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RESEARCH ARTICLE

“Fenton’s reagent dose calculation with respect to COD value and the process requirement optimization for effective oxidation of Aqueous Mother Liquor Effluent of an API manufacturing industry” at large scale

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Abstract

The pre-oxidation of high COD value (varying from 40000 mg/l to 90000 mg/l) containing Aqueous Mother Liquor Effluent (AMLE) by using the Fenton’s reagent (FeSO_4 and H_2O_2 in acidic medium) with effective air mixing in reactors were studied.

The theoretically calculated H_2O_2 doses are higher and are neither cost effective nor shows good reduction in COD value when it used alone. The theoretically calculated H_2O_2 dose consumption reduced more than 90 % when it used along with ferrous sulphate by providing favorable oxidation condition for AMLE.

The parameters which showed their great influence on pre-oxidation of Aqueous Mother Liquor Effluent (AMLE) were pH, concentration of ferrous ion, Hydrogen peroxide and reaction time. These parameters were optimized for COD reduction more than 80 %.

Fenton’s reagent dose were applied to AMLE (e.g. FeSO_4 (anhydrous physical form of commercial grade): H_2O_2 (on assay basis) = 1:10) on pH 3-3.5. The Fenton’s oxidation enhances the biodegradability of AMLE which further treated by coagulation and Activated Sludge Treatment Process (ASP). The biodegradable organic matter present in waste water removes in ASP by biosorption, biooxidation including nitrification and bioflocculation but due to the high organic load, biorecalcitrant compound, surfactants or biotoxicity in AMLE the Activated Sludge Treatment Process (ASP) did not perform effective treatment as a result we obtained biologically treated effluent with high COD, TSS and TDS value, loss of biomass in treated effluent, biomass rupturing in aeration tank and poor settling of biomass in secondary clarifier. Therefore to deactivate the biocidal property and to prevent shock loading and to improve the biodegradability for ASP the Advanced Oxidation played very important role.

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Introduction

The treatment of AMLE of an Active Pharmaceutical Ingredients (API) manufacturing industries by Reverse osmosis (RO) and biological treatment having big global problem because of the traces of solvent and biorecalcitrant compounds present in AMLE which show the adverse impact on biological treatment process and membranes of RO plant. The AMLE becomes acidic in nature and COD (chemical oxygen demand) value ranges from 40000 mg/l to 90000 mg/l. Fenton’s oxidation reduces the shock

organic load and biocides property of AMLE before biological treatment.

The Fenton’s reagent produces hydroxyl radicals which having second highest powerful electrochemical oxidation potential after fluorine for complex chemical compound present in AMLE. The combination of ferrous salt, hydrogen peroxide in acidic medium is known as Fenton’s reagent. The hydroxyl radicals oxidizes complex compound into simple forms e.g. CO_2 , H_2O , salts and other intermediate compounds. The hydroxyl radicals

oxidizes variety of complex compound e.g. Acids, Alcohols, Aldehydes, Aromatics, Amines, Dyes, Ethers and ketones (Bigda 1995).

The Fenton's oxidation process requires adjustment of pH in between 3 to 3.5, FeSO₄: H₂O₂ ratio 1:10 (FeSO₄ used taken in its physical form of commercial grade while H₂O₂ used on the assay basis) with respect to COD value of AMLE. The hydroxyl radicals produced during oxidation process, attack organic molecules by either abstracting a hydrogen atom or adding hydrogen atom to the double bonds. It makes new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization.

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 [H₃O₂]⁺ 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 (Huseyin Tekin et al 2005).

Material and Methods

AMLE collection:

Aqueous Mother Liquor Effluent (AMLE) collected from API production unit of M/S Symbiotec Pharmed Ltd. The quantity of AMLE varying from 1000 liters to 8000 liters depend upon batch size of API production. This stream of effluent was extremely polluted measured in terms of its COD value. The experiments were completed during the period of October 2011 to March 2012.

The results of characterization of AMLE is mentioned in Table 1 and COD removal obtained by the Fenton's oxidation of AMLE mentioned in Table 2, 3, 4 & 5 under different operational conditions.

