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APPLICATION OF ADVANCED OXIDATION PROCESS (AOP) FOR THE PRE-TREATMENT OF HOSPITAL WASTEWATER WITH A CASE STUDY ON ARAMBAGH SUB DIVISIONAL HOSPITAL WASTEWATER, HOOGHLY, WEST BENGAL, INDIA

[1]Harjeet Kaur, [2*]Srimanta Gupta and [3]Tirthankar Mallick

[1,2]Department of Environmental Science, The University of Burdwan, West Bengal

[3]Netaji Mahavidyalaya, Arambagh, West Bengal

Emails: [1]harjeet0909@gmail.com, [3]tirthamallickahm@gmail.com

[2]srimatagupta@yahoo.co.in (*Corresponding Author*)

Abstract: The present research work deals with the suitability study of advanced oxidation processes (Fenton's, Photo and Photo-Fenton's oxidation processes) for the treatment of synthetic solution as well as hospital wastewater. Synthetic solution was prepared with a mixture of potassium hydrogen phthalate and antibiotic wastewater containing amoxicillin and cloxacillin, to evaluate the effect of different operating conditions (***viz***. H_2O_2/COD molar ratio 1:1 and H_2O_2/Fe^{2+}molar ratio 50:0·5, 50:1, 50:1·5 respectively). The degradation of wastewater has been investigated in terms of removal efficiency of COD under advanced oxidation processes. The results obtained from Fenton's oxidation were quite appreciable as it reduced COD of synthetic solution and hospital wastewater by 93% and 88% respectively.

Keywords: Hospital wastewater; Advanced Oxidation Processes (AOPs) and Chemical Oxygen Demand (COD).

1. INTRODUCTION

Hospital wastewater contains antibiotics, pharmaceuticals, heavy metals, x-ray contrast and some organic substances that are resistant to biological degradation (Sorensen *et al.*, 1998). 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 (Emmanuel *et al.*, 2005).

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 compounds (Pera-Titus *et al.*, 2004). However, the development of oxidation processes is showing higher removal rates, oxidation reactions have primarily been used to supplement

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rather than replace conventional systems and to enhance the treatment of refractory organic pollutants (Balcioglu *et al*., 2003).

With this back drop 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 COD from synthetic as well as hospital wastewater.

2. MATERIALS AND METHODS

2.1 ***Preparation of synthetic sample: -*** Synthetic solution was prepared with potassium hydrogen phthalate and antibiotic wastewater containing amoxicillin and cloxacillin. Preparation of synthetic solution was done according to the standard methods (APHA. 1998).

2.2 ***Collection and preservation of sample: -*** Grab wastewater samples are collected from the different disposal sites of Arambagh 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 $4^{\circ}C$ until analysis or experiments.

2.3 Physico-chemical characterization of hospital wastewater: - Temperature, pH and conductivity were measured at the sampling site with the help of portable analyzer. Other parameters such as pH, conductivity(EC), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Suspended Solid (TSS), Total Dissolved Solids (TDS), Dissolved Oxygen (DO), Residual Chlorine (Res Cl^-), Sulphate(SO_4^{--}), and Phosphate(PO_4^{3-}) were analysed as per the standard methods (APHA. 1998).

2.4 Advanced oxidation processes

2.4.1 Fenton's Oxidation: - Fenton's reaction is based on the catalyzed decomposition of hydrogen peroxide by iron (II) to produce very reactive hydroxyl radicals:

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

The efficiency of Fenton's oxidation depends on H_2O_2 and Fe^{2+} concentrations, time and pH of the reaction. The pH value should be in the range of 2·5 to 4·0 (Kang *et al.*, 2000).Several runs were carried out in a one litre glass reactor with constant mixing using a magnetic stirrer. One litre wastewater solution was first adjusted with pH 3·2-3·3 and then prepared a solution according to operating condition H_2O_2/Fe^{2+} molar ratio of 50:0·5, 50:1, 50:1·5 and H_2O_2 /COD molar ratio 1:1. Where the Fe^{2+} catalyst was added in different proportion (H_2O_2: Fe^{2+} = 50:0·5, 50:1, 50:1·5) as $FeSO_4$ crystal. Entire experiment was conducted with the span of three hours. Where, COD and residual peroxide of solutions were analyzed from time to time.

