Feasibility of combined Fenton & coagulation method for the treatment of pesticides waste water.

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Abstract

The uses of Fenton's reagent for the degradation of pesticides wastewater has been investigated. Optimization of process parameters like pH, dosages of H_2O_2 & $FeSO_4$,Contact time(Aeration time) has been checked pH, contact time & concentration of Fenton's reagents are playing a key role in treatment process. At the first stage of the experiment different combination of the sets has been done with respect to $FeSO_4$ & H_2O_2 to check the efficiency of COD & BOD removal. After getting optimum dosage of Fenton reagent(FeSO4+H2O2)with different contact time(Aeration hrs-2,3,4,) has been observed. At second stage, Coagulation will be given as pre-treatment to increase efficiency of Fenton & to reduce cost & amount of Fenton reagents. So throughout study wastewater treated with coagulants (Al2SO4 +lime) with combination of Fenton process to give the maximum COD & BOD removal efficiency from pesticides waste water sample.

***Key words**: Fenton reagent ,Pesticides effluent, COD-BOD, Removal efficiency, Coagulation.*

1. Introduction.

Industrial effluents from various industries like textile, dyestuffs, Pesticides, paper and pulp, medicinal products, drugs, dying olive oil mill and metal industries etc. are the major contributors to water pollution as they create more subtle effects on behaviour, reproduction or eve even survival of biotic communities. Pesticides used in India are of different types such as orgonachloride, organophoshrous, urea, anilidesect. insecticides are of great significance in pest control & are increasingly in used. the pesticides & chemical industries are consider to generate wastewater containing toxic & non-biodegradable compounds that remain in the environment even after their waste have been subjected to conventional processing. Pesticides include a large amount of organic matter that makes the environment challenging .The appearance of toxic ,carcinogenic are difficult to degrade by biological method, So for the solution of this problem has involved Advanced oxidation process(AOP).

Among AOPs, the Fenton's reagent (K. Barbusinski) has been efficiently used as a chemical process for wastewater treatment and pre-treatment. The Fenton's system consists of ferrous salts combined with hydrogen peroxide under acidic conditions. Oxidation with ozone or hydrogen peroxide has been found to be an important alternative to chlorination, because the oxidation does not result in toxic chlorinated organic compounds

The high COD concentration is found typically in pesticides effluent required special treatment. The presence of toxic substance would have an effect on ecosystem but also on conventional system. The application of coagulation-Fenton's process for the treatment of pesticides wastewater has received considerable attention due to hid COD removal efficiency & cost effectiveness. The effectiveness varies with nature of organic compound & properties of waste water. To improve efficiency of COD-BOD removal, the uses of Fenton's followed by coagulation process is helpful.

1.1Fenton Treatment .

In 1894, chemists first discovered organic Fenton in (H2O2) and Fe2+ can be mixed solution consisting of the rapid oxidation, and to such a system known as the standard Fenton reagent can be that many of the known organic compounds such as carboxylic acid, alcohols, esters of inorganic oxidation, oxidized effect is very obvious . Fenton reagent was mixed by H2O2, Fe2+ gets a strong oxidant; in particular, apply to certain difficult to control, or biological toxic industrial wastewater.

The Fenton's treatment has been widely applied in the treatment of non-biodegradable wastewater in field of AOP. the efficiency of Fenton's depends on properties of wastewater, pH values,Fe+2 :H2O2 conc., &

reaction time(Aeration). Moreover, iron(Fe+2) is highly abundant & non toxic element & hydrogen peroxide (H2O2) is easy to handle environmentally. this treatment have proved worthy in this treatment have proved worthy in this field ,achieving good results in destruction of pollutants. the objectives of this study was to investigate the performance of Fenton's reagents & couple application of coagulation plus Fenton.
Fenton's chemistry uses hydrogen peroxides (H_2O_2) and iron salts where the effectiveness of H_2O_2 is improved by iron through generation of highly reactive hydroxyl radicals.

