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Removal of Refractory COD from Pharmaceutical Wastewater using HCO_3^- and Fenton Oxidation Process

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Abstract

The increasing concern on the presence of pharmaceutical compounds in the drinking water has increased nowadays mainly due to the potential risk to the health of human being. Advanced oxidation processes (AOPs) are widely used for the removal of recalcitrant organic constituents from industrial wastewater. This study mainly aimed to investigate removal of chemical oxygen demand (COD) from pharmaceutical wastewater using HCO_3^- and Fenton oxidation process in a batch reactor. Experiments were conducted under the various pHs (3-7) and temperatures (19-27°C) condition. Various amounts of H_2O_2, Fe^{2+} and HCO_3^- were taken in order to optimize the refractory COD reduction.COD reduction was found 70% and 15% in Fenton oxidation process and HCO_3^- process subsequently. Moreover the results showed that Fenton oxidation process is capable of achieving high refractory COD removal at about pH-3.

Keywords*-pharmaceutical compounds; advanced oxidation processes; recalcitrant organic constituents; industrial wastewater; refractory COD.*

I. INTRODUCTION

Water is one of the most valuable resources on planet earth. It is the lifeline of almost all living thing on earth. Although this fact is widely recognized, pollution of water resources is a common occurrence. During the last few decades, the rise of world population as well as industrial revolution has caused serious environmental pollution.

India is the third largest producer of pharmaceutical chemicals after the USA and Europe, and its turnover is expected to reach US$74 billion per year by 2020. Production and use of large quantities of pharmaceuticals for human and veterinary applications could lead to the release of more pharmaceuticals substances into the environment. (CCI 2012)

The need for high quality drinking water is one of the most challenging problems of our times, but still only little knowledge exists on the impact of these compounds on ecosystems, animals and man. Reliable access to clean and affordable water is considered one of the most basic humanitarian goals, and remains a major global challenge for the 21st century. Worldwide, some 780 million people still lack access to improved drinking water sources. (WHO 2012)

Pharmaceutical industry

Pharmaceutical industry mainly covers the following process operations for manufacturing of product.

I. Fermentation
II. Chemical synthesis
III. Biological and Natural Extraction
IV. Formulation and packaging
V. Research and development.

Fermentation

Most antibiotics and steroids are produced by the fermentation process, which involves three basic steps:

I. Inoculum and seed preparation
II. Fermentation
III. Product recovery.

Solvents most often used in fermentation operations are acetone, methanol, isopropanol, ethanol, amyl alcohol and MIBK. Copper and zinc are priority pollutant metals known to be used in the precipitation process.

Chemical synthesis

Most of the active ingredients marketed and sold as drugs are manufactured by chemical synthesis. Chemical synthesis is the process of manufacturing pharmaceuticals using organic and inorganic chemical reactions. Since most of these compounds are produced in batch operations, the conventional batch reaction vessel is the major piece of equipment used on the process line.

Biological and Natural Extraction

Many materials used as pharmaceuticals are derived from such natural sources as the roots and leaves of plants, animal glands and parasitic fungi. These products have numerous and diverse pharmaceutical applications ranging from tranquilizers and allergy-relief medications to insulin and morphine.

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Formulation and packaging

Pharmaceutically active ingredients are generally produced by batch processes in bulk form and must be converted to dosage form for consumer use. Common dosage forms for the consumer market are tablets, capsules, liquids and ointments.

The primary objective of mixing, compounding or formulating operations is to convert the manufactured products into a final usable form. The necessary production steps typically have small wastewater flows because very few of the unit operations generate wastewater. The primary use of water is in the actual formulating process, where it is used for cooling and for equipment and floor washing.

Research and development

Research works in laboratories also generate wastewater, but quantity is negligible in compare to above processes and this wastewater is readily treatable by biological treatment systems. (S.C. n.d.)

In a general term "refractory" means not responding to treatment or unresponsiveness. A variety of organic compounds are classified as refractory when they are poorly biodegraded and/or exhibit a low value for the ratio of biological oxygen demand to chemical oxygen demand (BOD:COD).