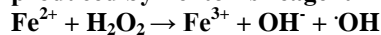
Analytical Procedure:

Analytical procedures for the determination of chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), and pH were conducted according to Standard Methods. Precautions taken for suspected interferences of residual H₂O₂ in COD and BOD test. **Fenton's Oxidation:**

Fenton's oxidation was conducted at ambient temperature and pressure in excess of atmospheric oxygen added by air blower for effective mixing and faster oxidation process. The H₂O₂ and FeSO₄ used in oxidation process. FeSO₄ used in the process taken in its anhydrous physical form of commercial grade and H₂O₂ taken on assay basis to maintained FeSO₄

and H₂O₂ ratio 1:10. The Fenton's oxidation processes for AMLE observed in 1 to 5 days.

Chemical reactions of the hydroxyl radical produced by Fenton's reagent

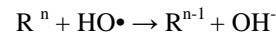


The chemical reactions of the hydroxyl radical in water are of four types:

The hydroxyl radical (HO•) can attack organic molecules found in highly polluted effluents by radical addition, hydrogen abstraction, electron transfer, and radical combination.

Radical addition: R + HO• → ROH where R = reacting organic compound

Electron transfer: Results in the formation of ions of a higher valence



Hydrogen Abstraction: R + HO• → R' + H₂O

Radical Combination: HO• + HO• → H₂O₂

In general, the reaction of HO• with organic compounds, at completion will produce H₂O, CO₂, and salts (www.h2o2.com).

H₂O₂ dose Calculation with respect to COD

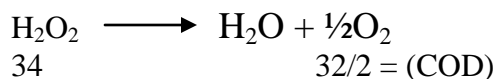
(A) Theoretical H₂O₂ doses:



Oxidant dosage (mg/l) = (Molecular wt of oxidant / 16 n) * COD

Where Mw is the molecular weight of the oxidant, n is the number of reactive oxygens generated and COD is the Chemical Oxygen Demand of the AMLE.

(B) Theoretical H₂O₂ doses:



M.w. Of H₂O₂ is 34.01 g so the 2.13 mg/l of H₂O₂ is required to oxidize 1 mg/l of COD (34/16=2.13).

(C) Process for Fenton's reagent Dose Calculation:

Step 1: Total COD load in AMLE (kg) = [(COD of AMLE (mg/l) * Quantity of AMLE (M³)]/1000

Step 2: Theoretical H_2O_2 dose required (kg) = 2.13 * Total COD load in AMLE (kg).

Step 3: Required H_2O_2 dose in Fenton's reagent (kg) = 3% of Theoretical H_2O_2 dose required (kg)

Step 4: For Fenton's reagent H_2O_2 dose (kg) = 1/2 of Required H_2O_2 dose in Fenton's reagent (kg)

Step 5: $FeSO_4$ required = (Fenton's reagent H_2O_2 dose /10) kg to maintain the $FeSO_4$ and H_2O_2 ratio 1:10

After 24 hrs drawn the sample and checked the COD value and repeated the step 1 to 5 up to getting desired COD value.

The 50% H_2O_2 means it contain 500g/l (0.5 kg H_2O_2 /Liter of H_2O_2).

Fenton's treatment and procedure requirement:

The calculated theoretical kg dose of H_2O_2 reduced

The procedure required:

- adjusted the pH of AMLE 3 to 3.5
- added the iron catalyst (as a solution of $FeSO_4$); and
- Added slowly the H_2O_2 .
- Started the air bubbling for mixing as well increase the reaction faster

90 % to 95 % when it is used along with Ferrous Sulfate (Fenton Treatment) because H_2O_2 catalyzed by addition of ferrous sulphate and becomes more powerful by producing hydroxyl radicals having second highest electro oxidation potential (Rein MUNTER). The fenton treatment is applicable for highly polluted stream of industrial effluent. Therefore separate treatment system is must for highly polluted stream before discharging to collection / neutralization tank to prevent the shock loading on Activated Sludge Treatment Process. Treatment time took 4 to 5 days depend on chemical properties of the effluent.

