste water was evaluated with BOD_5/COD ratio. The results are depicted in figure11. The biodegradability value increased from 0.20 to 0.54.The results indicated that Fenton process could breakdown or rearrange molecular structures of organic matters to biodegradable forms.

Table 2 Biodegradability values during Fenton process

BOD	**COD**	**Time**	**Biodegradability**
mg/L	**mg/L**	**Minutes**	
41	**200**	**0**	**0.20**
34	**150**	**10**	**0.23**
24	**100**	**20**	**0.24**
22	**85**	**30**	**0.26**
24	**80**	**40**	**0.30**
28	**73**	**50**	**0.38**
33	**68**	**60**	**0.49**
23	**42**	**90**	**0.54**

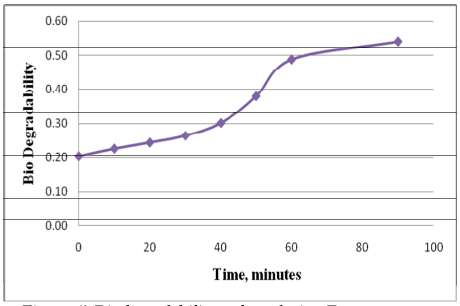

Figure 4) Biodegradability values during Fenton process

Waste water Treatment by Fenton Process:

The results showed that the waste water treatment by Fenton process for remove organic matter were for 94% COD removal and 85% for BOD.

Table 3. Characteristics of influent and effluent waste water

Sl No	Parameter	Influent Mean values (mg/l)	Effluent (after treatment)	Standards
1	pH	8.35	8	8 to 9
2	BOD	158	23	30
3	COD	770	42	100
4	TSS	172	28	100
5	Biodegradability	0.201	0.54	

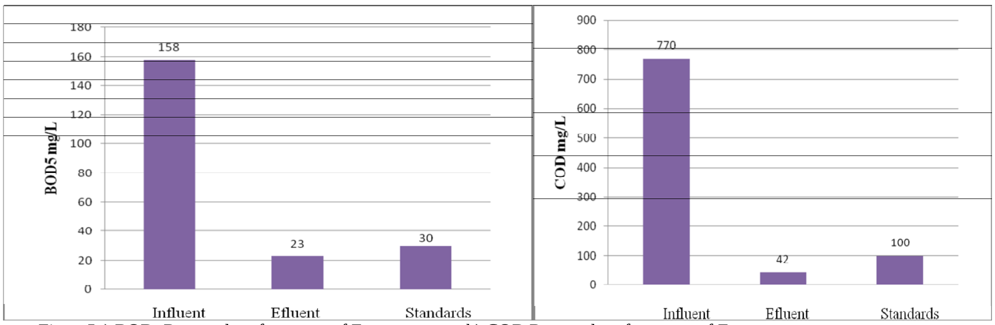

Figure5a) BOD_5 Removal performance of Fenton process b) COD Removal performance of Fenton process

IV.CONCLUSION

Fenton Treatment is used for removing COD and enhancement of biodegradability of waste water. Both oxidation and coagulation contributed to COD removal through Fenton treatment of waste water. Relative contributions depend primarily on pH, molar ratio of reagents.

From the results of the experiments for treating the non biodegradable waste water by Fenton's oxidation, the following conclusions can be drawn:

1. The COD removal efficiency by oxidation was effected by the pH value .The most effective reaction was observed at pH=3.0
2. The reaction time of Fenton process was 90 minutes to complete the reaction between ferrous sulphate and hydrogen peroxide.
3. The optimum H2O2/Fe2+ was 1.2:1 according to the results of ferrous Sulphate and hydrogen peroxide.
4. The removal efficiency of COD 89.87% and
5. Improved the biodegradability of waste water from 0.205 of influent to 0.54 of effluent waste water.

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