

# Studies on Application of Advanced Oxidation Processes for Degradation of p-Anisaldehyde and Dimethylsulphoxide in Combined Wastewaters From Bulk Drugs Manufacturing Processes

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Recent progress in chemical water treatment has led to the development of advanced oxidation processes (AOPs). AOPs are based on the generation of hydroxyl radicals that can often achieve oxidative destruction of compounds refractory to the conventional ozonation or  $H_2O_2$  oxidation. Therefore, industrial wastewaters from bulk drugs (diltiazem hydrochloride and ketoconazole) manufacturing processes were treated with UV/ $H_2O_2$ , UV/Fentons reagent, UV/ $TiO_2$  heterogenous photo oxidation process as pretreatment step. Experiments were conducted by combining the two wastewater streams of two different bulk drugs manufacturing processes for determining the effectiveness of AOPs suited for the effective degradation of p-anisaldehyde (initial concentrations 22,355 ppm, COD 2,08000 mg/L, BOD 34000 mg/L) and dimethylsulphoxide (initial concentration 27444 ppm, COD 70147 mg/L, BOD 15150 mg/L). A UV/Fenton AOP was found to cost effectively treat the majority of refractory toxic organics with upto 70% COD removal and 89% compound degradation. This UV/Fenton treatment was affected by pH at 3. The UV/Fenton treatment process was compared with the conventional biological treatment process to evaluate the cost effectiveness.

## KEYWORD

Refractory toxic organics, Advanced oxidation processes, UV/ $H_2O_2$ , UV/Fenton, UV/ $TiO_2$  heterogeneous photo oxidation, Biological treatment.

## INTRODUCTION

Recent progress in chemical wastewater treatment has led to the development of advanced oxidation processes (AOPs). AOPs are based on the generation of hydroxyl radicals that can often achieve oxidative destruction of compounds refractory to the conventional ozonation or  $H_2O_2$  oxidation. AOPs can sometimes completely convert the organic contaminant into carbon dioxide and water (Ruppert and Gares, 1994; Anderozzi *et al.*, 2000). The UV/ $H_2O_2$  systems are in practical use (Ligo and Guel, 1995; De Last

*et al.*, 1999; Esplugas *et al.*, 2002). The effectiveness of the UV/ $H_2O_2$  system in the treatment of aromatic compounds, such as phenol and nitrobenzene has been widely studied (Alton and Balcioglu, 2002). UV/ $H_2O_2$  as pretreatment step in combination with other advanced oxidation process in the treatment of textile wastewater has been studied by Alebayah *et al.* (2003) and Hung-Yee Shu Ming (2005). A comprehensive experimental investigation was done by Mandel *et al.* (2004). On removal of catechol from aqueous solution by advanced photo oxidation with  $H_2O_2$ /UV light. The effectiveness of photo Fenton process in the mineralisation of aromatic organic compounds in aqueous solutions is well known (Lipozynsks-kochang, 1992; Li and Comfort, 1996; Bauq *et al.*, 2003). Application of photo-Fenton process for degradation of

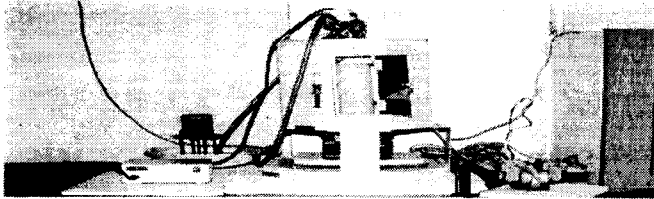


Figure 1. Photographic internal view of 16 W - UV photo reactor

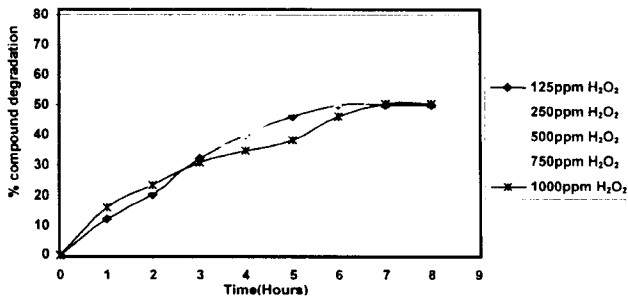


Figure 2. *p*-anisaldehyde and dimethylsulphoxide percentage degradation trend in combined wastewater by UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process at varying H<sub>2</sub>O<sub>2</sub> dosages and irradiation

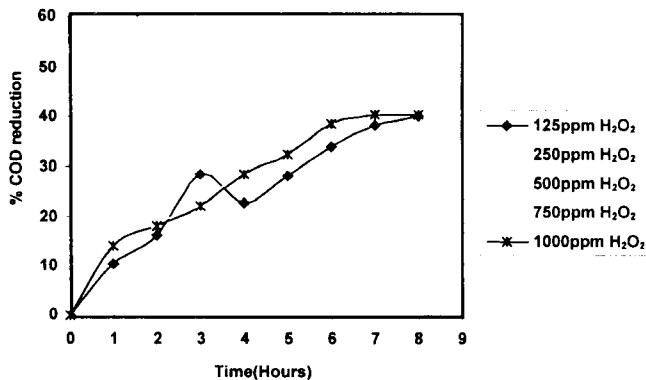


Figure 3. COD percentage reduction trend of *p*-anisaldehyde and dimethylsulphoxide by UV/H<sub>2</sub>O<sub>2</sub> oxidation in the combined wastewater with time and varying H<sub>2</sub>O<sub>2</sub> dosages

phenol in industrial wastewater was studied by Chedeville (2005), Fallman (1999) and Zheng-Zhan-Wang (2004).