$$Fe_2^{+} + H_2O_2 \rightarrow Fe_3^{+} + \bullet OH + OH^{-} \quad \ldots\ldots\ldots\ldots\ldots 1.0$$

The hydroxyl radical(•OH) is a powerful, chemical oxidant, which acts very rapidly with organic compounds .

$$\bullet OH + pollutants \rightarrow mineralization\ or\ (CO_2 + H_2O) \ldots 1.2$$

According to reaction (1), Fe_2^{+} is oxidized to Fe_3^{+} and then regenerated through the reduction of ferric ion by H_2O_2 , as shown in Eq. (1.2)

$$Fe_3^{+} + H_2O_2 \rightarrow Fe_2^{+} + HO_2\bullet + H^{+} \quad \ldots\ldots\ldots\ldots\ldots 1.3$$

1.2.1 Factors affecting Fenton reagent

I] Effect of Iron Concentration.

In the absence of iron, there is no evidence of hydroxyl radical formation when, for example, H_2O_2 is added to a phenolic wastewater (i.e., no reduction in the level of phenol occurs). As the concentration of iron is increased, phenol removal accelerates until a point is reached where further addition of iron becomes inefficient. This feature (an optimal dose range for iron catalyst) is characteristic of Fenton's Reagent, although the definition of the range varies according to wastewaters.

II] Effect of H_2O_2 Concentration .

Because of the indiscriminate nature by which hydroxyl radicals oxidize organic materials, it is important to profile the reaction in the laboratory for each waste to be treated. This is frequently seen when pretreating a complex organic wastewater for toxicity reduction. As the H_2O_2 dose is increased, a steady reduction in COD may occur with little or no change in toxicity until a threshold is attained, whereupon further addition of H_2O_2 results in a rapid decrease in wastewater toxicity.

III] Effect of pH.

The optimal pH occurs between pH 3 and pH 6. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals. The effect of pH on reaction efficiency is illustrated below.

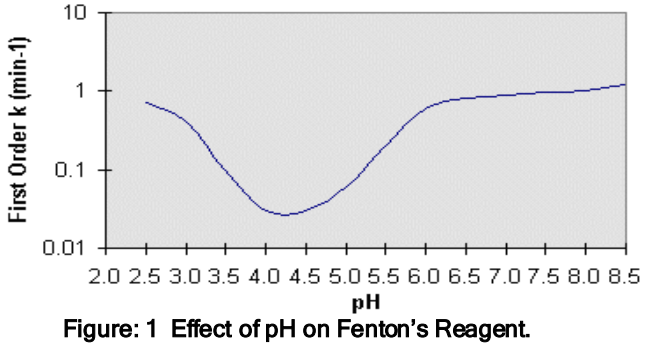


Figure: 1 Effect of pH on Fenton's Reagent.

The optimal pH occurs between pH 3 and pH 6. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In the latter form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals.

IV] Effect of Reaction Time.

The time needed to complete a Fenton reaction will depend on the many variables discussed above, most notably catalyst dose and wastewater strength. After getting optimum dosage of Fenton reagent($FeSO_4$+ H_2O_2)with different contact time(Aeration hrs-2,3,4,6) has been observed to check efficiency of COD & BOD removal.

2. Methodology of Experiment.

At As the first stage of the experiment studies, Attempts were made to check the efficiency of Fenton's process. Different combination of the sets has been done with respect to $FeSO_4$ & H_2O_2 to check the efficiency of COD & BOD removal. After getting optimum dosage of Fenton reagent($FeSO_4$+ H_2O_2)with different contact time(Aeration hrs-2,3,4,6) has been observed to check efficiency of COD & BOD removal.

At second stage, Coagulation will be given as pre-treatment to increase efficiency of Fenton & to reduce cost & amount of Fenton reagents. So throughout study wastewater treated with coagulants (Al_2SO4 +lime) & ($FeSO_4$ +lime) with combination of Fenton process to give the maximum COD & BOD removal efficiency from pesticides waste water sample. This will decrease the amount of Fenton's reagent & increase efficiency of treatment .Thus, combine treatment will also decrease

treatment cost & bring down the limits of waste water effluent under the GPCB limits.