Wastewater produced from the pharmaceutical factories is hazardous, toxic and also often has intensive color and disgusting odor. The high concentration of chemical oxygen demand (COD) and low concentration of biological oxygen demand (BOD) in wastewater present a challenge for biological treatment technologies, because the components that are refractory in wastewater may greatly inhibit the activities of microorganisms. (W.Gebhardt 2007)

Pharmaceuticals are being released into the environment in extremely large quantities on a regular basis. The degradation of pharmaceuticals and their residues is of particular great interest due to the ubiquity of these compounds and to their capacity of affecting aquatic organisms even if they exit at trace concentrations.

Many researchers have been seeking suitable methods to treat pharmaceutical wastewater. Physical-chemical and biological methods are the main treatment processes with their own characters. Biological treatment is economical, but not so effective in refractory organic wastewater. Physical-chemical treatment can obtain high efficiency and is stable with a high quality effluent, but treatment cost is relatively high. (M.Klavarioti 2009)

Advanced wastewater treatment is defines as the additional treatment needed to remove suspended, colloidal and dissolved constituents remaining after conventional secondary treatment.(George Tchobanoglous 2003) Advanced Oxidation processes are used to oxidize complex organic constituents found in wastewater that are difficult to degrade biologically into simpler end products.

Advanced oxidation processes although making use of different reacting systems, are all characterized by the same chemical feature: production of OH radicals.

A suitable application of AOP to waste water treatments must consider that they make use of expensive reactants as H_2O_2, and/or O_3 and therefore it is obvious that their application should not replace, whenever possible, the more economic treatments as the biological degradation. A list of the different possibilities offered by AOP is given in the Fig. 1. (Roberto A. 1999)

- H_2O_2 / Fe^{2+}	(Fenton)
- H_2O_2 / Fe^{3+}	(Fenton - like)
- $H_2O_2 / Fe^{2+} (Fe^{3+}) / UV$	(Photo assisted Fenton)
- H_2O_2 / Fe^{3+}- Oxalate	
- Mn^{2+}/Oxalic acid/Ozone	
- $TiO_2 / hv / O_2$	(Photocatalysis)
- O_3 / H_2O_2	
- O_3 / UV	
- H_2O_2 / UV	

Figure 1 Advanced oxidation processes.

Another aspect concerning the opportunity of AOP application is that referring to the polluting load of wastes normally expressed as COD. Only wastes with relatively small COD contents ($\leq$5.0 g/l) can be suitably treated by means of these techniques since higher COD contents would require the consumption of too large amounts of expensive reactants. Wastes with more massive pollutants contents can be more conveniently treated by means of wet oxidation or incineration (Fig. 2). (V.S. Mishra 1995)

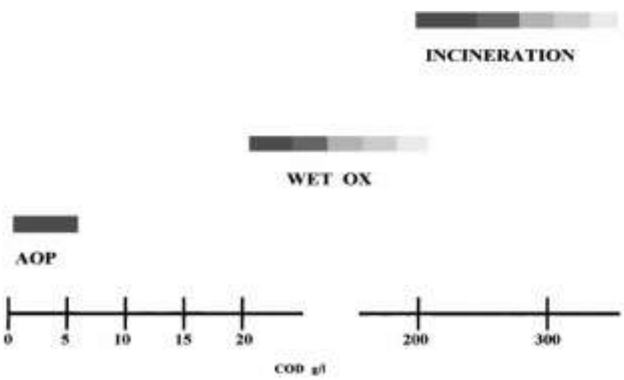

Figure 2 Suitability of water treatment technologies according to COD contents.

Fenton processes

The renewed interest of researchers for this classic, old reactive system discovered by Fenton the last century (Fenton 1894) is today underlined by a significant number of investigations devoted to its applications in wastewater treatments.

It has been demonstrated that Fenton's reagent is able to destroy toxic compounds in waste waters such as phenols and herbicides. Production of OH radicals by Fenton reagent (F. Haber 1934) occurs by means of addition of H_2O_2 to Fe^{2+} salts

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH\bullet \quad (1)$$

This is a very simple way of producing OH radicals neither special reactants nor special apparatus being required. This reactant is an attractive oxidative system for wastewater treatment due to the fact that iron is very abundant and nontoxic element and hydrogen peroxide is easy to handle and environmentally safe.