Table1: Characterization of Waste water streams

Waste water streams	Quantity M3	pH	BOD (mg/l)	COD (mg/l)	TDS (mg/l)	TSS (mg/l)
(Stream1)Floor washing/ Equipment washing/ Laboratory / Cooling / Boiler blow down,waste water	12 - 15	5 - 7	300 – 400	800 – 1000	500 – 700	50 – 150
(Stream2)AMLE	2 – 10	3 - 5	2000 – 3000	40000 - 80000	1000 - 2000	100 - 150
After Fenton treatment of AMLE	2 – 10	3 – 4	1500 – 2000	7000 – 9000	1500 - 2500	200 - 300
(Stream3)Domestic Waste Water	8 – 10	7 - 7.5	200 – 300	300 – 600	300 – 500	80 - 200
After coagulation and flocculation of mixed streams (except domestic waste water)	24 -35	7 – 7.5	400 – 700	2000 – 3000	800-1500	40 – 80
Equalized Waste Water, Required Parameter for ASP (According to Design)	55	7 - 7.5	700	2500	-----	50 – 100

Qty. AMLE m3	Initial COD mg/l	Initial COD load kg	Theoretically calculated. H2O2 dose Alone (kg)	F.S. kg	1/2 Qty of 3% of R.T. H2O2 dose kg	After 24 hrs COD mg/l	F.S. kg	1/2 Qty of 3% of R.T. H2O2 dose kg	After 24 hrs COD mg/l	F.S. kg	1/2 Qty of 3% of R.T. H2O2 dose kg	After 24 hrs COD mg/l	F.S. kg	1/2 Qty. of 3% of R.T. H2O2 dose kg	After 24 hrs COD mg/l	F.S. kg	1/2 Qty. of 3% of R.T. H2O2 dose kg	After 24 hrs COD mg/l
1	86000	86	183.18	0.27	2.75	54200	0.17	1.73	30200	0.10	0.96	13200	0.05	0.45	9800	0.031	0.31	7226
1	72500	72.5	154.43	0.23	2.32	48600	0.16	1.55	27000	0.09	0.86	12800	0.04	0.44	8700	0.028	0.28	6540
2	69400	138.8	295.64	0.44	4.43	37000	0.24	2.36	20800	0.13	1.33	13360	0.09	0.92	11000	0.070	0.70	8452
2	56200	112.4	239.41	0.36	3.59	34500	0.22	2.20	19000	0.12	1.21	12280	0.07	0.78	10760	0.069	0.69	7240
2	76000	152	323.76	0.49	4.86	47000	0.30	3.00	26400	0.17	1.69	15350	0.09	0.98	12900	0.082	0.82	8464
2	84500	169	359.97	0.54	5.40	68000	0.44	4.35	32700	0.21	2.09	14320	0.09	0.92	11780	0.075	0.75	8680
2	68400	136.8	291.38	0.44	4.37	37200	0.24	2.38	21000	0.13	1.34	12600	0.08	0.81	10456	0.067	0.67	9200
2	57000	114	242.82	0.36	3.64	36000	0.23	2.30	19300	0.12	1.23	11340	0.07	0.72	9248	0.059	0.59	8750
4	78000	312	664.56	0.99	9.97	43400	0.56	5.55	23000	0.29	2.94	12260	0.18	1.82	10700	0.137	1.37	9220
4	44300	177.2	377.44	0.57	5.66	23000	0.29	2.94	16000	0.20	2.04	12230	0.16	1.56	9654	0.123	1.23	8654
4	65700	262.8	559.76	0.84	8.40	39000	0.50	4.98	19600	0.25	2.50	11620	0.15	1.49	10200	0.130	1.30	9112
8	56000	448	954.24	1.31	14.31	16800	0.43	4.29	12470	0.32	3.19	9436	0.24	2.41	9200	0.235	2.35	8220
8	49200	393.6	838.37	1.26	12.58	14000	0.36	3.58	11860	0.30	3.03	7424	0.19	1.90	7242	0.185	1.85	7200
8	56800	454.4	967.87	1.45	14.52	18700	0.48	4.78	13200	0.34	3.37	8760	0.22	2.24	8526	0.218	2.18	8300
8	39200	313.6	667.97	1.00	10.02	15300	0.40	3.91	12000	0.31	3.07	8120	0.21	2.08	7974	0.204	2.04	7856