Over the last few years, the tendency has been to carryout chemical oxidation in the presence of a catalyst that serves as a generator of hydroxyl radicals and therefore, the addition of an oxidizer in the medium is not necessary. Heterogeneous photo catalytic

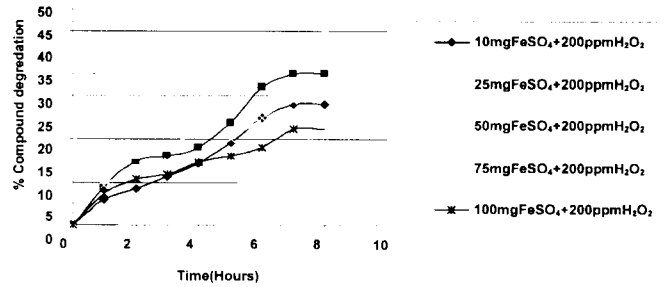


Figure 4. *p*-anisaldehyde and dimethylsulphoxide percentage degradation trend of combined wastewater by Fenton oxidation process at varying FeSO<sub>4</sub> dosages and optimum 200 ppm H<sub>2</sub>O<sub>2</sub> dosages and time

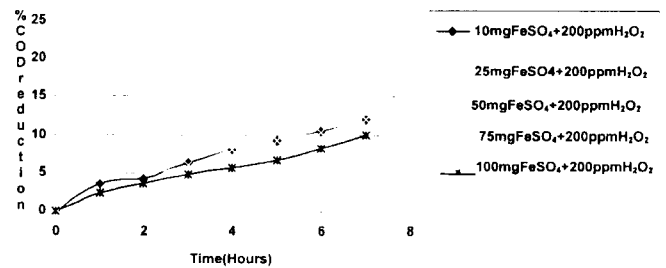


Figure 5. COD percentage degradation trend of combined wastewater containing *p*-anisaldehyde and dimethylsulphoxide by at varying FeSO<sub>4</sub> and optimum 200 ppm H<sub>2</sub>O<sub>2</sub> dosages and time by Fenton oxidation process

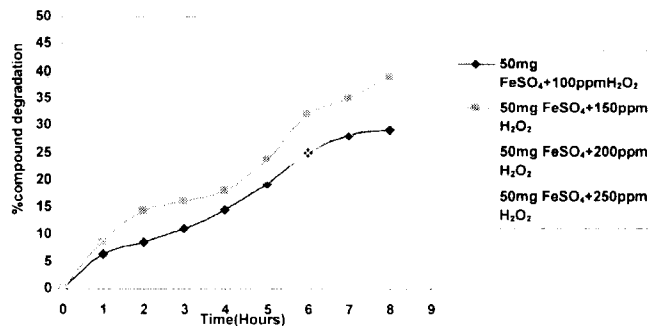
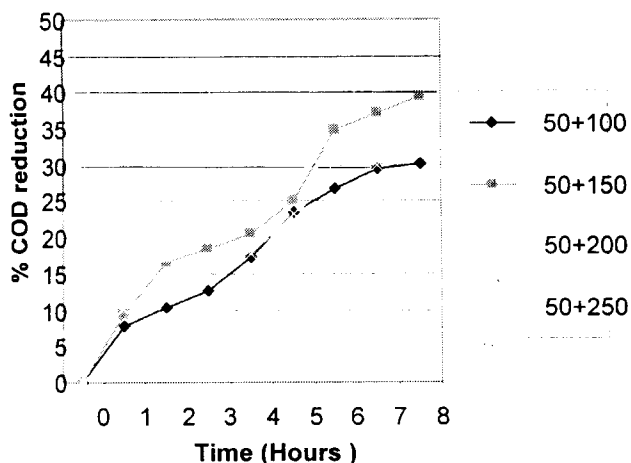
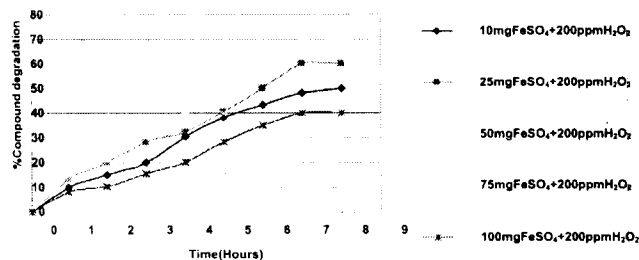


Figure 6. *p*-anisaldehyde and dimethylsulphoxide percentage degradation trend of combined wastewater by Fenton oxidation process at varying H<sub>2</sub>O<sub>2</sub> dosages and time

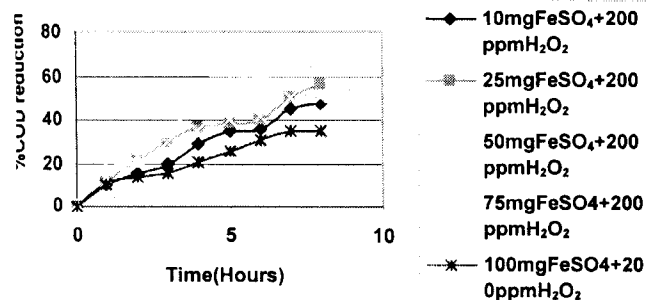
process consists on utilizing the near UV radiation to photo excite a semiconductor catalyst (TiO<sub>2</sub>) in the presence of oxygen. Under these circumstances oxidizing species, either bound hydroxyl radical or free holes are generated. TiO<sub>2</sub> in the anatase



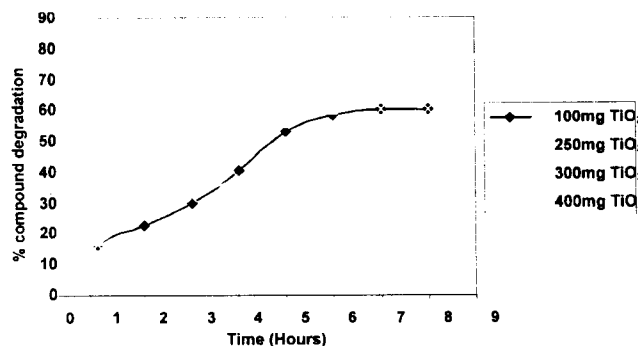
**Figure 7.** COD percentage degradation trend of combined wastewater containing *p*-anisaldehyde and dimethylsulphoxide by UV/ $H_2O_2$  oxidation process at varying  $H_2O_2$  dosages and time