In fact, as it has been pointed out in many recent studies (Fenton 1894) the adoption of a proper value of pH (2.7-2.8) can result into the reduction of Fe^{3+} to Fe^{2+} (Fenton-like)

$$Fe^{3+} + H_2O_2 \rightleftharpoons H^+ + FeOOH^{2+} \quad (2)$$

$$FeOOH^{2+} \longrightarrow HO_2\bullet + Fe^{2+} \quad (3)$$

proceeding at an appreciable rate. In these conditions, iron can be considered as a real catalyst.

In this work, the Fenton's reagent is used to remove COD from an industrial wastewater characterized by its extremely high value of COD and a low value of BOD, probably due to the presence of toxic compounds, which hamper a direct biological treatment.

Wastewater sampling

The untreated wastewater samples were collected after the first centrifuges of Pharmaceutical intermediate products manufacturing industry located at Vapi, (Gujarat) India. The sampling bottle was cleaned and rinsed carefully with distilled water, filled and seal air tightly. About 5.0 cm air space is left in the bottle to facilitate mixing by shaking. The sample was stored at 4°C within one to two hours of sample collection.

Characterization of wastewater

Sample Collection Site: - AMA first centrifuges ML.

Table 1 Physical and chemical characteristic of wastewater

Para.	Results	Test method
pH	12.02	IS 3025(PART 11) 1983, (APHA 22nd Ed.,2012,4500-H^+B)
BOD_3	3220	IS 3025(PART 44) 1993
COD	20140	IS 3025(PART 58) 2006, (APHA 22nd Ed.,2012,5220-B)
TDS	2160	IS 3025(PART 16) 1984, (APHA 22nd Ed.,2012,2540-C)
TSS	868	IS 3025(PART 17) 1984, (APHA 22nd Ed.,2012,2540-D)

II. MATERIALS AND METHODS

Various methods and devices were used to both characterize and monitor the oxidation processes. Some of these methods and devices are briefly described here. The chemicals used in this study were manufactured by Merck Specialties Pvt. Ltd., Mumbai (H_2O_2 30%, $FeSO_4.7H_2O$, Na_2CO_3, H_2SO_4 98%, NaOH 20%).Various devices were used like pH meter (Supplied by HANNA Instruments, Model- pH211 Microprocessor pH Meter), Beaker, COD apparatus and Magnetic Stirrer (Supplied by REMI-2L capacity).

Experimental Procedure

The procedure of Fenton's reaction was as follows: the wastewater was put into beaker of 500mL volume and then pH was adjusted at neutral by addition of alum. Add some polyelectrolyte and settle down the solids for 30minutes. Fenton's reaction is only effective in the acidic pH range. Hence, when the initial pH of wastewater was above 7-8, the samples were acidified by H_2SO_4 to the selected value, in the pH range of 3.0–4.0, in order to estimate the pH effect on COD removal.

After that, the various amounts of hydrogen peroxide solutions and $FeSO_4{\cdot}7H_2O$ (in a solid state) were added with continuous magnetic stirring. After 1hour reaction time, the wastewater was neutralized with solution of NaOH upto about pH-7. After sedimentation, the residual amount of H_2O_2 was removed by using Na_2SO_3, because the effect of H_2O_2 on $K_2Cr_2O_7$ and they showed linear relationships between concentrations of H_2O_2 and COD.

In HCO_3^- process, the wastewater was put into beaker of 500mL volume and then pH was adjusted at neutral by addition of alum. Add some polyelectrolyte and settle down the solids for 30minutes.

After that, the various amounts of Na_2CO_3 were added with continuous magnetic stirring. After 1hour reaction time the wastewater was neutralized with solution of H_2SO_4 upto about pH-7.

