# Removal of Paracetamol from Pharmaceutical Wastewater by Integrated MBR

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**ABSTRACT**

In present scenario, concerns regarding the presence of active pharmaceutical ingredients have gained increasing attention. The ingredients may be present in water and wastewater in the form of solvents, intermediates and raw materials. Conventional water treatment methods for the removal of sludge content from water such as Activated sludge may not be sufficient for the removal of active pharmaceutical constituents in water. With a view to achieve better results, other treatment methods like activated carbon, membrane filtration and reverse osmosis are used in addition with the traditional treatment methods. This study aims at demonstrating the integrating biological process and Fenton oxidation in a system. The system is operated in recycling.

A lab-scale system integrating a membrane bioreactor (MBR) and a Fenton reactor was fed on simulated wastewater containing refractory drug acetaminophen (Paracetamol) and also it demonstrates the use of AOP-MBR system for pharmaceutical wastewater treatment.

**KEY WORDS**: Integrated process, Membrane bioreactor, advanced oxidation process, Waste water.

## 1. INTRODUCTION

The study of pharmaceuticals and the various pharmaceutical residues are of high concern because of their ability to affect the aquatic organisms even when they are present in trace amount. There is supposed to be an increase in the percentage of pharmaceutical concentration and the pharmaceutical residues due to an increasing practice of reuse of water due to water scarcity. Hence much importance must be given to the segregation of the pharmaceutical residues from the effluent of pharmaceutical production industry. Steps must be taken to reduce this source of water pollution and also direct and indirect discharge of drugs must be avoided.

Pharmaceutical effluent contains lot of analgesic, antibiotics, cardiovascular drugs etc., a wide variety of products are manufactured by the Pharmaceutical industry. The pharmaceutical industry makes use of organic and inorganic substances as raw materials. The organic substances may be of animal, vegetable or of synthetic origin. The waste effluents from these industries have in them a large number of pathogenic organisms, radioactive elements and many other.

The segregation of pharmaceutical residues from the pharmaceutical industrial wastewater is very complicated due to the presence of:

- non-biodegradable solvents
- and lower amounts of recalcitrant organics
- salinity content

Paracetamol is a major component in a number of medicines because of its analgesic and antipyretic properties. During its synthesis, a total of 10 process-related impurities are observed. Acetaminophen is a medication usually prescribed to reduce the body temperature and body pain. Paracetamol is a weak inhibitor of cyclooxygenase. Although the anti-inflammatory effect of this drug is weak, the impact on the environment from other NSAIDs is not different.

Recently, in a review of the potential of fenton processes (AOP), it was concluded that AOP application is best only for drinking water plants and for the treatment of pharmaceutical waste water.

In order to reduce the high treatment cost of chemical oxidation and also to treat wastewater containing refractory compounds, biological treatment is usually adopted. Chemical oxidation can be done either as a pretreatment for the purpose of reducing toxicity or as post treatment for the final polishing of waste water. Generally pharmaceutical effluent mostly contains trace amount of refractory or inhibitory organic compounds. When post treatment is done in this type of effluent, some byproducts with unknown harmfulness may be left. At some cases it reaches complete mineralization. In such case, the chemical and biological processes are integrated. The main objective of the chemical oxidation process is to achieve the biodegradability of inhibitory compounds and avoid their complete mineralization.

Comparing the various methods of AOP, it is found that the Fenton process is very advantageous since the reaction takes place at a room temperature and pressure thus making the process inexpensive.

Membrane bioreactors method (MBRs) have been chosen for the purpose of integrating with the fenton oxidation. This has been selected so as to offer greater operational flexibility and higher performance as in case of removing the micro pollutants and suspended residues. Also adopting this system of MBR gives a greater advantage in case of high sludge retention time, by giving more potential for biomass acclimation.

With a view to investigate the behavior, feasibility and potentiality of an integrated MBR–AOP system, pharmaceutical effluent from the production of analgesic acetaminophen (Paracetamol) has been simulated in this study. Paracetamol is a widely administered drug and has been found to be refractory to biological degradation during wastewater treatment. Scarce or no accumulation has been detected in soil and sediments.

The main objective of this study was to assess the feasibility and advantages of the integrated approach for the treatment of Pharmaceutical wastewater. To this aim, integrated MBR-AOP was performed.

## 2. METHODS

**Simulated waste water:** For quantification of drugs, 10 tablets of 500 mg paracetamol each were weighed and crushed. A crushed powder 2g of paracetamol was transferred into a 100 ml volumetric flask, diluted with 15 ml of methanol and further diluted for 3 litres using distilled water. Then the resulting solution as allowed to stand for some time, filtered through Whatman filter paper No. 44 and the filtrate.

