TREATABILITY STUDY OF FENTON ACTIVATED CARBON CATALYTICAL OXIDATION FOR PHARMACEUTICAL WASTE WATER TRATMENT

Ravi J. Acharya[1], Dr. Dipak S. Vyas[2], Mr. Purvesh Shah[3]

[1] *M.E. Student, Environmental engineering, BVM Engineering College, Vallabh Vidyanagar, Gujarat*
[2] *Professor, Civil Engineering Department, BVM Engineering College, Vallabh Vidyanagar, Gujarat*
[3] *Director , Siddhi Green Excellence Pvt.Ltd , Ankleshwar , Gujarat*

ABSTRACT

This Study has been carried out to study treatability of Fenton activated carbon catalytical oxidation for pharmaceutical waste water treatment. Pharmaceutical waste water containing high amount of organic content of non biodegradable nature , these substance are resistance to biodegradation because of low BOD/COD values. The conventional treatment may not be effective for removal of such pollutant. So, advanced oxidation processes can be a good choice for pharmaceutical waste water abetment. Of all the AOP's , the use of Fe for the degradation of organic compound in pharmaceutical industries effluent in pre-oxidation process has recently emerged as an active research area. In last decade the homogeneous Fenton process encountered major drawbacks even though receiving much attention with more emphasis on heterogeneous catalysts. FACCO as a treatment can be good option to increase biodegradability of pharmaceutical waste water.

Keyword : - *FACCO (Fenton activated carbon catalytical oxidation) , Pharmaceutical wastewater, Biodegradability , Biochemical oxygen demand, Chemical oxygen demand*

1. INTRODUCTION

An active ingredient is ingredient in a pharmaceutical drug or a pesticide that is biologically active. The similar term active pharmaceutical ingredient (API) and bulk active are also used in medicine , and the term active may be used for pesticide formulation. Some medications and pesticide products may contain more than one ingredient, the traditional word for the API is pharmacon or pharmakon (from Greek word pharmacos) which originally denoted a magical substance or drug. [1]Chemical reaction engineering is being increasingly utilized in the pharmaceutical industry, This is particularly for the products which have been on market for a while and their manufacturers may thus be more easily subjected to optimize in terms of desired product yield. [1]

Pharmaceutical manufacturing occurs in two general steps. First , firms convert raw material into Active pharmaceutical ingredient (APIs). API production is a highly sophisticated , technically demanding chemical and biochemical fermentation and / or synthesis process. In these process different unit processes & operations takes part. For example Mixing, heat exchange , Chemical & biochemical reactions in reactors , Distillation & condensation , Drying in tray dryers, Grinding & pulverising in jet mills.[1]Production of Active Pharmaceutical ingredients(APIs) by chemical synthesis is commonly carried out from the starting material through the chain of intermediate forming the final product, the transformation from one intermediate to another is done by chemical reaction, often accomplished by undesired pathway forming impurities and reducing yield. A different temperature sensitivity of main and side reaction , the presence of more phases, and transport effects due to mixing can make process scale-up-difficult and unpredictable. the characterization and understanding of reaction kinetics is therefore

an important, Nonetheless, it has been often neglected in past, because of pressing market/regulatory demands, leaving little room for optimization.[2]The second step in Pharmaceutical manufacturing is the final formulation of the drug, Unlike the chemical business of API production, final formulation belong to the manufacturing sector. During this processes, first mix APIs and excipients(other non-active ingredients),then either press the mixture into pills and tablets or prepare powder for solution or filling of capsules, and finally, package the product for public. In these processes Different unit operations are used , For example pelletization lines (Fluid bed coaters) , Rapid mixer granulator, Tablet compression machine , Tablet coating machine , Bulk packing machine , Automatic capsule filling machine etc.[1]

Followings are examples of Active pharmaceutical ingredients(APIs):-

(Table no-1.1)[3]