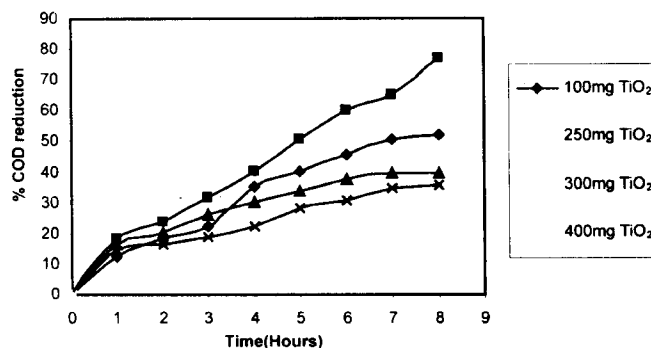
**Figure 8.** *p*-anisaldehyde and dimethylsulphoxide percentage degradation trend of combined wastewater by UV/Fenton oxidation process at varying  $FeSO_4$  and optimum 200 ppm  $H_2O_2$  dosages and time



**Figure 9.** COD percentage reduction trend of combined wastewater containing *p*-anisaldehyde and dimethylsulphoxide at varying pH and optimum 200 ppm  $H_2O_2$  and  $[Fe^{2+}]$  dosages and time by UV/Fenton oxidation process



**Figure 10.** Percentage degradation trend of *p*-anisaldehyde and dimethylsulphoxide in combined wastewater by UV/ $TiO_2$  advanced oxidation process at varying  $TiO_2$  dosage and irradiation time



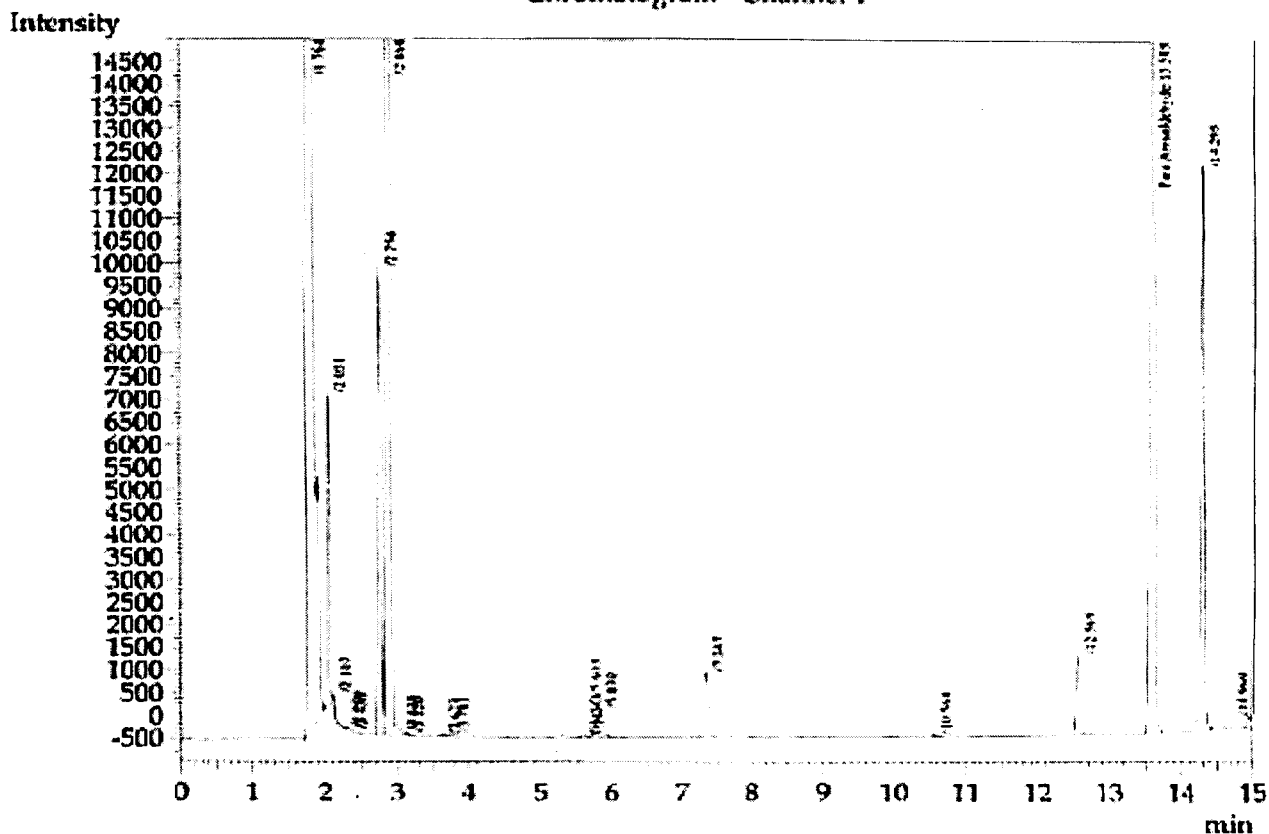
**Figure 11.** COD percentage reduction trend of *p*-anisaldehyde and dimethylesulphoxide in the combined wastewater by UV/ $TiO_2$  oxidation process at varying  $TiO_2$  dosages and optimum pH

form seems to possess the most interesting features, such as high stability, good performance and low cost. A lot of work has been done on UV/ $TiO_2$  heterogeneous photocatalysis for the treatment of highly polluted industrial wastewater. Minero *et al.* (1994) studied the photo catalytic degradation of nitrobenzene on  $TiO_2$  and ZnO, reporting that complete mineralisation with  $TiO_2$  was achieved. Ding-Wang Chen *et al.* (2001) verified the effect of optimal catalyst layer thickness for the photo catalytic process. Other author (Luane *et al.*, 2002) investigated the degradation of elemental chlorine free bleaching effluents by using two catalytic systems:  $O_2/TiO_2/UV$  and  $O_2/ZnO/UV$  at different periods of irradiation. The degradation of 4-chloro-2-methylphenol

**Sample Information**

Analysis Date & Time : 5/2/2005 3:07:16 PM  
 User Name : S.R Mittal  
 Sample Name : DMSO+PARA  
 Sample ID : DMSO+PARA  
 Injection Volume : 1ml  
 Data Name : D:\GCsolution\Data\Project 1\2005\FEB-05\2010-Nicholas (Para)Actual-E  
 Method Name : D:\GCsolution\Data\NICHOLAS-EFLUENT.gcm