2.1 Fenton Process.

- 300 ml wastewater sample was added in a flask, measure the pH.
- The sample's pH was adjusted to desired values (pH 3) using sulphuric acid.
- The scheduled ferrous ions (Fe^{+2}) dosage was achieved by adding necessary amount of solid $FeSO_4.7H_2O$.
- A given volume of 35% (w/w) hydrogen peroxide (H_2O2) solution was added to start up the Fenton's reaction.
- For vigorous & adequate mixing using Air pump with capacity (250 ml/hr) for different reaction time 2,3,4, hrs.
- Subsequently, final pH was neutralized or adjusted to pH=7 with sodium hydroxide and is followed by sedimentation for 1 hour.
- After sedimentation the supernatant was taken for analyzed for BOD-COD.

2.2 Coagulation Process.

Take 300ml of sample in beaker of 1litre size. Optimized dosage of Al_2SO_4 is added to fixed volume(300ml) of sample. pH of sample is adjusted to 8-9 with use of lime. then place it in jar test apparatus. Mixed it for 20mins,at 120rpm.Then the sample is standstill for 30mins to settle out flocs. After 30mins,withdrawn supernatant & filter it. The filtrate is checked for COD-BOD analysis to check the degradation efficiency by coagulation.

2.3 Combined coagulation-Fenton's process

In this set of experiment first of all coagulation process is carried out with optimized dosage of coagulation Aluminium sulphate (3.5gm/300ml ,pH:8-9,rpm:120,time:20mins)with jar test apparatus. Here also, batch experiments are carried out. Standstill 30min for settling of flocs. Withdrawn supernatant & filter it ,checked for COD-BOD analysis.

After getting significant reduction of COD-BOD(55-66%) with coagulation process,In which ,pH of sample is alkaline so adjusted to acidic pH by sulphuric acid(98% conc.).Then Fenton experiment is carried out with optimized dosages of H2O2-FeSO4(1.8gm+18ml,2.5gm+20ml,3.5gm+22) respectively, at fixed pH 3 & differ reaction time(2,3,4 hrs)air pump was attached for vigorous mixing.

2.4 Characteristics of Pesticide waste water.

Waste water or raw effluent was collected from pesticides industry A situated at ankleshwar. waste water collected in 15liter container. The sample was immediately acidified at pH 2 & it is kept for the preservation into freezer.

Parameters	Values
pH	7.32
COD	8700 ± 200
BOD	3450 ± 100
Sulphate	7.61 mg/l
Ammonical Nitrogen	6.5 mg/l
Chloride	2300 mg/l
TSS	736mg/l
TDS	18,250 mg/l

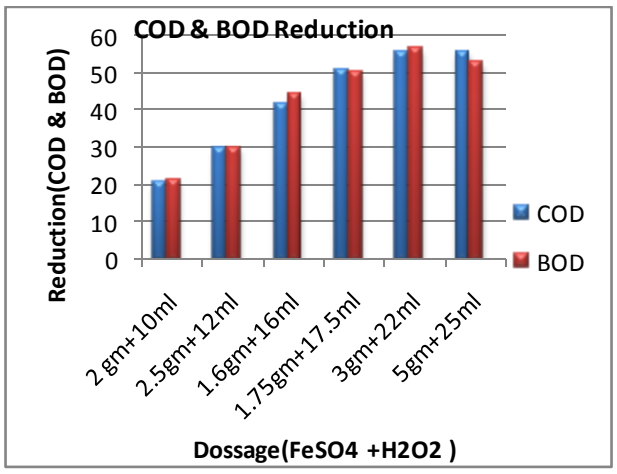
Table no : 1 Characteristics of Pesticide waste water

3. Results & Discussion.

To observe optimum concentration of hydrogen peroxide(H_2O_2) & Ferrous sulphate($FeSO_4$) for degradation or removal of COD & BOD experiments were conducted by varying dosage of hydrogen peroxide(H_2O_2) & ferrous sulfate at fixed pH & reaction time(2 hr)