SR.NO	NAME OF API	IUPAC NAME	CHEMICAL FORMULA
1	Lamotrigine	6-(2,3-dichlorophenyl)-1,2,4-triazine-3,5-diamine	$C_9H_7Cl_2N_5$
2	Metformin	*N*,*N*-Dimethylimidodicarbonimidic diamide	$C_4H_{11}N_5$
3	Divalproex sodium	2-propylpentanoic acid	$C_8H_{16}O_2$
4	Deuloxitine	*N*-Methyl-3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propan-1-amine	$C_{18}H_{19}NOS$
5	Mesalamine	5-amino-2-hydroxybenzoic acid	$C_7H_7NO_3$

2. GLOBAL & INDIAN SCENARIO OF PHARMACEUTICAL INDUSTRY

World-over the pharmaceuticals industry is focused on Allopathy , the most common modern medicine . other types of medical treatment such as Homeopathy, Ayurveda and Unani are more Prevalent in third world countries.[4]. The pharmaceutical industry is growing at a rapid rate in emerging countries, such as India , china , Brazil, Russia, among others, while a slowdown in growth has been encountered in the US and European countries. [4]. A distinct shift is expected in the market shares across the globe, with the US and Europe share of global spending declining meanwhile, 17 high growth emerging markets including chine. India, brazil, Russia will contribute 28 % of total spending by 2015, up to from only 12 % in 2005. The next 5 years will also seen an accelerating shift in spending toward generics, rising to 39% of spending in 2015,up from 20 % in 2005, [4]

Followings are the Leading international APIs manufacturers.

1) Pfizer, USA
2) Novartis, Switzerland
3) Merk & Co., USA
4) GlaxoSmithKline, UK
5) AstraZeneca, UK

The Indian pharmaceutical industry is estimated to grow at 20 % compound annual growth rate over the next five years. India is now among the top five pharmaceutical emerging markets. There will be new drug launches, new drug filings, and Phase II clinic throughout and a greater penetration in rural markets, the domestic pharma market to grow at 10-12 % in FY15 as compared to 9 % in FY14. [5]

Following are leading Indian pharmaceutical industries.

1) Sun pharma.
2) Lupin ltd.
3) Glenmark ltd.
4) Zydus Cadila Health care.
5) Cadila pharmaceuticals.

3. ENVIRONMENTAL CONCERNES OF API'S AND EFFECT PHARMACEUTICAL FACTORY DISCHARGES ON AQUATIC LIFE.

Human and veterinary active pharmaceutical ingredients are involved in contamination of surface water , ground water , effluents, sediments and biota. Effluent of waste water treatment plant and hospitals are considered as major source of such contamination. However , recent evidences reveals high concentration of large numbers if APIs in effluent of pharmaceutical industries and in receiving aquatic ecosystems. moreover, laboratory exposures to those effluents and field experiments reveal various physiological disturbance in exposed aquatic organisms, also it seems to be relevant to increase knowledge on this route of contamination but also to develop scientific approach for further environmental monitoring. [6]. First discovered in Missouri river basin where metabolites of clofibrate and aspirin (chlorophynoxyisobutyrate and salicylic acid respectively) were quantified in effluent of sewage disposed plant discharging into the river, it is now recognized by scientists, environmental managers and decisions makers that active pharmaceutical ingredient (APIs)and their metabolites are involved in the contamination of water bodies around the world. many publication reported contraceptive, beta-blockers, antiepileptic and anti-inflammatory drugs or antibiotics at concentrations between a few ng/L to µg/L in surface and groundwater around the world. In aquatic ecosystem terms, these chemicals induce adverse effects in wild organisms due to interaction with wide range of physiological processes including reactive oxygen species regulation , hormone synthesis and reproduction. [6]

Following the discovery of high API concentration in the effluent from patancheru industrial area , the question of adverse effects in aquatic organisms exposed to effluent emerged. To address the hazard associated with the waste water of pharmaceutical factories , aquatic vertebrates such as fish and amphibians were laboratory-exposed to the effluent and a set of ,molecular, biochemical, physiological, and behavioural indicators were assessed..The results of these experiments confirm that highly diluted patancheru industrial effluent affects physiological process in fish and amphibians. Indeed, rainbow trout exposed for 5 days to effluent dilated 1:500 exhibited up and down regulation of more than 2000 genes involved in response to xenobiotic such as estrogens receptors or heat shock proteins.[6]

(Table-1.2)[6]