**Chromatogram - Channel 1**

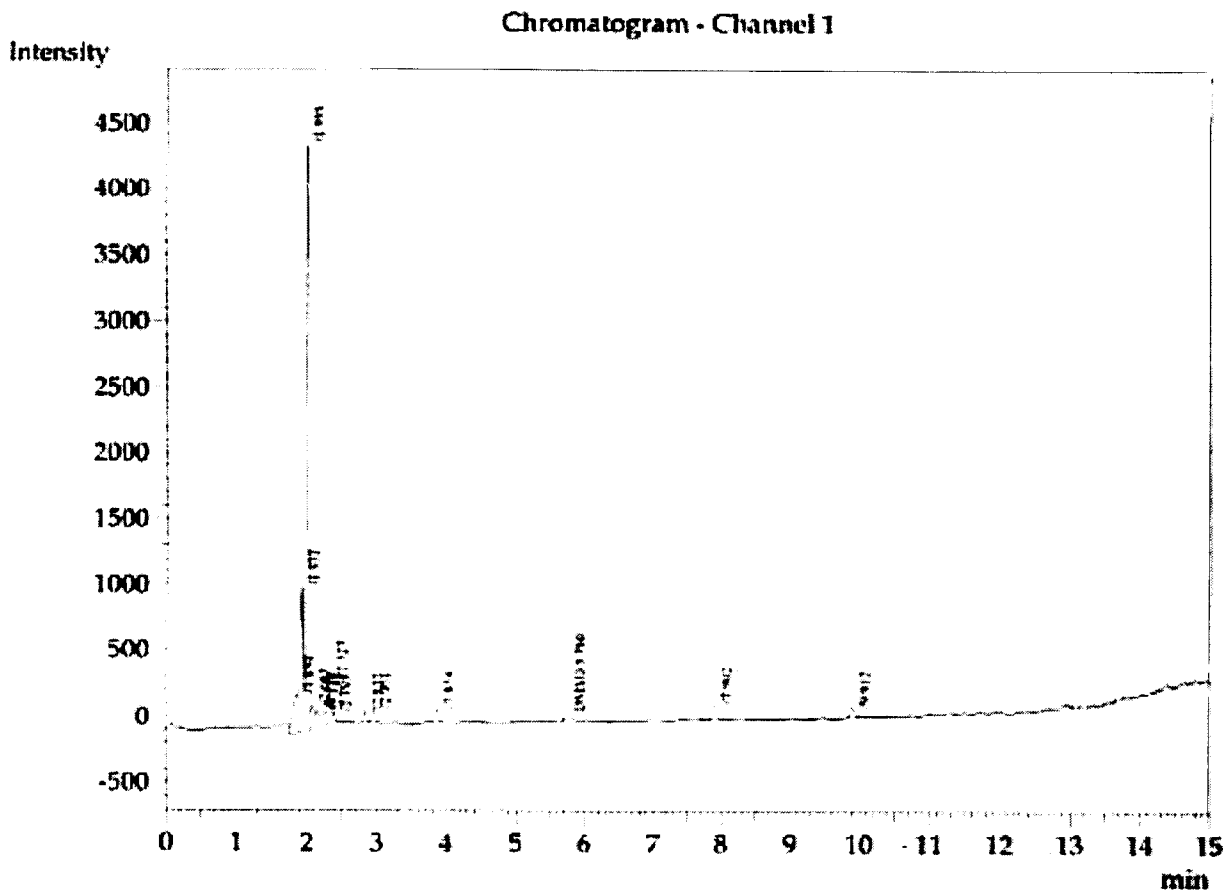


Peak Table - Channel 1				
Peak#	Ret.Time	Area	Area%	Cmpd Name
1	1.764	1960098	83.8781	
2	2.031	16153	0.6912	
3	2.107	747	0.0320	
4	2.270	52	0.0022	
5	2.330	45	0.0019	
6	2.754	32505	1.3910	
7	2.868	170925	7.3143	
8	3.030	20	0.0008	
9	3.120	85	0.0036	
10	3.623	293	0.0125	
11	3.743	361	0.0154	
12	5.603	213	0.0091	DMSO
13	5.830	3955	0.1692	
14	7.347	6954	0.2976	
15	10.564	202	0.0087	
16	12.569	6919	0.2961	
17	13.589	71287	3.0506	Para Anisaldehyde

**Figure 12.** GC headspace chromatograms of *p*-anisaldehyde and dimethylsulphoxide in the actual combined wastewater indicating peaks for *p*-anisaldehyde and dimethylsulphoxide and peaks for other volatile organics

Sample Information

Analysis Date & Time : 5/3/2005 1:44:12 PM  
 User Name : S.R Mittal  
 Sample Name : Combined Effluent(Treated)  
 Sample ID : UV-H2O2(500ppm)-3hrs  
 Injection Volume : 1ml  
 Data Name : D:\GCsolution\Data\Project 1\2005\MAY-05\2010-Nicholas (Para)\Combined  
 Method Name : D:\GCsolution\Data\NICHOLAS-EFLUENT.gcm