Dosage ($FeSo_4$+H_2O_2)	paramet er	Initi al conc. (mg/ l)	Final conc. (mg/l)	(%) reducti on
2.0gm+10m l	COD	8700	6936.3 9	20.70%
	BOD	3450	2711.3 5	21.41%
2.5gm+12m l	COD	8700	6090	37.00%
	BOD	3450	2408	34.20%
1.6gm+16m l	COD	8700	5007.7 2	42.06%
	BOD	3450	1914	44.50%
3.0gm+22m l	COD	8700	3674	57.77%
	BOD	3450	1552	55.75%
5gm + 25ml	COD	8700	3828	56.00%
	BOD	3450	1621	53.15%

Table no:2 pH=3, Reaction time=2hrs, Dosage=Vary

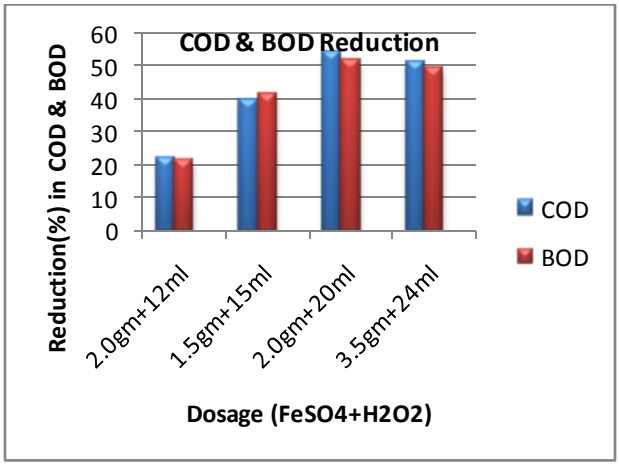


Graph no:1 Removal Efficiency of COD & BOD

Dosage	paramet	Initial conc.	Final conc.	(%) reductio

($FeSo_4$+ H_2O_2)	er	(mg/l)	(mg/l)	n
1.5gm+1 2ml	COD	8700	6772	22.15
	BOD	3450	2711	21.42%
1.5gm+1 5ml	COD	8700	5233	39.85%
	BOD	3450	2004	41.89%
2.5gm+2 0ml	COD	8700	3934	54.78%
	BOD	3450	1656	52.00%
3.5gm+2 4ml	COD	8700	4497	51.70%
	BOD	3450	1728.45	49.90%

Table no:3 pH=3, Reaction time=2hrs, Dosage=Vary.



Graph no:2 Removal Efficiency of COD & BOD

From previous two crude sets significant reduction observed with ,(pH=3 ,R.T=2hrs)

a)COD(57.77%) & BOD(55.75%) with dosage 3gm $FeSO_4$ + 22ml H_2O_2 .

b) COD(51.23%) & BOD(50.59%) with dosage 1.75gm $FeSO_4$ + 17.5ml H_2O_2.

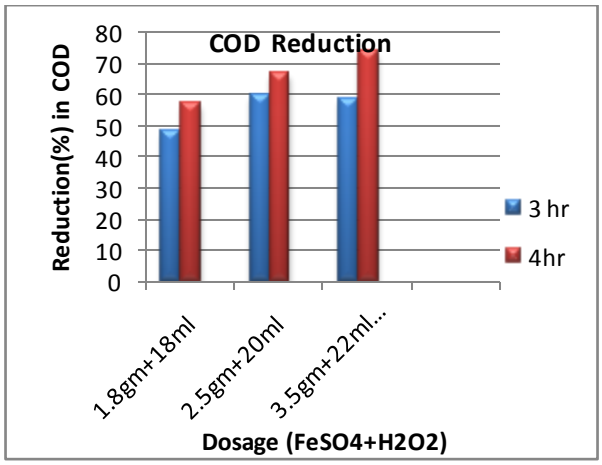
c) COD(54.78%) & BOD(52%) with dosage 2.0gm $FeSO_4$ + 20ml H_2O_2.

sAbove results indicate that good reduction is achieved with Fe+2:H_2O_2-1:10 ratio.& also indicate that degradation of COD-BOD increase with increase

dosage of Fenton's reagents.A further increase of the H_2O_2 & Fe+2 ratio actually decreases the extent of degradation of COD-BOD.