Pharmaceuticals	Therapeutic class	Localisation	Concentrations ($\mu g L^{-1}$)	
			Effluent	Surface (SW)–Ground (GW) or Dinking (DW) waters
Ciprofloxacin	Antibiotic	India	>10000	>10000 (SW)
Cetirizine	Antiallergic		1000–10000	1000–10000 (SW)
Losartan	Anti-hypertensive		1000–10000	10–100 (GW)
Citalopram	Antidepressant		100–1000	
Enrofloxacine	Antibiotic		100–1000	
Metoprolol	Anti-hypertensive		100–1000	
Norfloxacine	Antibiotic		100–1000	
Ofloxacine	Antibiotic		100–1000	
Enalapril	Anti-hypertensive		10–100	
Ramipril	Anti-hypertensive		10–100	
Ranitidine	Gastric acidity lowering agent		10–100	
Salbutamol	Bronchodilalator		10–100	
Amlodipine	Anti-hypertensive		1–10	
Atenolol	Anti-hypertensive		1–10	
Atorvastatine	Blood lipid lowering agent		1–10	
Dextropropoxyphene	Antalgic		1–10	
Erythromycine	Antibiotic		1–10	
Sertraline	Antidepressant		1–10	
Terbutaline	Bronchodilalator		1–10	
Trimetoprim	Antibiotic		1–10	
Zolpidem	Hypnotic		0.1–1	
Fluoxetine	Antidepressant		0.1–1	
Omeprazole	Gastric acidity lowering agent		0.1–1	
Warfarin	Antithrombotic agent		0.1–1	

4. OBJECTIVES OF STUDY.

The main objective of study is to examine the efficiency of FACCO treatment for pharmaceutical waste water.

1) To determine characteristics of pharmaceutical effluent.
2) To prepare a lab scale model of FACCO reactor & other experimental setups.
3) To determine optimum dose of ferric sulphate & hydrogen peroxide for Fenton reaction.
4) To carry out Experiment based study for FACCO treatment.
5) To increase Biodegradability of pharmaceutical effluent by Increasing the BOD/COD ratio.

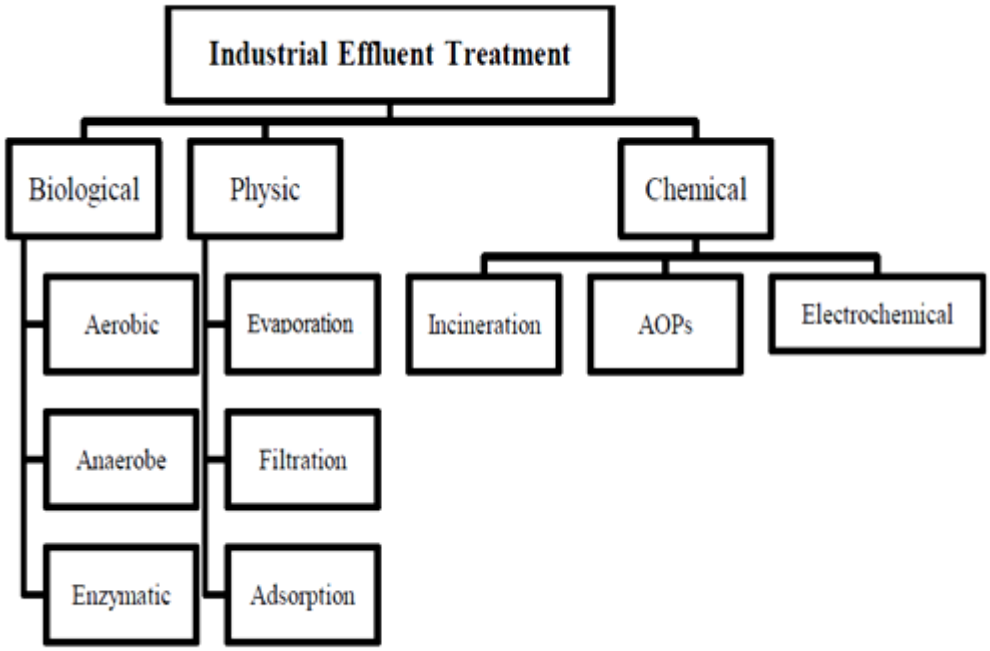
5. PHARMACEUTICAL WASTEAWTER TREATMENT.

