FENTON ACTIVATED CARBON CATALYTICAL OXIDATION (FACCO) FOR PESTICIDES WASTE WATER TREATMENT USING TWO DIFFERENT (FE(II) AND FE(III)) IRON

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Abstract : This study is aimed to find treatability using Fenton Activated Carbon Catalytical Oxidation (FACCO)for treatment of Pesticide industry effluent. Pesticide effluent is not easily biodegradable so, FACCO as treatment is a good option to increase biodegradability of pesticide wastewater. The research was carried on the untreated waste effluent of Pesticide industry for the removal of COD. The optimum ratio of $[H_2O_2]$ to $[Fe^{2+}]$ was 10:1 and 20:1 and the [COD] to $[H_2O_2]$ ratio was 10:1, 6:1, 2:1 finalize at the pH value of 2.5 and 3.5. Lowering of pH was from 2.5 to 3.5 using sulphuric acid and sodium hydroxide, chemical dosed with hydrogen peroxide and Ferrous sulphate and ferric chloride (known as Fenton's reagent) was added. In this study, treatment of Pesticide effluent was carried out using combined system of Fenton oxidation process followed by adsorption on powder activated carbon (PAC). The effect of operating condition on Fenton oxidation process such as hydrogen peroxide and iron concentration were investigated. About 60-65% COD reduction was obtained without any pre-treatment of the waste effluent at pH 2.5. The experimental results shows that maximum COD removal was obtain at 6:1 of COD:H₂O₂ ratio. The lad scale model suggested that the rate of reaction was highly affected by the concentration of hydrogen peroxide. So it is suitable for Advanced Oxidation process due to its non bio-degradable nature.

Index Terms : COD removal, Fenton Activated Carbon Catalytical Oxidation (FACCO), Ferrous sulphate, Hydrogen peroxide, Pesticide waste water

I. INTRODUCTION

The most contamination of surface water observed in agricultural area and water that come from agricultural area due to the use of pesticide. Another source of the pesticide contain wastewater is from pesticide production plant. The Pesticide usually have direct adverse effect on the living organism[1]. These compounds are toxic and carcinogenic in nature[1]. Municipal point sources and industrial discharges, urban storm water runoff has been identified as a sources water with pesticides[26]. The most of the ground water and surface water contamination is due to the pesticide use, pesticide production, industrial discharge and agricultural activity[10]. The pesticide removal from industrial wastewater is of great importance because of well known pesticide resistance to microbial degradation and its ability of accumulation in the environment as well as possible carcinogenic and mutagenic properties[19,20]. The possible treatment for the pesticide wastewater for degradation and COD removal is advance oxidation process using different method like O_3/H_2O_2 , $O_2/H_2O_2/UV$, O_3/UV , H_2O_2/UV , Fenton reaction like FACCO[24]. These processes involve highly oxidize hydroxyl radical, which react quickly with organic pollutant. Fenton's reaction is one of the most effective methods of oxidation of the organic pollutant that are degraded by hydroxyl radicals generated from H_2O_2 in the presence of Fe iron as catalyst. the efficiency of the Fenton's reaction depends on the concentration of Fe²⁺ and H_2O_2 and the pH of the reaction[2].

Waste minimization in the pesticide industry is the most important step to avoid the production of the waste[23]. The aim of the study to treat the pesticide wastewater using FACCO (Fenton activated carbon catalytical oxidation) treatment[23]. The objective of this study are to determine characteristics of pesticide effluent; to perform the FACCO treatment and the other experimental setup; to determine the optimum dose of the ferric chloride, ferric sulphate and hydrogen peroxide for Fenton reaction; to carry out experiment based study for FACCO treatment and to treat pesticide wastewater by improving parameters such as pH, COD, TSS. The AOPs techniques are mainly used as a pre-treatment stage for industrial wastewater treatment[8]. Among the many treatment the Fenton treatment is found to be most effective for the treatment of the organic pollutant. The Fenton reagent has been found most effective for the industrial wastewater containing amine, dye and many other substance e.g. pesticide and the surfactant [12]. The most important advantage of the FACCO reaction is on energy is require to generate the hydroxyl radical. So this method is cost effective and easy to handle. But there is also a disadvantages of the process that is produce high amount of sludge because of the iron salt.[22]

II. FACCO TREATMENT

The Fenton reaction was discovered by Fenton in 1984[6]. 40 year later Harber-Weiss[13] mechanism is found which say that the hydroxyl radical is the effective oxidative reagent in the Fenton reaction. The HO[•] radical mostly attack all the organic compound, The most accepted scheme is described in the following equation[25].