Peak Table - Channel 1

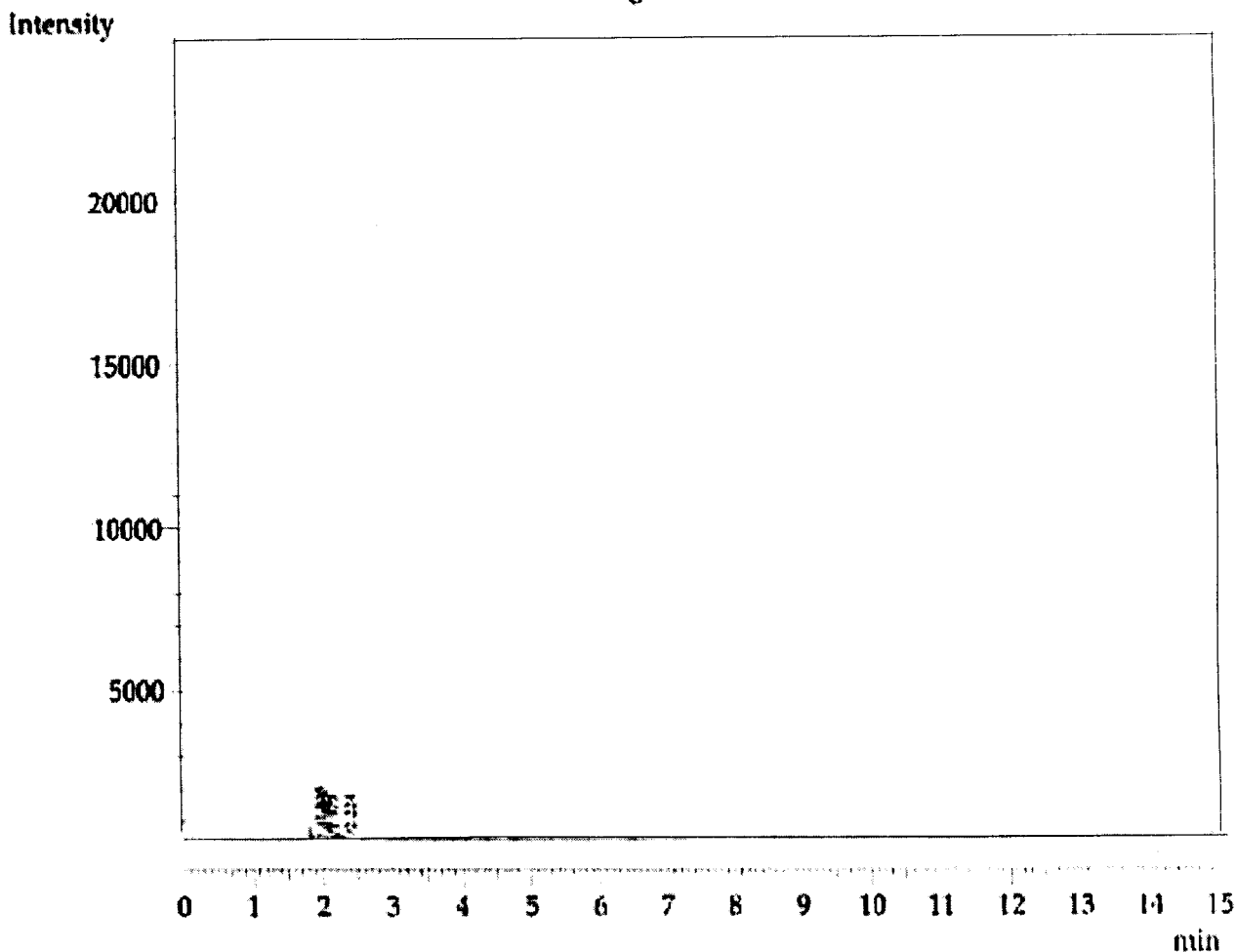
Peak#	Ret.Time	Area	Area%	Cmpd Name
1	1.850	1377	7.0246	
2	1.932	3266	16.6651	
3	1.995	9806	50.0362	
4	2.087	668	3.4088	
5	2.158	468	2.3864	
6	2.248	541	2.7623	
7	2.327	931	4.7488	
8	2.395	224	1.1416	
9	2.837	301	1.5354	
10	2.951	328	1.6738	
11	3.854	383	1.9555	
12	5.760	374	1.9103	DMSO
13	7.902	612	3.1214	
14	9.912	319	1.6300	
Total		19598	100.0000	

Figure 13. GC headspace chromatogram of *p*-anisaldehyde and dimethylsulphoxide in the combined wastewater treated with UV/H<sub>2</sub>O<sub>2</sub> (500 ppm) irradiated for 3 hr at pH 7 indicating 100% *p*-anisaldehyde and 99.54% dimethylsulphoxide degradation

Sample Information

Analysis Date & Time : 5/6/2005 10:38:58 AM  
 User Name : S.R Mittal  
 Sample Name : Combined Effluent(Treated)  
 Sample ID : UV-Fentone(5hrs)  
 Injection Volume : 1ml  
 Data Name : D:\GCsolution\Data\Project 1\2005\MAY-05\2010-Nicholas (Para)\Effluent\1  
 Method Name : D:\GCsolution\Data\NICHOLAS-EFLUENT.gcm

Chromatogram - Channel 1



Peak Table - Channel 1

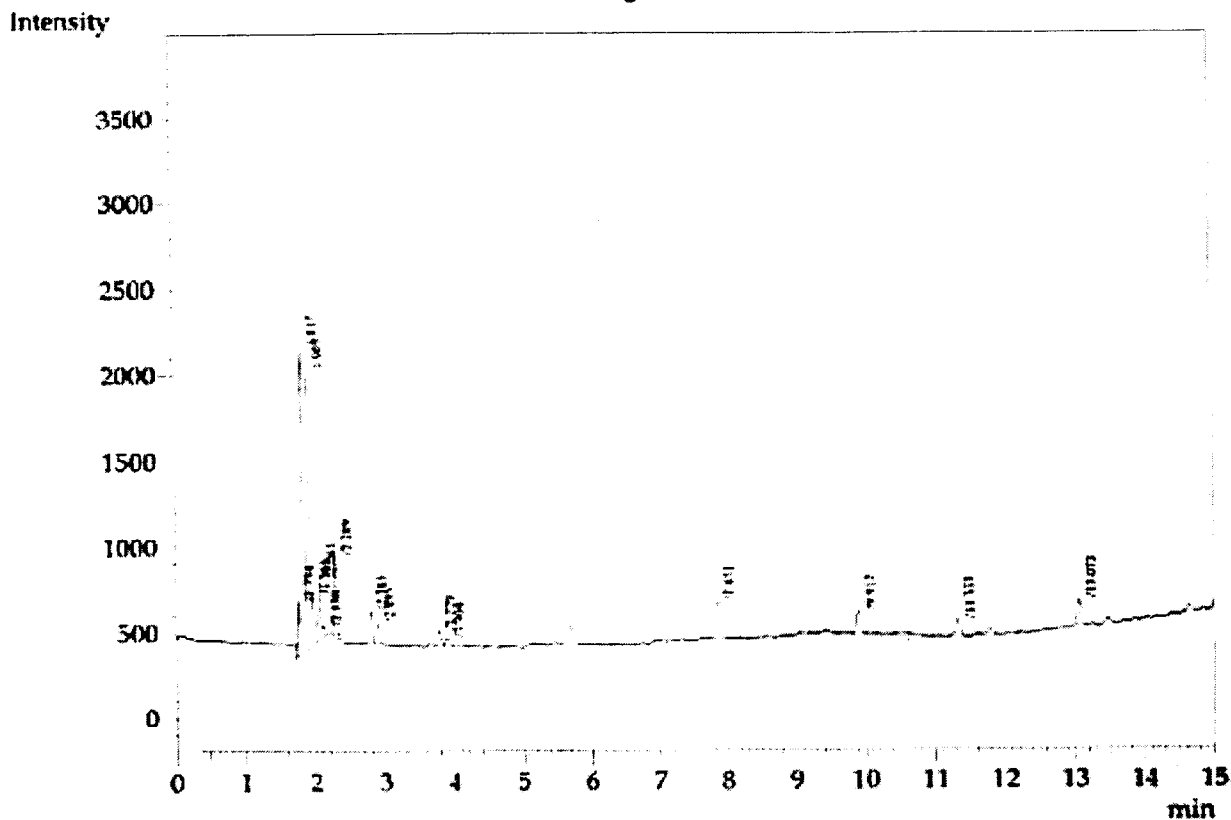
Peak#	Ret.Time	Area	Area%	Cmpd Name
1	1.805	707	36.7370	
2	1.887	754	39.2105	
3	1.975	123	6.3764	
4	2.224	340	17.6761	
Total		1924	100.0000	