A rising subject in environmental and engineer science is the development of processes, which promote the definite removal of drugs from industrial wastewaters, before ecosystems contamination. Since common water and effluents treatment are unable to destroy definitely persevering compounds, it is necessary to introduce additional advanced treatment technologies.[9]
Treatment of pharmaceutical wastewater can be carried out in following treatments.

1) Physical treatment.
2) Chemical treatment.
3) Biological treatment.

following figure shows organogram for different treatment of pharmaceutical wastewater.

Fig-2.1(Organogram for different treatments) [9]



5.1. EVAPORATION.

Disposal of effluent from pharmaceutical industry is an increasing problem in India and worldwide. The bulk drug manufacturing process involves usage of more organic and inorganic salts, which is becoming major part of high chemical oxygen demand and total dissolved solids. Evaporation and cooling are the common techniques used to extract available salts and reusable water. The pharmaceutical industry of the study uses multiple effect falling and forced circulation evaporator to achieve zero liquid discharge process for pharmaceutical effluent. Reverse osmosis reject is conveyed to multiple effect falling film evaporator to separate salt and reusable water. This study aims to diagnose the ills of the multiple effect evaporator to improve the efficiency and energy consumption. Diagnosis involves vacuum testing and hydro testing. The former tests revealed leakages in various parts of the multiple effect evaporator. The leakages were arrested and high pressure cleaning along with chemical cleaning was performed to remove the scaling in the evaporator. This improved the efficiency of the multiple effect evaporator significantly resulting in reduction of chemical oxygen demand and total dissolved solids by 91.5% and 96% respectively. This also achieved reduction in energy consumption by 40% reducing the overall live steam consumption from 0.55 to 0.32 kg/kg of effluent treatment.[10]

5.2. ADVANCED OXIDATION PROCESSES.

Active pharmaceutical intermediates (API) in waste waters have adverse effects on aquatic life and environment. The API have high COD value and low BOD3 and hence difficult to treat biologically. In this study, advanced oxidation processes (AOPs) utilizing the H_2O_2/Fe^{+2}, Fenton reactions were investigated in lab-scale experiments for the degradation of Atenolol containing waste water streams. The experimental results showed that the Fenton process using H_2O_2/Fe^{+2} was the most effective treatment process. With Fenton processes, COD reduction of wastewater can be achieved successfully. It is suggested that Fenton processes are viable techniques for the degradation of Atenolol from the waste water stream with relatively low toxic by-products in the effluent which can be easily biodegraded in the activated sludge process. Hence, the Fenton process with H_2O_2/Fe^{+2} is considered a suitable pre treatment method to degrade the active pharmaceutical molecules and to improve the biodegradability of waste water. After the treatment 66 % COD removal can be achieved.[15]

5.3. BIOLOGICAL TREATMENT.

This study was designed a wastewater treatment plant with an aim at minimizing and/or removing of suspended solids, dissolved solids, nutrients, and toxic compounds, before it releases into a water body. A lab scale batch type integrated aerobic biological treatment plant was constructed and operated for pharmaceutical wastewater treatment and its performance was evaluated. A cylindrical open tank was used as a reactor and passed air through the bottom of the tank. The maximum hydraulic retention time was 15 days. The treated water samples were collected every day and tested for its chemical oxygen demand (COD), total suspended solids (TSS), pH, conductivity, and total dissolved solids (TDS) to evaluate the efficiency of the plant. About 75% removal of COD was achieved employing hydraulic residence times of 15 days. The analyses results of the treated wastewater reveal that the parameters pH, BOD, COD, TSS, TDS and colour were found within the prescribed permissible limits indicating the efficiency of the plant. The results of this study demonstrate the potential for air injection to accelerate the biological treatment process, with greatest influence on COD removal from the wastewater [13].