$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+} + HO \bullet$	(1)
$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \bullet + H^+$	(2)
$Fe2++HO\bullet \rightarrow Fe^{3+}+HO\bullet-$	(3)
$\mathrm{HO} \bullet + \mathrm{H}_2\mathrm{O}_2 \to \mathrm{HO}_2 \bullet + \mathrm{H}_2\mathrm{O}$	(4)
$Fe^{3+} + HO \bullet \rightarrow Fe^{2+} + H + + O_2$	(5)
$Fe^{3+} + O_2 \bullet - \rightarrow Fe^{2+} + O_2$	(6)
$\mathrm{Fe}^{2+} + \mathrm{HO}^2 \cdot \longrightarrow \mathrm{Fe}^{3+} + \mathrm{HO}^{2-}$	(7)

In the FACCO treatment oxidation process using the activated carbon and Fenton reagent [21]. FACCO treatment is the good option to increase biodegradability of pesticide wastewater. Treatment of pesticide wastewater using combine system of Fenton oxidation process follow by adsorption on Activated carbon [23]. The FACCO treatment is happen at lower pH with the range of 2 to 4 using sulphuric acid with the chemical dose of hydrogen peroxide and ferrous ion known as Fenton reagent [23]. Adding PAC (Powdered Activated Carbon) to the waste water sample. Filtering the sample after adsorption. Acidify sample by adding H₂SO₄. Addition of hydrogen peroxide and ferrous ion as a Fenton's reagent. Allowing agitation by magnetic stirrer. Settle down of sample, collection of supernatant. Check pH value. Find out percentage reduction in COD.

The characteristics of the pesticide wastewater is pH-2.77, COD-40250, TSS-2800. The wastewater is treat with the Fenton activated carbon catalytical oxidation (FACCO). The wastewater first treat with the Powdered activated carbon (PAC) at the 100 RPM for 1 hr in JAR test after 1 hr filter the water . The treatment is decided to given at pH at 2.5 and 3.5. So the pH 1st adjusted with the help of H_2SO_4 and NaOH. Then the process is done at the COD: H_2O_2 ratio10:1, 6:1 and 2:1. For that individual COD: H_2O_2 ratio the H_2O_2 :Fe ratio is 10:1, 20:1 decided. These process is done for both the iron salt (ferric chloride and ferrous sulphate).



Fig. 1: Jar apparatus

III. RESULT AND DISCCUTION

A. Initial characteristics of the wastewater

Sampling of the wastewater was carried out at different days and their characteristics are as shown in below table.

Sr.	Parameter	Unit	Result at different sampling days					
No.			21/12/2018	28/12/2018	04/01/2019	11/01/2019	25/01/2019	
1	pН	-	2.77	2.98	2.57	3.20	2.85	
2	COD	mg/l	41820	40290	42052	46520	39569	
3	TSS	mg/l	2800	3224	2500	1700	2860	

From the above table it's been clear that the pH is between 2.57 to 3.2, COD from 39569 to 46520, TSS from 1700 to 3224. Thus the further study is carried out to determine the dose of Hydrogen peroxide, Ferric chloride and Ferrous sulphate.

