ADVANCED OXIDATION PROCESSES FOR COD REDUCTION

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ABSTRACT

Most of the synthetic dyes are non-biodegradable and are toxic to the microorganisms. The effluent containing dyes is difficult to treat by conventional biological processes. These dyes can be easily treated if the conventional treatment methods are incorporated with the advanced oxidation processes (AOPs). AOPs can break the complex structure of dyes making them more amicable to bio-degradation. This paper deals with different AOPs like hydrogen peroxide, sonolysis and their combination like sono-chemical process for remediation of dye wastewater effluent and comparison of treatment efficiencies. It is observed that the efficiencies of various options were found to be dependent on characteristics of the wastewater to be treated. The paper also discusses the important parameters to scale-up AOPs on large scale for better efficiency in actual practice.

Keywords-Effluent; Dyes; Advanced Oxidation Processes (AOPs); Revamp

INTRODUCTION

The dye wastewater is characterized by high content of dyestuff, salts, high chemical oxygen demand (COD) derived from additives, suspended solid (SS) and fluctuating pH. Conventional processes to treat wastewater from dyes and textile industries includes chemical precipitation with alum or ferrous sulphate which suffers from drawbacks such as generation of a large volume of sludge, the contamination of chemical substances in the treated wastewater, etc. Moreover these processes are inefficient towards completely oxidizing dyestuffs and organic compounds of complex structure. To overcome these problems advanced oxidation processes (AOPs) have been developed to generate hydroxyl free radicals by different techniques. AOPs include hydrogen peroxide (H_2O_2), Ozone (O_3) and UV irradiation, which have proved to be much efficient in effluent treatment processes [1] [2].

The most efficient and feasible process which reduces the COD by maximum percent is selected for revamping of Effluent Treatment Plant of a particular chemical industry. The design related to modification of installed vessel would be done for large scale application of one of the AOPs in accordance with plant capacity.

The aim of AOP is the generation of free hydroxyl radical (OH●), a highly reactive, non-selective oxidizing agent, which can destroy even the recalcitrant pollutants. The generation of hydroxyl radical is highly accelerated by combining ozone (O_3), hydrogen peroxide (H_2O_2), titanium dioxide (TiO_2), heterogeneous photo-catalysis, UV radiation or high electron beam radiation. Various types of AOPs include Ozone/H_2O_2, Ozone/UV/H_2O_2, Ozone/TiO_2/H_2O_2, Ozone/TiO_2/Electron beam irradiation, H_2O_2/UV, H_2O_2/Fe^{+2}, H_2O_2/UV/Fe^{+2}, Ozone/UV [3,9]. In this paper Fenton's method, ultrasonication & sonochemical processes are discussed.

METHODOLOGY & MATERIALS

1. FENTON'S METHOD
The Fenton's process generates great amount of HO● radicals with powerful oxidizing potential which has a very short life, but is reactive and attack dyes by either abstracting a hydrogen atom or adding itself to double bonds The Fenton process can be defined as the oxidation of

organic compounds in an aqueous solution. Initially an increase in colour removal was observed with the increase in amount of ferrous sulphate for all concentrations of green cationic dyes. The fact that the rate of decolourization increases with an increase in the concentration of ferrous ions was shown in the study performed by [4] on green cationic dyes in textile wastewater. The pH of the solution, amount of ferrous ions, and concentration of H_2O_2, initial concentration of the pollutant and presence of other ions considerably affects the Fenton's process [5]. Fenton's reagent can be electro-produced with abundant and cheap feedstock: oxygen saturated wastewater and solar energy [6].

Procedure for Fenton's method:
First of all the pH of Effluent was measured and then the pH was adjusted to 3 by adding concentrated H_2SO_4. 600 mL of effluent sample was taken in a 1 Litre beaker. Fenton's reagent was prepared by adding 3gm of $FeSO_4.7H_2O$ in 30 ml of 30% Hydrogen Peroxide. Prepared Fenton's reagent was added to the beaker containing effluent sample. The beaker was then set on a magnetic stirrer at room temperature. After regular intervals of 30 min, 50ml sample from the beaker was collected for 30, 60, 90 minutes mixing time. In each sample 2-3 drops of H_2SO_4 was added to prevent further reaction. The samples were kept in incubators and COD was measured [7, 10].