Effluents from manufacturing operations in the pharmaceutical industry, such as antibiotic formulation, usually contain recalcitrant compounds. An approach towards appropriate technology for the treatment of pharmaceutical wastewaters has become imperative due to strict water quality legislation for environmental protection. Typically, pharmaceutical wastewater is characterized by high chemical oxygen demand (COD) concentration, and some pharmaceutical wastewaters can have COD as high as 80,000 mg.L-1. Due to high organic content, anaerobic technology is a promising alternative for pharmaceutical wastewater treatment. Consequently, in the present study, an anaerobic packed bed reactor was employed to treat highly polluted pharmaceutical wastewater. The effect of organic loading rate (OLR) was assessed by adjusting feed substrate concentration and

hydraulic retention time (HRT). The reactor performance was characterized in terms of chemical oxygen demand (COD) removal, volatile fatty acid (VFA), gas production, methane yield and pH. At an average reactor OLR of 1.58 kg COD.m3/d (HRT 5.6 d), the average soluble COD reduction was 73%. However, when the OLR was increased to 2.21 and 4.66 kg COD.m3/d the COD removal efficiency decreased gradually until 60 - 70% soluble COD removal was observed. Further increase of the OLR resulted in only around 53% soluble COD removal (average) was observed at an OLR of 5.71 kg COD.m3/d, signifying as OLR was increased; the increasing load of complex pharmaceutical wastewater may have affected the methanogens.[14] .

5.4. FACCO TREATMENT.

The treatment of pharmaceutical wastewater in terms of organic content (COD, TOC) has been investigated using advanced catalytic per-oxidation with granular activated carbon supported nano zero valent iron (nFe0/GAC). The characteristics of pharmaceutical wastewater and optimization of reaction parameters that influence the process efficiency have also been evaluated. The pharmaceutical wastewater contains a high amount of organic content of non-biodegradable nature. At optimum conditions, 81% COD and 76% TOC removal was attained. Moreover, advanced catalytic per-oxidation process was more favourable to the complete oxidation. The two-step kinetics can be attributed primarily to the oxidation of organic compound first to short chain molecular structures (organic acids) followed by their complete oxidation to produce carbon dioxide and water. Moreover, the average oxidation state (AOS) got raised from 1.8 to 2.1, which represents the strong mineralization and the generation of highly oxidized intermediates. Thus, the treatment of pharmaceutical wastewater using nFe0/GAC + H_2O_2 could be considered to be an effective alternative treatment option.[25].

6. MATERIAL AND METHOD.

For experimental study following materials were obtained.

1) FACCO reactor body :- Specially prepared toughen glass reactor is purchased from lab equipment supplier from Ankleshwar .

2) Chemicals:- Laboratory grade Ferrous sulphate , Hydrogen peroxide , Activated carbon was purchased from RANKEM ankleshwar.

3) Sand & gravels is purchased from construction material suppliers.

4) Pharmaceutical wastewater is collected from a API manufacturing pharmaceutical industry in Ankleshwar.

The reactor used in this study had a total volume of 1000 ml , with dimensions of 6.5 cm diameter and height of 40 cm. It consisted of 2.5 cm layer of gravel (diameter 5mm) separated by a 2.5cm layer of gravel(diameter 3 mm). This was followed by a 10 cm layer of coarse sand (diameter 1mm). A 10 cm void space was left at the base to facilitate collection of the filtered water. The collection system consisted perforated plate over which media is supported and filtrate flows through the perforated Teflon plate and collected in bottom space . The reactor was filled with activated carbon to a bed height of 15 cm. The size and dimensions of FACCO reactor used in this study were arbitrarily chosen for ease of observation. The Fenton reagent treated wastewater is distributed onto the surface of the carbon bed via valve system .The treated wastewater is collected from bottom of reactor.

6.1 CHARACTERISTICS OF PHARMACEUTICAL WASTWATER.

Wastewater samples are collected from primary treatment outlet (Outlet of PST) at different date as shown in table below.