Table: 2. COD value of Treated AMLE at pH 3.5 and FeSO₄: H₂O₂ ratio 1:10

R.T. = required theoretical, F.S. = Ferrous sulphate, Qty. = quantity

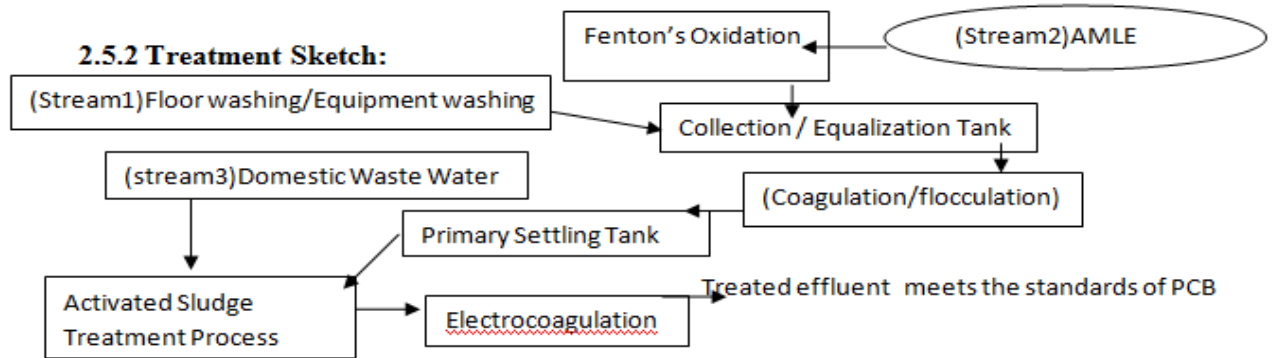


Table: 3. COD value of Treated AMLE at pH 4 to 5 and FeSO₄: H₂O₂ ratio 1:10

Qty. AMLE m3	Initial COD mg/l	Initial COD load kg	R.T. H2O2 dose Alone (kg)	FeSO4 added kg	Added 1/2 Qty of 3% of R.T. H2O2 dose Kg	After 24 hrs COD mg/l	FeSO4 added kg	Added 1/2 Qty of 3% of R.T. H2O2 dose kg	After 24 hrs COD mg/l	FeSO4 added kg	Added 1/2 Qty of 3% of R.T. H2O2 dose kg	After 24 hrs COD mg/l	FeSO4 added kg	Added 1/2 Qty of 3% of R.T. H2O2 dose kg	After 24 hrs COD mg/l
0.5	48400	24.2	51.55	0.08	0.77	32400	0.052	0.52	21400	0.034	0.34	17300	0.028	0.28	15480
0.5	65000	32.5	69.23	0.10	1.04	43000	0.069	0.69	24000	0.038	0.38	20500	0.033	0.33	17230

Table: 4. COD value of Treated AMLE at pH 4 to 5 and FeSO₄: H₂O₂ ratio 1:5

Qty. AMLE m ³	Initial COD mg/l	Initial COD load kg	R.T. H ₂ O ₂ dose Alone (kg)	FeSO ₄ added kg	Added 1/2 Qty of 3% of R.T. H ₂ O ₂ dose Kg	After 24 hrs COD mg/l	FeSO ₄ added kg	Added 1/2 Qty of 3% of R.T. H ₂ O ₂ dose kg	After 24 hrs COD mg/l	FeSO ₄ added kg	Added 1/2 Qty of 3% of R.T. H ₂ O ₂ dose kg	After 24 hrs COD mg/l	FeSO ₄ added kg	Added 1/2 Qty of 3% of R.T. H ₂ O ₂ dose kg	After 24 hrs COD mg/l
0.5	48400	24.2	51.55	0.154	0.77	36000	0.116	0.58	29260	0.094	0.47	24840	0.08	0.40	21320
0.5	65000	32.5	69.23	0.208	1.04	49300	0.158	0.79	35420	0.114	0.57	31000	0.1	0.50	26400