2. SONOCHEMICAL METHOD

When ultrasound was applied to effluent, water undergoes thermal dissociation to hydrogen and OH radicals. OH radical is highly reactive and can oxidise almost all contaminants in water. This primary oxidation is the reason for the degradation of contaminants in water [8,14]. Sonochemical reactions are normally characterised by the simultaneous occurrence of pyrolysis and radical reactions, especially at high solute concentrations. Phenols, chloro-phenols, nitrophenols, parathion, etc. are among a few regularly observed contaminants in industrial effluent. They are known to get degraded by the cavitation phenomenon. Degradation pathway is likely to change with the change in the intensity of ultrasound, concentration of the contaminant in water, etc. An unanticipated advantage is that sonication also kills some microorganisms and hence disinfects water [8, 11].

Procedure for sonochemical treatment :
The same procedure was repeated for effluent treatment as described under Fenton's Method but it was carried out under the ultrasonic cleaner at 20Hz fixed frequency for the cycle of 144/36 (on/off) seconds [7, 10].

Fig.1: Various Ultrasonic Experimental Data [12, 13] for comparison

Contaminants degraded	Concentration		Ultra sound concentration		
		Frequency (KHZ)	Iron typ[e and dosage	Power (w)	Reactor (ml)
Dye reactive Brillient Red	10-100mgL^{-1}	20	Fe^{+2}:1-5 µm	150	150
2,4 dinitro phenol	20 mgL^{-1}	20	Fe^{+2} 60 mgL^{-1}	200-800	75
1,4 dioxane	100 mgL^{-1}	20	Fe^{+2}or Fe^0 0.5 mgL^{-1}	300	-
Dinitrotoluenes and 2,4,6 tri nitrotoluene	DOC 150 mgL^{-1}	20	-	52-227W cm^{-2}	300
Pentacholrophenol	15 mgL^{-1}	25	FeO@Fe$_2$O$_3$ core –shell neneowires:100mg	100	150
P-Nitro phenol	0.5 and 1.0 %	25	FeSO$_4$:H$_2$O$_2$=1:5,1:7.5 and 1:10	1000	500
2,4-D and DNOC	2,4-D(1mM) DNOC(0.5mM)	28 and 460	Fe^{+3}: 0.1mM	20-80	250
Azo dye acid orange -7	1000 mgL^{-1}	40	Fe^0/GAC:12g/2.3g	100	250
Pentachlorophenol	37.5µm	40	Fe^0:2gL^{-1}	600	75
Azo dye Acid Black-I	0.041-0.162mm	40	Fe^{+2}:0.01-0.05Mm	20-50	100
Chlorobenzene	100 mgL^{-1}	200	Fe^{+2}:0.45mM Fe^{+2}:0.90mM	200	150
Methylene Blue	3.0µm	200-1063	Fe^{+3}:1x10^{-3}-1x10^{-2} M	35	300
Anthraquinonic dye,C.IAcid Blue25	10-50 mgL^{-1}	22.5 and 1,700	Fe^{+2} :10^{-3}M	14	100

OBSERVATIONS & RESULTS

Fenton's Method
Table 1 and 2 respectively depict the COD and % COD reduction at different time intervals for Fenton's method employing 1:10 (FeSO$_4$: H$_2$O$_2$) and 1:5 (FeSO$_4$: H$_2$O$_2$) reagent at 3 pH.