Table 3.1 (Different Characteristics of waste water)

Sr no	Para--meter	Method specification	Permi--ssible limit	Unit	Result at different sampling days					Average value	Standard deviation
					25/1/16	26/1/16	27/1/16	28/1/16	29/1/16		
1	pH	Standard Method by APHA Ed.22nd .2012,4500 - H+B	6.5-8.5	-	7.5	7.8	7.3	7.0	7.7	7.4	0.320936
2	TDS	Standard Method by APHA Ed.22nd .2012,2540 – C	2100	mg/l	3250	3020	2960	3100	3000	3066	114.8042
3	COD	Standard Method by APHA Ed.22nd .2012,5220 – B	250	mg/l	7886	8120	7964	8120	7886	8000	118.2929
4	BOD	Standard Method by APHA Ed.20th .1998,5210 - B	30	mg/l	2602	2680	2628	2680	2602	2640	39.43095

6.2. TREATMENT TRAIN FOR PRESENT STUDY.

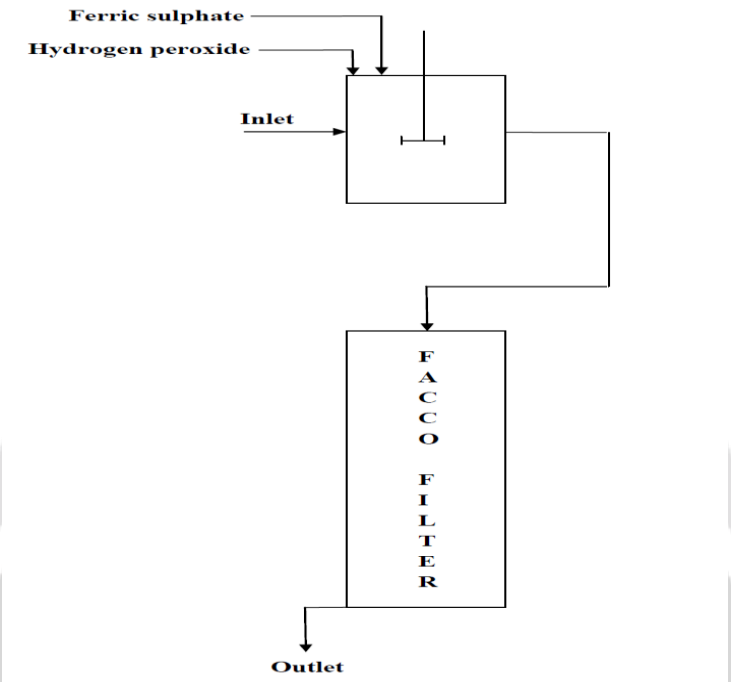


Figure-3.1 (Treatment train)

6.3. LAB SCALE MODEL FOR PRESENT STUDY.

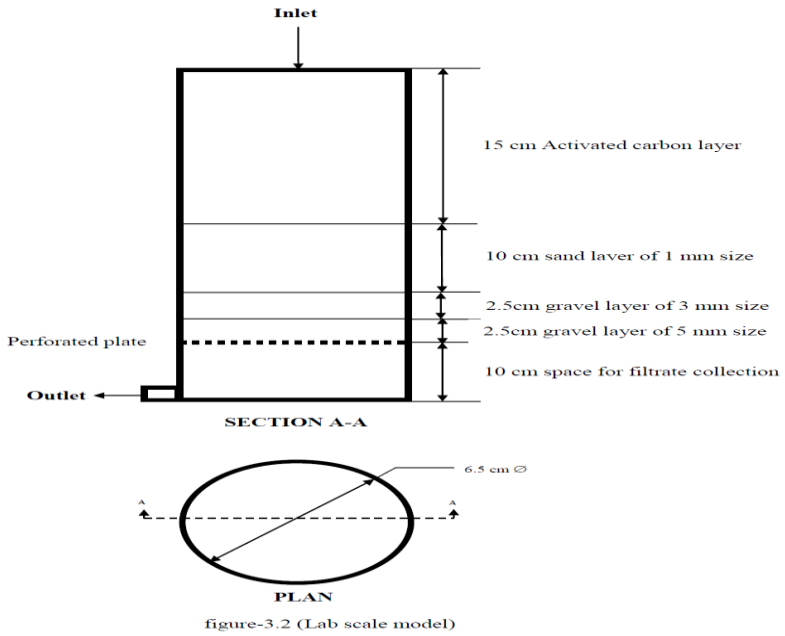


Figure-3.2 (Lab scale model)