Table: 5. the end result of Experiment No. 1 & 2 of Table 2 repeated at higher H₂O₂ dose on pH 3 to 3.5

Qty. AMLE m ³	Initial COD mg/l	Initial COD load kg	Required Theoretical (R.T.) H ₂ O ₂ dose Alone (kg)	FeSO ₄ added kg	Added 50 % dose of Required Theoretical (R.T.) H ₂ O ₂ kg	After 24 hrs COD mg/l
1	7226	7.23	15.39	0.77	7.70	6150
1	6540	6.54	13.93	0.697	6.97	5926

Result and Discussion

Effect of H₂O₂ Dose:

Only lower or higher dose of H₂O₂ cannot be an important factor for COD reduction because various radicals and anions (hydroxyl radical (OH[•]), superoxide radical (O₂^{•-}), and perhydroxyl radical (HO₂[•]) produced in oxidation process and nature of the AMLE play important role.

Effective dose of H₂O₂ optimized by the dose calculated and their addition in treatment system at regular interval of 24 hrs as described above under heading process of Fenton's reagent dose calculation. The H₂O₂ dosing started at very low quantity e.g. only ½ of 3% of theoretical calculated H₂O₂ dose. The reason behind this dose is maximum hydroxyl radical utilization in AMLE as well reducing the quantity of H₂O₂.

The higher dose of H₂O₂ does not mean that it will reduce the COD value more and more. H₂O₂ dose works at certain level above that dose COD reduction will not improve (Table 5). Similar observations were reported by several authors in different conditions (Nora San Sebastián Martínez, et al. 2003 and S. Sinnaraprasat et al. 2011).

COD reduction occur very fast at initial dose of H₂O₂ on higher COD value containing effluent as compare to effluent having lower COD value because hydroxyl radicals attacks on organic matter very fast on first and second time dosing.

Effect of Ferrous sulphate dose:

Ferrous ion play very important role for generation of hydroxyl radicals by splitting of ferrous ion to ferric ion and ferric ion to ferrous ion in acidic medium. The ferrous ion dose directly optimized in physical anhydrous form of Ferrous sulphate. The sulphate dose decided on the basis of H₂O₂ dose to maintain the FeSO₄: H₂O₂ ratio 1:10 and 1:5. The ferrous sulphate dose were set to control on TDS value of AMLE because more addition of ferrous sulphate increases the TDS value in AMLE which will further create problem in next stage (biological) treatment process due to higher TDS. Although FeSO₄: H₂O₂ ratio 1:5 showing COD reduction in Table 4 but by increasing FeSO₄ dose it did not show good result as compare to FeSO₄: H₂O₂ ratio 1:10 mentioned in Table 3. Similar observations were reported by several authors in different conditions. (Supawadee Sinnaraprasat and Prayoon Fongsatitkul 2011)

Effect of Initial pH on Oxidation process:

Oxidation process gives good reduction in COD value at pH 3 to 3.5 as compare to reduction observed in Table 2, 3 and 4. The acidic medium at optimum

pH 3 to 3.5 is best to start the oxidation reaction and showed good reduction in COD value. Similar observations were reported by Huseyin Tekin et al. 2005 and Tamal Mandal et al. 2010 in AMLE as compared reaction started at pH in between 4 to 5.

Effect of Reaction Time:

Reaction time maintained 1 to 5 days for maximum utilization of hydroxyl radicals and to reduce the consumption of H₂O₂. Oxidation process continues up to getting desired COD reduction.

Conclusion

After getting results in different experimental conditions, we conclude:

1. pH 3 to 3.5 is best to start the oxidation of AMLE
2. FeSO₄: H₂O₂ ratio 1:10 is best as compare to FeSO₄: H₂O₂ ratio 1:5 (FeSO₄ used in oxidation process possess its anhydrous physical form of commercial grade and H₂O₂ used on its assay basis).
3. The H₂O₂ dosing started in treatment process decided by technical calculation used in all experiments and FeSO₄ dose decided on basis of H₂O₂ dose
4. Reaction time may take 1 to 5 days to get desirable COD reduction in AMLE.
5. Complete oxidation of organic matter present in AMLE is not possible either by increasing H₂O₂ dose or reaction time.

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