Table.1: COD by Fenton's method (1:10) At pH =3, Dosage = 1:10 (FeSO$_4$: H$_2$O$_2$)

Time (min)	COD	% COD reduction
0	2300	-
30	1940	15.61
60	1761	23.43
90	1517	34.03
120	1344	41.56
150	1136	50.6
180	960	58.26

Table.2: COD by Fenton's method (1:5)
- At pH =3
- Dosage = 1:5 ($FeSO_4$: H_2O_2)

Time (min)	COD	% COD reduction
0	2300	-
30	2041	11.25
60	1845	19.91
90	1628	29.2
120	1458	36.6
150	1235	46.8
180	1053	54.21

Sono-Chemical Method

Table 3 and 4 respectively represent the result in terms of COD and % COD reduction at different time intervals for Fenton's method employing 1:10 ($FeSO_4$: H_2O_2) and 1:5 ($FeSO_4$: H_2O_2) reagent at 3 pH under sonication at fixed 20Hz.

In each case COD is found to decrease and % COD reduction increases with time interval starting from 30 min to 180 min. 1:10:: $FeSO_4$: H_2O_2 is observed to be more efficient than 1:5::$FeSO_4$: H_2O_2 with and without sonication. A maximum of 74% reduction in COD was achieved by sonochemical method.

Table.3: COD by sonochemical method
- At pH =3
- Dosage = 1:10 ($FeSO_4$: H_2O_2)

Time (min)	COD	For ratio 1:10
0	2300	-
30	1794	21.97
60	1608	30.08
90	1365	40.62
120	1125	51.08
150	798	65.23
180	596	74.08

Table.4: COD by sonochemical method
- At pH =3
- Dosage = 1:5 ($FeSO_4$: H_2O_2)

Time (min)	COD	For ratio 1:5
0	2300	-
30	1806	18.33
60	1689	26.56
90	1450	36.3
120	1263	45.08
150	935	59.34
180	714	68.95

CONCLUSION

Comparision of Fenton's and sono-chemical process for different ratio of $FeSO_4$:H_2O_2 employed for the treatment of dye effluent is presented below in the bar diagram (Fig 2) and Table 5.
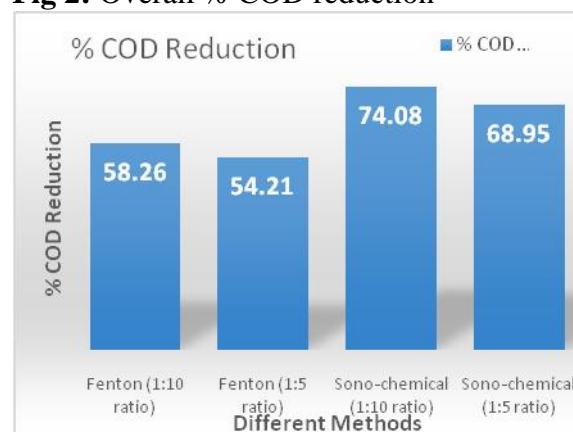
Fig 2: Overall % COD reduction

Table 5: Comparative Result

Methods	Fe^{2+}:H_2O_2 Ratio	COD	% COD Reduction
Initial sample	-	2300	-
Fenton	1:10	960	58.26
Fenton	1:5	1053	54.21
Sono-Chemical	1:10	596	74.08
Sono-Chemical	1:5	714	68.95

From the result, it is concluded that it is better to opt for sono-chemical process in the ETP plant with 20Hz frequency and 1:10 Fenton ratio. Approach for designing ETP should address following issues.

1. Quantity of wastewater generated
2. Characterization of wastewater
3. Inlet feed water quality
4. Wastewater treatability and treatment option
5. Mode of disposal of treated effluent
6. Disposal of sludge
7. Recycle/reuse of treated water
8. Modular process, scalable and flexible

Modifications Suggested

1. Feed : H_2O_2 ratio = 20 : 1 (30% H_2O_2)
2. $FeSO_4$:H_2O_2 ratio = 1:10
3. Frequency for Sonicator – 20 kHz
4. Vessel agitator should be connected along with Sonicator stirrer
5. Maintain pH between 2–3.
6. Reactor of 20000 kg requires 10 L (for usage of 50% concentration H_2SO_4) and 4 L (for usage of 98% concentration H_2SO_4).
7. Sound proof walls for reactor are recommended if high frequency sonicator is economically not feasible.

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