III. EXPERIMENTAL SETUP

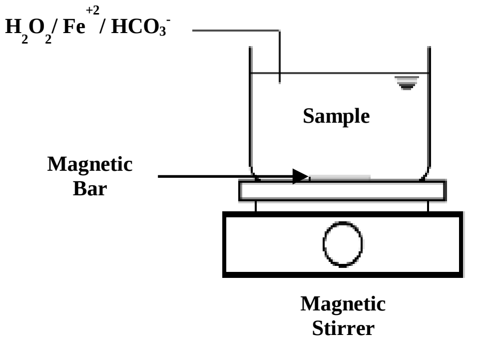

Figure 3 Experimental set-up

IV. RESULTS AND DISCUSSION

A. Effect of Fe^{2+}/ H_2O_2 on COD Removal

Generally hydroxyl free radicals can be increased with the increase of H_2O_2, however, excess H_2O_2 can directly oxidize Fe^{2+} to Fe^{3+}, which decreases the production of free radicals and leads to the decrease of COD removal. (Xing J N 2002)

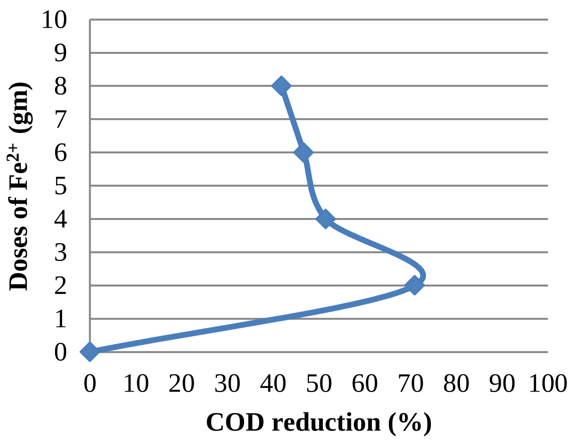

Figure 4 Effect of Fe^{2+}/ H_2O_2 on COD Removal

This was elucidated in Fig.4 with varies doses of $FeSO_4.7H_2O$ under fixed condition of H_2O_2=1mL/L, optimal reaction time = 60 minutes and optimal pH=3.0.

It can be seen from Fig.4 that the maximum COD removal was achieved at a dose of $FeSO_4.7H_2O$-2gms as 70.92%.

B. Effect of HCO_3^- on COD Removal

Addition of Na_2CO_3 was lead to pH change drastically towards the alkaline range due the nature of chemical and generation of NaOH during the chemical reaction. Initially from neutral to pH=10.57 were observed at 8gms dose of Na_2CO_3.

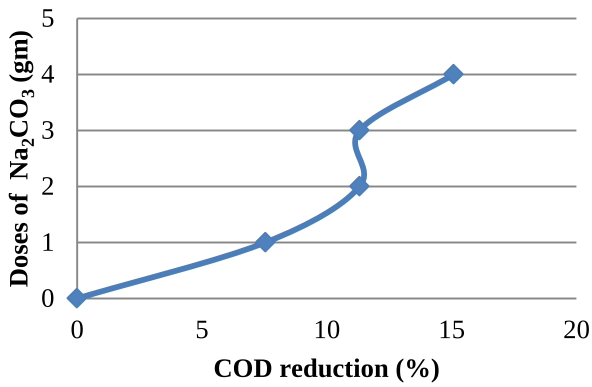

Figure 5 Effect of HCO_3^- on COD Removal

This was elucidated in Fig.5 with varies doses of Na_2CO_3 under fixed condition of optimal reaction time = 60 minutes and optimal pH=7.0.

It can be seen from Fig.5 that the maximum COD removal was achieved at a dose of Na_2CO_3-4gms as 15%.

V. CONCLUDING REMARKS

The results of the study can be summarized as follows:

1. In Fenton Process, maximum refractory COD removal was achieved at a dose of $FeSO_4.7H_2O$-2gm /L as 70%.
2. In HCO_3^- Process, maximum COD removal was achieved at a dose of Na_2CO_3-4gm/L as 15% with high pH variation.
3. Fenton oxidation process is a promising technique for the abatement of Refractory COD.
4. In combination with other AOP, Fenton Process will give more reduction in Refractory COD present in Pharmaceutical wastewater.

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