2.4.2 Photo – Fenton: - The oxidizing power of the Fenton system can be greatly enhanced by irradiation with UV or UV-visible light. The positive effect of irradiation on the degradation rate include the photo-reduction of Fe^{3+} to Fe^{2+} ions, which produce new HO• radicals with H_2O_2 , according to the following mechanism:

$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + HO^{\bullet} + H^+$ ------------------------- (II)

$H_2O_2 + hv \rightarrow 2HO^{\bullet}$ $(\lambda < 400\ nm)$ ------------------------ (III)

The pH of solution (3·2-3·3) was adjusted with H_2SO_4/NaOH. The required amount of iron ($FeSO_4.7H_2O$) was added to the wastewater and mixed by a magnetic stirrer to ensure complete homogeneity during reaction. Thereafter, necessary amount of hydrogen peroxide (H_2O_2) was added simultaneously under the operating conditions of H_2O_2: COD ratio of 1:1, 2:1and H_2O_2: Fe^{2+} molar ratio 50:1.75ml of both synthetic and hospital wastewater samples were subjected to UV irradiation at a temperature of 28 - 31^0C. The source of UV light was a UV lamp (125 W). COD and residual peroxide were analyzed with the time interval of 15 minutes.

2.4.3 Photo-oxidation: - 75ml of sample was taken in a beaker and UV light was passed through the sample by keeping the sample under UV (125 W) exposure. COD and residual peroxide were analyzed with the time interval of 15 minutes.

3. RESULTS AND DISCUSSION

3.1 The physico-chemical characteristics of hospital and synthetic wastewater: - The average value of the collected sample shows the level of COD and BOD_5 50·6 mg/L and 30·6 O_2 mg/L respectively. Others parameters like pH, EC, DO, SO_4^{--}, PO_4^{3-} , TDS and TSS were also measured. The average of value of pH, EC, DO, SO_4^{-}, PO_4^{3-}, TDS and TSS is 7·65, 696·6µm/sec, 0·14mg/L, 0·4mg/L, 0·3mg/L, 0·39mg/L and 0·023mg/L respectively. Synthetic solution has COD and BOD_5 level of 1270mg/L and 482 O_2 mg/L respectively.

3.2 Application of advanced oxidation processes for the treatment of synthetic as well as hospital wastewater

3.2.1Effect of Fenton's oxidation on COD removal: -

3.2.1.1 Effect of hydrogen peroxide: - Fig. 1 shows that the maximum COD removal of 50% is achieved at a dose of 0.4 ml/L. COD removal decreases with the increase in H_2O_2 concentration. It can be attributed to the fact that in alkaline medium the oxidizing species hydroperoxy anion (HO_2^-) is formed (HO_2^- anion is the conjugated base of H_2O_2) as given by Eq IV. This HO_2^- anion reacts with OH- radical and residual H_2O_2 as well [Eqs. (V), (VI)] consequently lowering the removal rate, though the exact mechanism is still not clear (Beltran et al., 1994).

$H_2O_2 \rightarrow HO_2^- + H^+$ ------------------------------ (IV)

$H_2O_2+HO_2^- \rightarrow H_2O+O_2+OH^-$ -------------------------------- (V)

$HO_2^-+OH^- \rightarrow H_2O+O_2^-$ ------------------------------- (VI)

Above reactions shows decrease probability of oxidation of substrate. That's why after a certain concentration of H_2O_2, no significant increase in degradation is observed.