Figure 14. GC headspace chromatogram of *p*-anisaldehyde and dimethylsulphoxide in combined wastewater treated with UV/Fenton advanced oxidation process irradiated for 5 hr at optimum 50 mg/L [Fe<sup>+2</sup>] and 200 ppm [H<sub>2</sub>O<sub>2</sub>] and at optimum pH 3 showing 99.92% degradation of other volatile organics & 100% degradation of compounds

**Sample Information**

Analysis Date & Time : 5/8/2005 11:25:12 AM  
 User Name : S.R Mittal  
 Sample Name : Combined Effluent(Treated)  
 Sample ID : UV-TiO<sub>2</sub>(5hrs)  
 Injection Volume : 1ml  
 Data Name : D:\GCsolution\Data\Project 1\2005\MAY-05\2010-Nicholas (Para)\Effluent\ E  
 Method Name : D:\GCsolution\Data\NICHOLAS-EFLUENT.gcm

**Chromatogram - Channel 1**

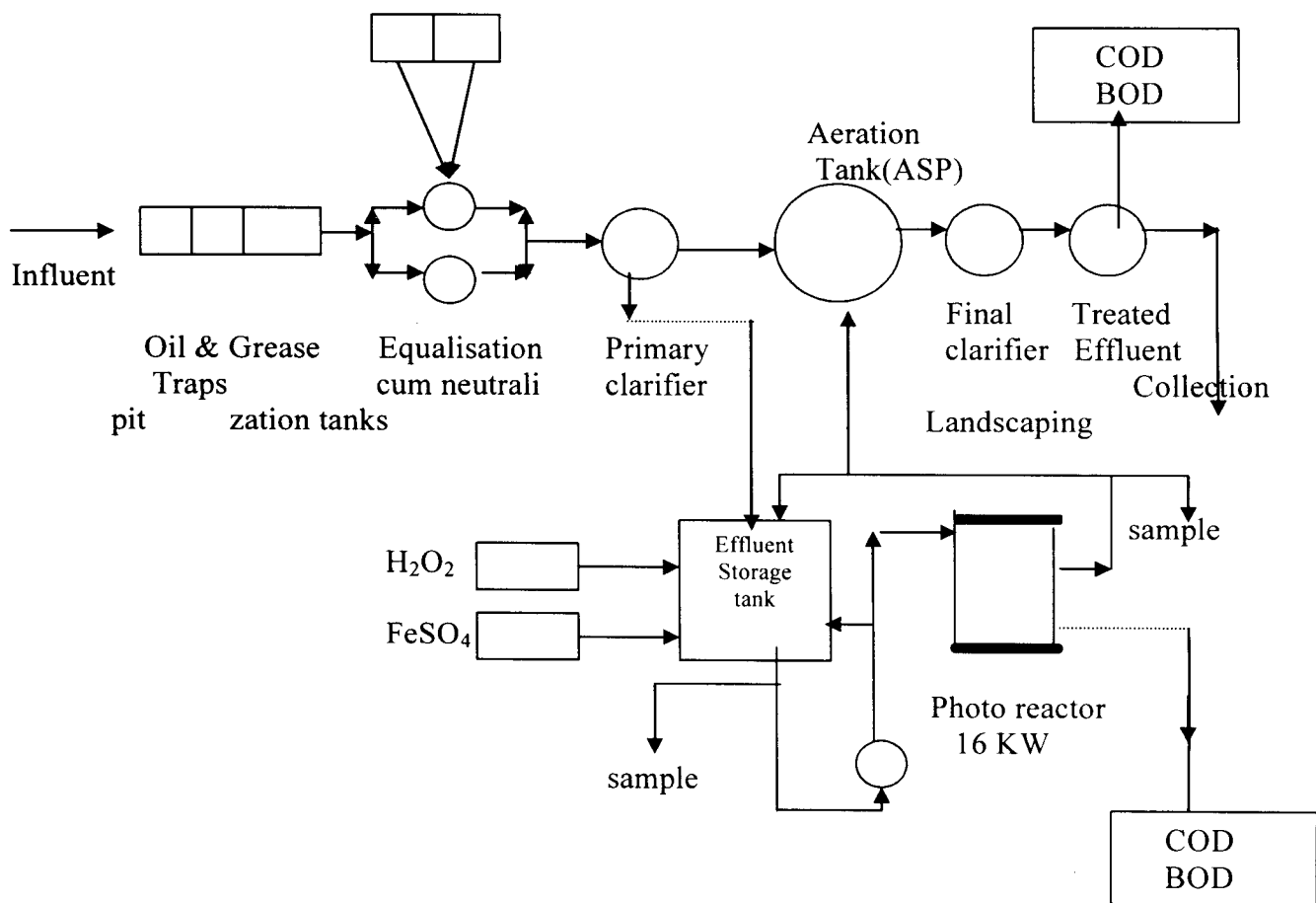


**Peak Table - Channel 1**

Peak#	Ret.Time	Area	Area%	Cmpd Name
1	1.754	552	3.0938	
2	1.817	5275	29.5871	
3	1.907	4050	22.7165	
4	1.966	948	5.3146	
5	2.061	983	5.5126	
6	2.130	192	1.0755	
7	2.289	1181	6.6267	
8	2.785	613	3.4395	
9	2.895	381	2.1371	
10	3.779	363	2.0383	
11	3.904	216	1.2094	
12	7.851	1077	6.0424	
13	9.917	631	3.5388	
14	11.333	401	2.2476	
15	13.073	689	3.8624	
16	15.002	278	1.5576	
<b>Total</b>		<b>17830</b>	<b>100.0000</b>	

Figure 15. GC headspace chromatogram of *p*-anisaldehyde and dimethylsulphoxide in combined wastewater treated with UV/TiO<sub>2</sub> advanced oxidation process irradiated for 5 hr at optimum 250 mg/L [TiO<sub>2</sub>] and at optimum pH of 7 showing 100% compounds, degradation and 99.21% degradation of other volatile organics

## Chemical Dosing Tanks



**Figure 16.** Proposed process flow diagram for photo Fenton and biological treatment

in aqueous solution by UV irradiation in the presence of  $\text{TiO}_2$  has been studied by Sibel *et al.* (2004). Hugul *et al.* (2002) studied the application of  $\text{TiO}_2$  as a photo activated catalyst under UV radiation emitted by an immersion well type quartz photo reactor for the degradation of chlorophenols in aqueous solutions.

The characteristics of wastewater of p-anisaldehyde and dimethylsulphoxide (Table 1) indicates that p-anisaldehyde wastewater stream has COD value 2,08,000 mg/L and pH is about 6.5 and that of dimethylsulphoxide is having COD value of 70147 mg/L and the pH of 12 and difficult to treat by the conventional biological treatment. About 60 KL/day of wastewater is generated from the manufacturing processes of two bulk drugs, namely diltiazem hydrochloride

and ketoconazole. The objective of this study was to treat industrial wastewater cost effectively and determine the effectiveness of UV/ $\text{H}_2\text{O}_2$ , UV/Fenton and UV/ $\text{TiO}_2$  heterogeneous photo oxidation processes. Therefore, the experiments were conducted by combining the two wastewater streams of two different bulk drugs manufacturing processes.