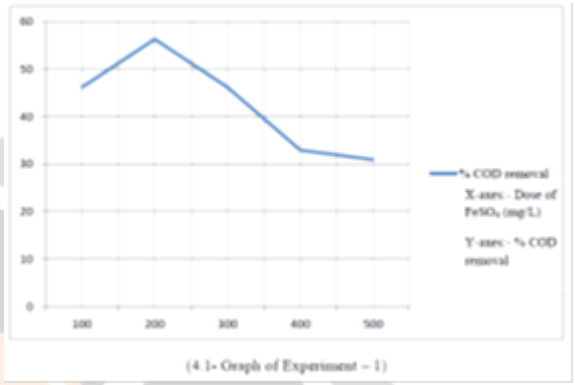
7.RESULT & DISCUSSION.

7.1. DETERMINING OPTIMUM DOSE OF FERROUS SULPHATE ($FeSO_4$) AND HYDROGEN PEROXIDE (H_2O_2).

Experiment -1 (Dose of H_2O_2 (Fixed):- 400 mg/L,Dose of $FeSO_4$:- Varying)

Sr.No	Dose of $FeSO_4$ (mg/L)	COD before treatment(mg/L)	COD after treatment(mg/L)	% COD removal
1	0 (Initial)	8000(Initial)	8000(Initial)	0(Initial)
2	100	8000	4307	46.16
3	200	8000	3495	56.31
4	300	8000	4367	46.16
5	400	8000	5364	32.95
6	500	8000	5527	30.91

(Table-4.1- Experiment-1)

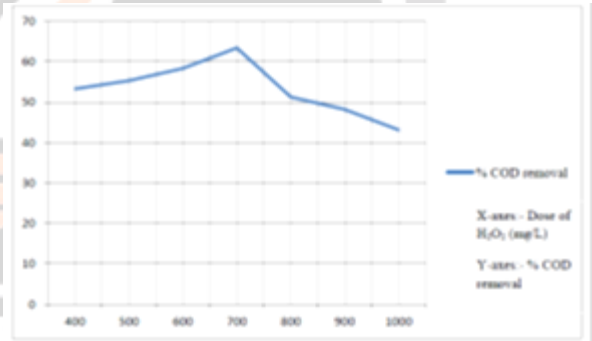


(4.1- Graph of Experiment – 1)

Experiment -2 (Dose of H_2O_2:- Varying , Dose of $FeSO_4$ (Fixed):-200 mg/L)

Sr.no	Dose of H_2O_2 (mg/L)	COD before treatment(mg/L)	COD after treatment(mg/L)	% COD removal
1	0 (Initial)	8000(Initial)	8000(Initial)	0(Initial)
2	400	8000	3788	53.27
3	500	8000	3576	55.30
4	600	8000	3332	58.35
5	700	8000	2926	63.42
6	800	8000	3901	51.23
7	900	8000	4145	48.18
8	1000	8000	4551	43.11

(Table-4.2- Experiment-2)

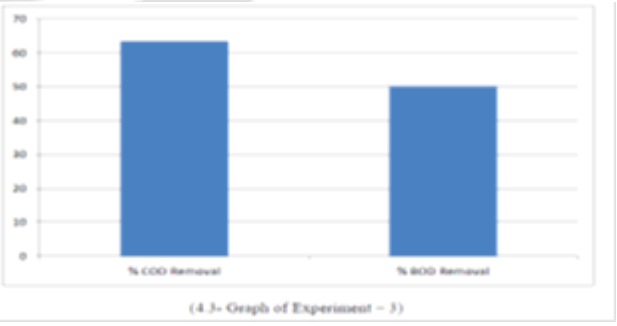


(4.2- Graph of Experiment – 2)

Experiment -3 (Dose of H_2O_2:- 700 mg/L,Dose of $FeSO_4$:- 200 mg/L)

Sr.No	COD Before treatment (mg/L)	COD After treatment (mg/L)	% COD Removal	BOD Before treatment (mg/L)	BOD After treatment (mg/L)	% BOD Removal
1	**8000**	**2926**	**63.42**	**2640**	**1316**	**50.15**

(Table-4.3- Experiment-3)



(4.3- Graph of Experiment – 3)