Dosage ($FeSO_4$+ H_2O_2	Reaction Time			
	Reduction in %			
	3hrs		4hrs	
	COD	BOD	COD	BOD
1.8gm+ 18ml	48.38	51.32	57.42	57.9
2.5gm+ 20ml	60.09	58.66	67.02	66.49
3.5gm+ 22ml	57. 49	62.12	73.93	70

Table no:4 pH=3, Reaction time=2,3,4hrs, Dosage=Vary.

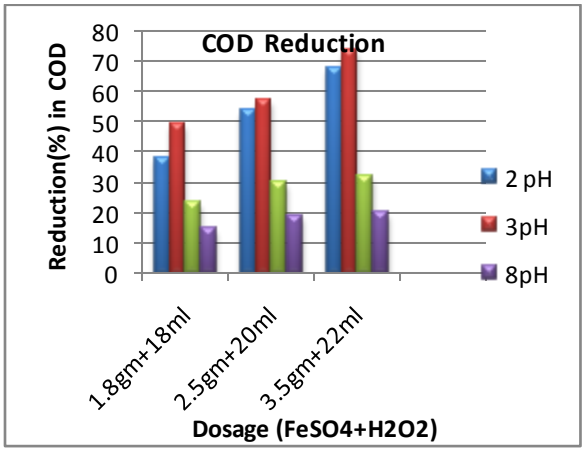


Graph no:3 Effect of reaction time on Removal Efficiency of COD.

pH has been observed to be highly important factor for the Fenton's process. Experiment demonstrated the effect if pH(2,3,5 & 8) on removal efficiency of COD & BOD. Hydrogen peroxide react very fast in acidic media to produced hydroxyl radicals(.OH). pH in acidic rang(2-4) reduction with models substance achieved range from 50-70% & maximum efficiency achieved with pH 3.

Dossage ($FeSO_4$+ H_2O_2)	Parameters	pH			
		2	3	5	8
		Reduction %			
1.8gm+ 18ml	COD	38.4	49.6	23.4	14.92
	BOD	35.90	51.92	29.83	17.22
2.5gm+ 20ml	COD	54	57.42	30.20	19.2
	BOD	55.3	57.09	26.03	15.30
3.5gm+ 22ml	COD	68.25	73.93	32.03	20.14
	BOD	65.01	70	29.15	18.5

Table no:5 pH=2,3,5,8 Reaction time=2 Dosage=Vary.



Graph no:4 Effect of pH on Removal Efficiency of COD.

Pesticides wastewater is subjected to chemical coagulation process. coagulation process removes COD,BOD & solids around 50-60% from wastewater .coagulation process is carried out to enhance removal of model substances. Here coagulation is provided with jar test(20mins,120rpm & dosage 1gm,2gm,3.5gm,4.5gm).lime is provide to adjust pH.

First coagulation is given before the Fenton's process as pre-treatment by use coagulant Al_2SO_4 to increase or enhance the efficiency of Fenton's process in removal of model substance. here 50-62% reduction(COD-BOD) is achieved with coagulation process.

Dosage (Al_2SO_4 +Lime)	parameter	Initial conc. (mg/l)	Final conc. (mg/l)	(%) reduction
1gm+1.5ml	COD	8700	3977.64	49.00
	BOD	3450	1880.25	46.90
2.0gm+1.5ml	COD	8700	3716.64	57.28
	BOD	3450	1424.16	58.72
3.5gm+1.5ml	COD	8700	3186.81	63.37
	BOD	3450	1380	60.00
4.5gm+1.5ml	COD	8700	3480	60.09
	BOD	3450	1373	59.89

Table no:6 Effect of coagulation (Al2SO4 +Lime).(pH=8-9,stirring time=20min,120rpm)