## MATERIAL AND METHOD

### Industrial wastewaters

Throughout this research the combined industrial wastewaters containing p-anisaldehyde (initial concentration 22355 ppm, COD 208000 mg/L, BOD 34000 mg/L, pH 6.5) and dimethylsulphoxide (initial concentration 27444 ppm, COD 70147 mg/L, BOD 15100 mg/L, pH 12) produced from the



**Table 1: Wastewater characterization, in mg/L**

TEST	p-anisaldehyde phenol waste-water	2-aminothio phenol waste-water	Dimethylsulfoxide waste-water
<b>Physical characteristics</b>			
Total solids	39856	2836	370490
Total volatile solids	11084	1358	61140
Total fixed solids	28714	1478	309350
Total suspended solids	104	288	280
Total dissolved solids	39752	2548	370210
Volatile dissolved solids	11084	1196	60990
Fixed dissolved solids	28668	1352	309220
Turbidity	62	180	210
Colour	Pale yellow	Brownish	Dark brown
Odour	Objectionable	Objectionable	Objectionable
Temperature	27°C	27°C	27°C
Conductivity	44000 $\mu\text{s/cm}$	1680 $\mu\text{s/cm}$	38000 $\mu\text{s/cm}$
<b>Inorganic chemical characteristics</b>			
Organic nitrogen	1.4	2.8	14
Nitrites	nil	nil	nil
Nitrates	nil	nil	nil
Total nitrogen	-	-	-
pH	6.35	5.6	Above 12
Alkalinity	65	nil	41250
Chlorides	12070	454	133
Sulphate	42	28	3702
<b>Organic chemical characteristics</b>			
BOD/COD ratio	0.16	0.24	0.21
Biochemical oxygen demand	34000	1800	15150
Chemical oxygen demand	208000	7400	70147
p-anisaldehyde	22355ppm	-	-
2-Amino thiophenol (2-ATP)	-	17030ppm	-
Dimethyl sulphoxide (DMSO)	-	-	27444 ppm

**Table 2. Optimization studies of p-anisaldehyde and dimethylsulphoxide degradation in the combined wastewater at varying H<sub>2</sub>O<sub>2</sub> concentration by UV/H<sub>2</sub>O<sub>2</sub> oxidation process**

Parameter	p-anisaldehyde and dimethylsulphoxide combined wastewater					
Initial concentration	1:10000 dilution					
Optimum pH	7					
	% COD reduction			% compound degradation		
Time (hr)	3	5	8	3	5	8
H <sub>2</sub> O <sub>2</sub> dosages (ppm)						
125	28.6	28.3	40	32	46	50.2
250	22.5	38.2	50	38	48	55.6
500	32.2	48.6	53.8	45	65.2	70.2
750	23	36.5	42	35	40.6	58
1000	22	32.5	40.3	30.8	38.2	50.3

**Table 3.** Optimization studies of *p*-anisaldehyde and dimethylsulphoxide degradation in the combined wastewater at optimum 200 ppm H<sub>2</sub>O<sub>2</sub> dosages and time and varying [Fe<sup>2+</sup>] by Fenton oxidation process

Parameter	p-anisaldehyde& dimethylsulphoxide combined wastewater					
Initial concentration	1:10000 dilution					
Optimum H <sub>2</sub> O <sub>2</sub> dosages(ppm)	200					
	% COD reduction			% compound degradation		
Time (Hours)	3	5	8	3	5	8
[Fe <sup>2+</sup> ], mg/L						
10	6.3	9.3	12	11.3	19.1	28
25	8	10.5	16	16.2	23.6	35
50	12	16.5	21.4	18.6	28	45
75	6	9.2	12	14.9	20	30
100	4.8	6.6	10	12	16.2	22.3