**Experimental Setup:** An MBR equipped with a flat sheet polyvinylidene fluoride membrane module (nominal pore size of 0.1 µm) with fine diffuser of size 2-4mm bubble size has been used for this study. The MBR was inoculated with biomass from the sewage treatment plant and it was operated at room temperature. A 2L Fenton reactor equipped with a magnetic stirrer was adopted.

**Analysis:** Paracetamol concentration was measured by HPLC, with the standard column (C-18), UV detector (254 nm), and mobile phase containing acetonitrile and HPLC water in the ratio of 3:1. Sample pre-treatment consisted of centrifugation at 1800 rpm for fenton process. Chemical oxygen demand (COD) was measured on fresh samples, without pretreatment and using COD digestor.

## 3. RESULTS AND DISCUSSION

**Characteristics of waste water:** The characteristics of the pharmaceutical effluent was summarized in the table and it was found that the average COD value of the effluent is 8100 mg/L, which is very high and thus, fenton oxidation will be the most preferable pretreatment technique to remove such heavy COD.

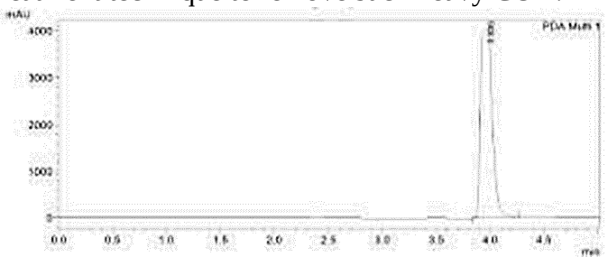

**Figure.1. HPLC observation for sample**

**Fenton oxidation: Fenton** oxidation was carried out using fenton's reagent at various dosages of ferrous sulphate salt and hydrogen per oxide and with the reaction time of 4 hours. The process is carried out at room temperature and pressure. Biological degradation and elimination from water are important factors to characterize the ecological behaviour of chemical substances and wastewater streams.

**COD Removal Efficiency:** Experiments were carried out and various results obtained were tabulated below.

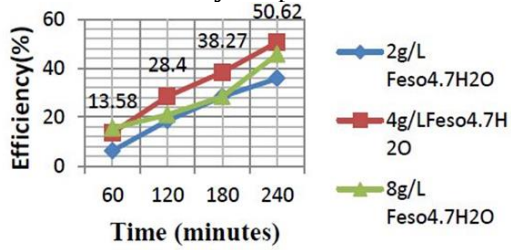


**Figure.2. COD Removal Efficiency by fenton process for H2O2 dosage 20ml/L**

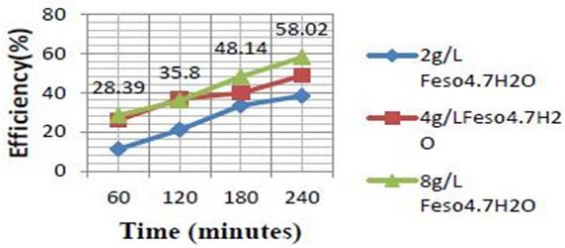


**Figure.3. COD Removal Efficiency by fenton process for H2O2 dosage 40ml/L**

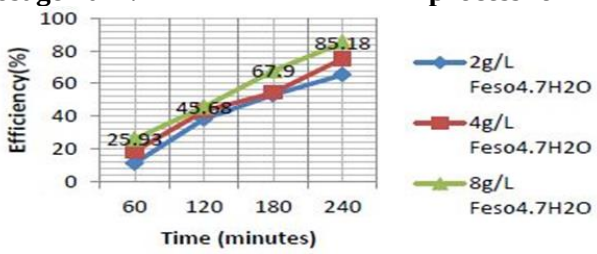


**Figure.4. COD Removal Efficiency by fenton process for H2O2 dosage 80ml/L**

**Paracetamol Removal Efficiency:** From the above experiments the optimum dosage were determined for the effluent for further treatment by MBR. The COD Removal Efficiency of 58.02% was achieved for the dosage of 8g/L of $FeSO_4.7H_2O$ and 40ml/L of $H_2O_2$ over a period of 4 hours. The paracetamol Removal Efficiency was determined by

high performance liquid chromatography and it was detected in the retention time 3.940 with the area of 500992. The paracetamol Removal after fenton process is observed.

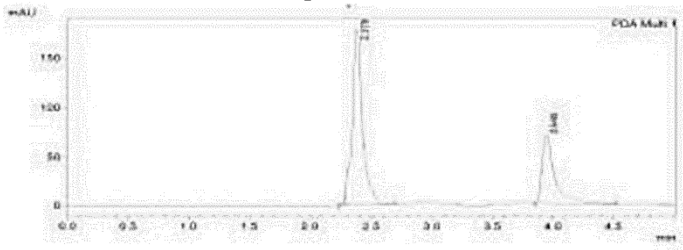

**Figure.5. HPLC observation after Fenton process**

**Integrated MBR:**

**COD Removal Efficiency:** Fenton oxidation is given as a pretreatment for the pharmaceutical effluent and then treated by Membrane Bio reactor for the effective Removal of COD and paracetamol. The COD Removal Efficiency obtained from both treatment at HRT of 5h, 6h and 8h is 89.20%, 91.87% and 93.32% respectively.