Table:1 Determining the optimum dose at pH 2.5 for Ferrous sulphate(FeSO₄)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe COD before		COD after	%COD
			treatment (mg/l)	treatment (mg/l)	removal
1	10:1	10:1	40914	22930	43.96
		20:1	40914	29036	29.05

Table:2 Determining the optimum dose at pH 2.5 for Ferrous sulphate(FeSO₄)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before	COD after	%COD
			treatment (mg/l)	treatment (mg/l)	removal
1	6:1	10:1	40914	20000	51.12
		20:1	40914	15509	62.09

Table:3 Determining the optimum dose at pH 2.5 for Ferrous sulphate(FeSO₄)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe COD before		COD after	%COD
			treatment (mg/l)	treatment (mg/l)	removal
1	2:1	10:1	40914	32080	21.59
		20:1	40914	27340	33.18

Table:4 Determining the optimum dose at pH 3.5 for Ferrous sulphate(FeSO₄)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe COD before		COD after	%COD
			treatment (mg/l)	treatment (mg/l)	removal
1	10:1	10:1	40914	20705	44.39
		20:1	40914	25195	38.42

	Table:5 Determining the optimum dose at pH 3.5 for Ferrous sulphate(FeSO ₄)										
No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before	COD after	%COD						
			treatment (mg/l)	treatment (mg/l)	removal						

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before	COD after	%COD
			treatment (mg/l)	treatment (mg/l)	removal
1	6:1	10:1	40914	29210	28.61
		20:1	40914	23510	43.52

Table:6 Determining the optimum dose at pH 3.5 for Ferrous sulphate(FeSO₄)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before	COD after	%COD
			treatment (mg/l)	treatment (mg/l)	removal
1	2:1	10:1	40914	26520	35.18
		20:1	40914	24416	40.32

Table:	7 Determining th	he optimum	dose at p	H 2.5 f	for Ferric C	Chloride(FeCl ₃)

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Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before	COD after	%COD
			treatment (mg/l)	treatment (mg/l)	removal
1	10:1	10:1	40914	26080	36.26
		20:1	40914	23220	43.25

Table:8 Determining the optimum dose at pH 2.5 for Ferric Chloride(FeCl₃)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before	COD after	%COD
			treatment (mg/l)	treatment (mg/l)	removal
1	6:1	10:1	40914	21220	48.14
		20:1	40914	23750	41.95

Table:9 Determining the optimum dose at pH 2.5 for Ferric Chloride(FeCl₃)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before	COD before COD after	
			treatment (mg/l)	treatment (mg/l)	removal
1	2:1	10:1	<mark>40</mark> 914	19020	53.51
		20:1	40914	21021	48.62

Table:10 Determining the optimum dose at pH 3.5 for Ferric Chloride(FeCl₃)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before	COD after	%COD
			tr <mark>eatme</mark> nt (mg/l)	treatment (mg/l)	removal
1	10:1	10:1	40914	22510	44.98
		20:1	40914	20795	49.17

Table:11 Determining the optimum dose at pH 3.5 for Ferric Chloride(FeCl₃)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before	COD after	%COD
			treatment (mg/l)	treatment (mg/l)	removal
1	6:1	10:1	40914	18080	55.81
		20:1	40914	21920	46.42

Table:1	2 Determining the	e optimum dose at	pH 3	3.5 for Ferric	c Chlo	ride(FeCl ₃)

Sr. No.	COD:H ₂ O ₂	H ₂ O ₂ :Fe	COD before treatment (mg/l)	COD after treatment (mg/l)	%COD removal
1	2:1	10:1 20:1	40914 40914	27520 23220	32.74 43.25

From the above table it is clear that when dose of $COD:H_2O_2$ is 6:1 and the $H_2O_2:Fe$ 20:1 the percentage COD reduction is maximum 62.09.

IV. CONCLUSION

The examined Fenton's reaction was found to be very efficient for removing pesticides from wastewater. Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron, is capable of hydroxyl radicals which may take part in oxidation of dissolved organics in pesticide containing wastewater. The study showed feasibility of the Fenton oxidation to decreases the organic load.

The treatment of pesticide wastewater resulted in substantial reduction of COD as well as in the biodegradability improvement. The H_2O_2 , FeSO₄ and FeCl₃ dosage should be carefully optimized. The COD/ H_2O_2 ratio of 6:1 was found to be the most effective for the pesticide wastewater treatment. The increase in the oxidation/catalyst doses led to a substantial increase in the cost of the treatment and to surplus sludge formation. The optimal H_2O_2 /Fe ratio was 20:1 for effective COD reduction.

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