7.2. DETERMINATION OF COD REMOVAL USING FACCO TREATMENT.

Experiment -4 (Dose of H_2O_2:- 700 mg/L,Dose of $FeSO_4$:- 200 mg/L)

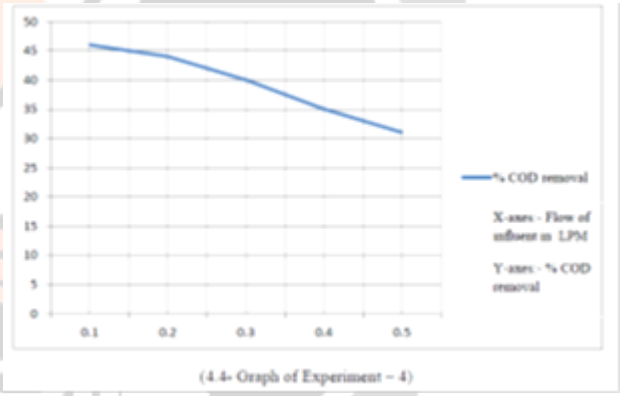
First of all determined dose of Fenton's reagent is dosed in wastewater and mixed, after mixing that wastewater is passed through FACCO reactor.COD removal at different flow, SLR, VLR were determined which are as below.

Sr.No	Flow (LPM)	Surface loading rate ($L/cm^2/Day$)	Volumetric loading rate ($L/cm^3/Day$)
1	0.1	4.33	0.28
2	0.2	8.57	0.57
3	0.3	13.01	0.86
4	0.4	17.35	1.15
5	0.5	21.70	1.44

(Table-4.4- Experiment-4)

Sr.No	Flow (LPM)	COD Before treatment (mg/L)	COD After treatment (mg/L)	% COD Removal
1	0.1	2926	1560	46
2	0.2	2926	1625	44
3	0.3	2926	1755	40
4	0.4	2926	1890	35
5	0.5	2926	2000	31

(Table-4.5- Experiment-4)



(4.4- Graph of Experiment – 4)

Considering flow at which maximum COD removal efficiency is achieved (0.1 LPM)

Sr.No	COD Before treatment (mg/L)	COD After treatment (mg/L)	% COD Removal	BOD Before treatment (mg/L)	BOD After treatment (mg/L)	% BOD Removal
1	2926	1560	46	1316	770	41.48

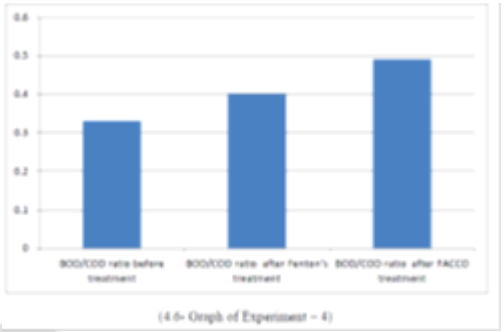
(Table-4.6- Experiment-4)

(4.5- Graph of Experiment – 4)

7.2.1 BOD/COD RATIO BEFORE AND AFTER TREATMENT.

Sr. No	BOD/COD ratio before treatment	BOD/COD ratio after Fenton's treatment	BOD/COD ratio after FACCO treatment
1	BOD:- 2640 COD:- 8000 BOD/COD ratio = 0.33	BOD:- 1316 COD:- 2926 BOD/COD ratio = 0.40	BOD:- 770 COD:- 1560 BOD/COD ratio = 0.49

(Table-4.7- Experiment-4)



(4.6- Graph of Experiment – 4)

8. CONCLUSION.

The present investigation draws the following conclusion:-

1) Waste water generated from pharmaceutical industries is less amenable to biological treatment which is due to the presence of drugs and other non biodegradable chemicals.

2) Primary clarification of wastewater removes suspended solids and less of dissolved organics.

3) Fenton's reagent , a mixture of hydrogen peroxide and ferrous iron, is capable of releasing hydroxy radicals which may take part in oxidation of dissolved organics in wastewater.

4) Fenton's reagent added salt laden wastewater was further catalytically oxidized in meso porous activated carbon packed column.

5) The oxidation of dissolved organics by Fenton's reagent resulted in the percentage removal of BOD, COD were 80.5 % , 70.83 % respectively.

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