3.2.1.2 Effect of catalyst: - The experimental result of catalyst dose of synthetic solution shows that COD reduction ranges 32·1% to 48·8% within 180 minutes (Fig. 2) with the dose of H_2O_2:Fe^{2+}, 50:0·5. The range of COD removal improved up to a maximum of 57·5% to 93·1% when dose of catalyst was improved up to 2 fold (H_2O_2: Fe^{2+} = 50:0·5 vs. 50:1) within 180 minutes reaction time (Fig. 3) and subsequently decreased range of COD to 52.6% to 84.6% with a further doubling of the catalyst concentration (H_2O_2: Fe^{2+} = 50:1·5) (Fig. 4).Thus H_2O_2: Fe^{2+} ratio 50:1 is regarded as the optimum dosage for Fe^{2+} catalyst for maximum COD reduction and was selected for all the subsequent experiment(Fig. 3) in synthetic wastewater.

The result of hospital wastewater shows that COD has been removed from 37·9%, 46·44%, 50% with the dose of H_2O_2:Fe^{2+} ,50:1 through the reaction of time (60,120 and 180 minutes) (fig. 5). In case of dose H_2O_2:Fe^{2+}(50:1·5), COD removal changes from 59·6%, 72·9% and 80·90% for 60,120 and 180 minutes respectively (fig. 6).COD removal in dose of H_2O_2 :Fe^{2+} (50:2) changes from 60·93%, 76·9% and 88.06% for 60,120 and 180 minutes (fig. 7). Similar kind of observation also investigated by El-Gohary *et al.,* (2008) in olive oil mill wastewater.

3.3.2 Photo Oxidation: - It shows that UV light alone give the 44·9% removal of COD of synthetic solution at 30 minutes UV exposure.

The study of hospital wastewater reveals that range of COD removal in 30 minutes is 44·8%. The enhancement of removal rate with enhanced exposure of UV light is due to the fact that high energy associated with UV radiation can photolysis water to yield $^{\bullet}OH$ and hydrogen radicals [Gonzalez *et al*, 1994].

3.3.3 Photo-Fenton's Oxidation: - The experimental results of synthetic solution depicts that in low dose of hydrogen peroxide range of COD removal efficiency is 53·5% in first 15 minutes and 58% in 30 minutes (H_2O_2: COD = 1:1 w/w ratio). But up to two fold increase in H_2O_2 dosage (H_2O_2: COD = 1:1 to 2:1) COD removal range reaches 77·3% in 30 minutes.

The experimental results of hospital wastewater depict that hydrogen peroxides dosage [H_2O_2: COD (w/w)]: 1:1 shows range of COD removal efficiency 53·99% to 64·4 %. But up to two fold increase in H_2O_2 dosage (H_2O_2: COD = 1:1 to 2:1) COD removal changes from 67·02 % in 15 minutes to 76·9% in 30 minutes. The low amount of removal is may be due to inhibition of peroxide because COD is low, as reported by Liou *et al*, 2003 also indicated that the hydroxyl radical inhibition effect could occur in the photo-Fenton reaction with high ferrous concentrations.