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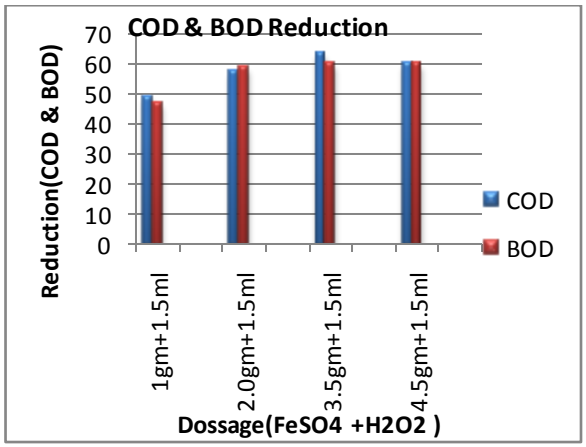

Graph no:5 Effect of Coagulation (Al_2SO_4) on Removal Efficiency of COD.

After observing good reduction with coagulation process as pre-treatment in third stage of this study wastewater is treated first with coagulation (Al_2SO_4 +lime) process & then treated effluent is subjected to Fenton 's process. First of all wastewater is treated with optimum coagulation(3.5gm Al_2SO_4 + 1.5ml lime ,pH:9-8 ,rpm:120 ,stirring time :20mins) & filtrate obtain from it subjected to Fenton process with optimum dosage ($FeSO_4$+H_2O_2=1.8gm+18ml ,2.5gm +20ml ,3.5gm +22ml) & different reaction time(2,3,4 hrs) to observe removal efficiency of coagulation + Fenton combined treatment.

Dossage ($FeSO_4$ +H_2O_2)	Para-meters	Process	Reaction Time		
			2hr	3hr	4hr
			Reduction %		
1.8 gm +18ml	COD	Fenton	**44.38**	**48.90**	**57.71**
		Coag+Fent	**72.48**	**75.00**	**79.50**
	BOD	Fenton	**43.21**	**51.32**	**56.91**
		Coag+Fent	**69.47**	**73.55**	**77.69**
2.5gm +20ml	COD	Fenton	**54.00**	**60.09**	**67.92**
		Coag+Fent	**85.03**	**87.16**	**87.92**
	BOD	Fenton	**52**	**58.62**	**66.49**
		Coag+Fent	**81.57**	**84.00**	**86.05**
3.5gm +22ml	COD	Fenton	**57.00**	**63.43**	**73.77**
		Coag+Fent	**88.50**	**89.02**	**90.40**
	BOD	Fenton	**55.75**	**62.12**	**70**
		Coag+Fent	**86.32**	**87.01**	**89.77**

Table no:7 Combined treatment of coagulation(3.5gm Al2SO4 + 1.5ml lime) + Fenton (Optimum dosage of FeSO4+H2O2=1.8gm+18ml ,2.5gm +20ml ,3.5gm +22ml).

4. Conclusion.

It is evident from result & discussion that good reduction is achieved with Fe^{+2}:H_2O_2-1:10 ratio. COD(57.77%) & BOD(55.75%) with dosage 2gm $FeSO_4$ + 20ml H_2O_2 & also indicate that degradation of COD-BOD increase with increase dosage of Fenton's reagents. A further increase of the H_2O_2 & Fe+2 ratio actually decreases the extent of degradation of COD-BOD. Here increasing the dosage above 4.5gm $FeSO_4$ & 24 ml H_2O_2 Removal efficiency is decrease.

Reaction time varies between 2-4 hrs for which removal efficiency vary between 49-73%. Fenton process is very sensitive to pH .it is not given good

results in neutral or alkaline media. It works at acidic pH range. In this study ,it gives max reduction in pH rang(2-4) .

pretreatment with coagulation found to be effective treatment which give around 30-60% BOD-COD removal efficiency with Al_2SO_4 coagulant. Pretreatment given with Fenton will reduce the quantity of Fenton reagents which affect cost factor at industrial scale. By combine (coagulation +Fenton) treatment maximum removal efficiency achieved, than Fenton alone.

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