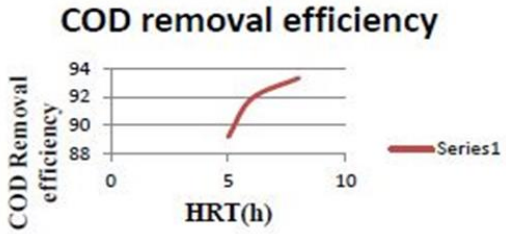


**Figure.6. COD Removal Efficiency BY integrated MBR**

**Paracetamol Removal Efficiency:** The paracetamol Removal Efficiency was observed at 5h, 6h and 8h HRT with the area of 976682, 269940 and 68196 respectively. Paracetamol area for various HRT is given below.

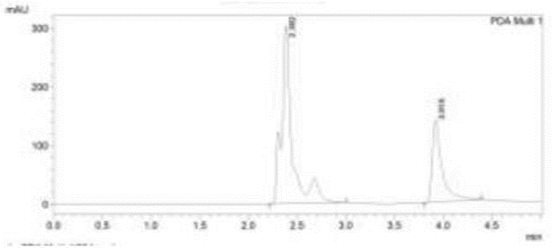

**Figure.7. Paracetamol Removal Efficiency for 5h HRT**

Initially effluent has a paracetamol area of 30587197 and after the treatment paracetamol area detected is 976682. Main disadvantage is iron concentration is increased in the effluent and it was detected in chromatography. The paracetamol Removal Efficiency was observed at 5h HRT is 96.85%.

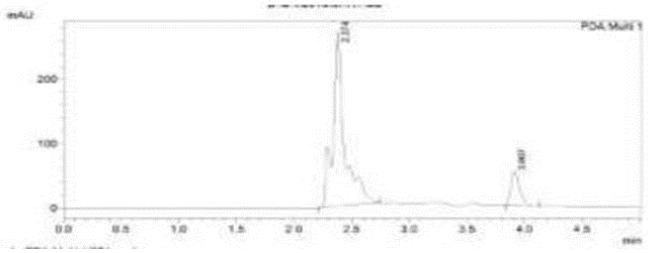

**Figure.8. Paracetamol Removal Efficiency for 6h HRT**

Initially effluent has a paracetamol area of 30587197 and after the treatment paracetamol area detected is 269940. Main disadvantage is iron concentration is increased in the effluent and it was detected in chromatography. The paracetamol Removal Efficiency was observed at 5h HRT is 99.11%.

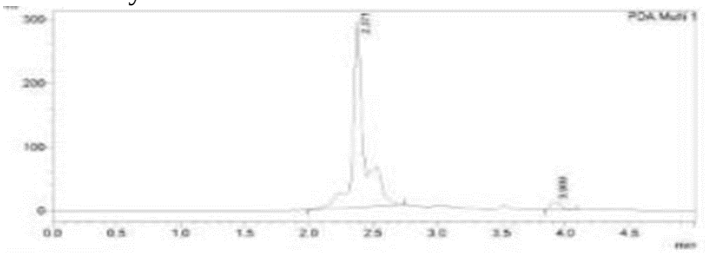

**Figure.9. Paracetamol Removal Efficiency for 8h HRT**

Initially effluent has a paracetamol area of 30587197 and after the treatment paracetamol area detected is 68196. Main disadvantage is iron concentration is increased in the effluent and it was detected in chromatography. The paracetamol Removal Efficiency was observed at 8h HRT is 99.77%.

## 4. CONCLUSION

The integrated process for Pharmaceutical effluent was carried out using Fenton's Oxidation and MBR in which the COD and paracetamol Removal Efficiency was investigated. In fenton process the maximum COD removal efficiency of 58.02% was obtained at the dosage of 8g/L and $H_2O_2$ dosage of 40ml/L. The iron salt, one of the major component of fenton process got oxidized and gave a brown colour to the treated effluent. Before carrying into the MBR the effluent is adjusted to pH 7 using sodium hydroxide pellets and sludge are settled, the effluent is filtered and used for further treatment in MBR. Based on various experiments carried out, a maximum Removal Efficiency of COD and paracetamol was about 93.32% and 99.77% respectively and it was achieved by combination of fenton process and MBR. Thus, the experimental results showed that the fenton process followed by MBR holds good for the treatment of pharmaceutical effluent.

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