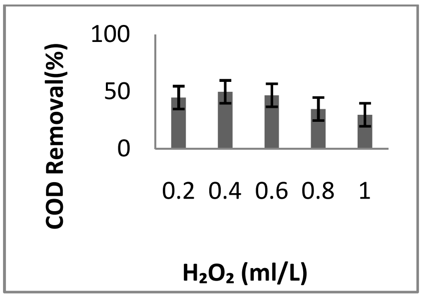

Fig. 1: Effect of hydrogen peroxide on COD removal

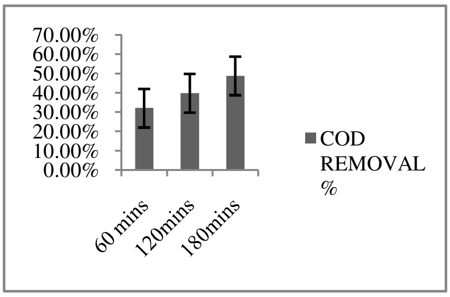

Fig. 2: % COD Reduction due to H_2O_2 Fe^{2+}(50:0·5) in synthetic wastewater

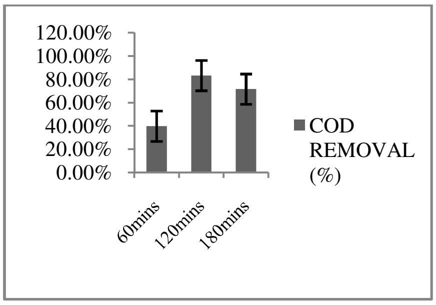

Fig. 3: % COD reduction due to H_2O_2:Fe^{2+} (50:1) in synthetic wastewater

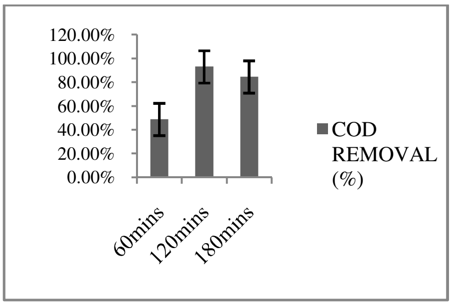

Fig. 4: % COD reduction due to H_2O_2:Fe^{2+} (50:1·5) in synthetic wastewater

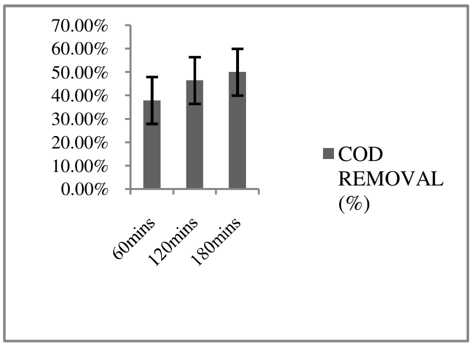

Fig. 5: % COD reduction due to H_2O_2:Fe^{2+} (50:1) in hospital wastewater

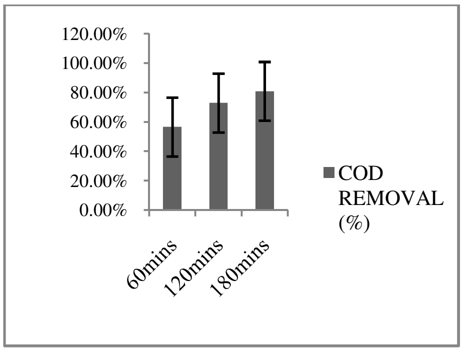

Fig. 6: %COD reduction due to H_2O_2:Fe^{2+} (50:1) in hospital wastewater

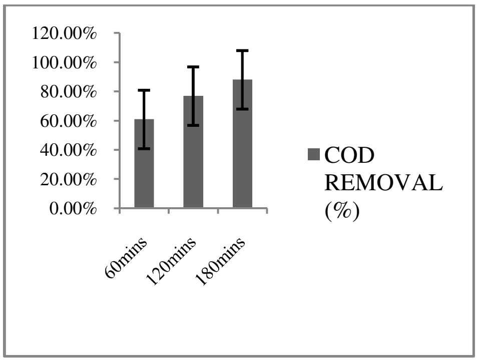

Fig. 7: % COD reduction due to H_2O_2:Fe^{2+} (50:2) in hospital wastewater

4. CONCLUSION

Advanced Oxidation Processes were applied to synthetic solution as well as hospital wastewater to know the feasibility of AOPs. Here these processes were initiated as a pre-treatment method to increase biodegradability and reduce toxicity of enhancement of biodegradability. The optimum conditions was fond as a dosage ratio of $FeSO_4$ catalyst (H_2O_2: Fe^{2+} molar ratio) 50:0·5, 50:1, 50:1·5 and a reaction pH of 3-3·5. Though, the amount of COD was significantly low in hospital wastewater the application of advanced oxidation processes seems to be very fruitful in case of high COD loaded hospital wastewater also. The result of Fenton's process has consistently achieved 93% and 88% removal of COD from synthetic as well as hospital wastewater respectively.

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