**Table 4.** Optimization studies of *p*-anisaldehyde and dimethylsulphoxide degradation in the combined wastewater at varying H<sub>2</sub>O<sub>2</sub> dosages by Fenton oxidation process

Parameter	p-anisaldehyde& dimethylsulfoxidecombined wastewater					
Initial concentration	1:10000 dilution					
Optimum pH	3					
	% COD reduction			% compound degradation		
Time (hr)	3	5	8	3	5	8
H <sub>2</sub> O <sub>2</sub> dosages (ppm)						
100	12.7	23.6	30.2	11.2	19.1	29
150	18.4	25.2	39.3	16	23.6	16
200	20.4	31	43.5	18.6	28	43.5
250	15.4	23.2	32	14.9	20	30

**Table 5.** Percentage degradation trend of *p*-anisaldehyde and dimethylsulphoxide in combined wastewater and COD removal at optimum H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub> dosages and time and varying pH by Fenton oxidation process

Parameter	p-anisaldehyde and dimethylsulphoxidecombined wastewater					
Initial concentration	1:10000 dilution					
Optimum Fenton dosages	FeSO <sub>4</sub> :50 mg/L, H <sub>2</sub> O <sub>2</sub> : 200 ppm					
	% COD reduction			% compound degradation		
Time (hr)	3	5	8	3	5	8
pH						
3	38	52.8	70	41.6	63.3	89
4	32	40.6	60.2	14.4	21.2	34.4
5	25	40.6	50	10	17.3	24.5

manufacturing processes of diltiazem hydro- chloride (a bulk drug) and ketoconazole (a

**Table 6.** Optimization studies of *p*-anisaldehyde and dimethylsulphoxide degradation in the combined wastewater at optimum Fenton dosages and varying pH and time by UV/Fenton oxidation process

Name of the compound	<i>p</i> -anisaldehyde and dimethylsulphoxide combined wastewater	
Initial concentration [1 : 10000 dilutions]		
Optimum pH	3	
Optimum dosage	[H <sub>2</sub> O <sub>2</sub> ] : 200 ppm, [Fe <sup>2+</sup> ] : 50 mg/L	
Treatment time,hr	3	8
% Compound	16.4	40.2*
COD reduction	12	21.4*

\*Optimum time and pH at optimum dosage of 200ppm (H<sub>2</sub>O<sub>2</sub>) and FeSO<sub>4</sub> for maximum *p*-anisaldehyde and dimethylsulfoxide degradation and COD removal of combined wastewater by Fenton oxidation process

bulk drug), respectively were used.

### Chemicals

Hydrogen peroxide 30% volume solution (Merck), and ferrous sulphate heptahydrate (FeSO<sub>4</sub>·2H<sub>2</sub>O) (Merck), were used in the experiments to generate hydroxyl radicals. Titanium dioxide particles of anatase form (Aldrich) used in this study were purchased from Aldrich. Its medium particle size was approximately 1µm, specific surface particle area 8.9 m<sup>2</sup>/g and zero point charge or pH at which the surface of an oxide is uncharged for TiO<sub>2</sub> is approximately 3.8. Other analytical reagents used in chemical oxidation demand estimation and buffer solutions of pH 4 and 7 were prepared by using double distilled water. The pH adjustment of effluents was made with 0.1M NaOH or 0.1 M H<sub>2</sub>SO<sub>4</sub> solutions accordingly for various photo oxidation processes for ascertaining the optimum pH for attaining maximum percentage compound degradation and COD reduction after treatment with AOPs.

### Experimental methodology

Oxidative degradation studies on laboratory scale batch mode were conducted in a 1000 mL cylindrical photochemical reactor (Heber-Chennai) made up of quartz having dimensions 30x3 cm (height x diameter) with water circulation arrangement to the jacket to ensure a constant temperature of 20-25°C inside the reactor. In each experiment, a 800 mL of the combined industrial wastewater sample of *p*-anisaldehyde and dimethylsulphoxide (1:10000 dilutions) was charged to the reactor (Figure 1). The solutions were subjected to irradiation time from 1 to 8 hr using a 16 W low pressure mercury arc lamp built into a lamp housing with polished anodized aluminum reflectors and placed 6.5 cm away from the reactor. The lamp emits predominantly UV radiation at a wavelength of 254 nm. The wastewaters were treated with varying H<sub>2</sub>O<sub>2</sub> concentration from 100 ppm to 1000 ppm for H<sub>2</sub>O<sub>2</sub>/UV oxidation process; Fentons reagent (H<sub>2</sub>O<sub>2</sub> concentration from 100 ppm to 250 ppm, Fe<sup>2+</sup> from 10 mg to 100 mg) for Fenton/UV oxidation process and TiO<sub>2</sub> dosage (from 100 mg to 400 mg) for TiO<sub>2</sub>/UV heterogeneous photo oxidation process. Wherever necessary, the pH of solutions was adjusted to optimum condition. The experiments were also conducted at different pH in the range of 3 to 6 for UV/Fenton oxidation process, 3 to 5 for UV/H<sub>2</sub>O<sub>2</sub> process, and 5 to 8 for UV/TiO<sub>2</sub> heterogeneous photo oxidation process for determining the optimum pH condition for achieving maximum percentage compound degradation and COD reduction. Selected samples (100 mL) of oxidized wastewater were treated biologically in 500 mL wide mouth round bottom flask, treated with 10 mL of mixed liquor suspended solid. The COD after every 8 hr of aeration and biological process was noted.

### Analysis

During the experiments, 10mL samples were withdrawn regularly after every 60 min of irradiation and treatment. The effect of H<sub>2</sub>O<sub>2</sub> dosages/UV irradiation, on the Fenton dosages/UV irradiation, TiO<sub>2</sub> dosages/UV irradiation, pH and irradiation time on the quantitative decrease in the concentration of *p*-

**Table 7.** Optimization studies of *p*-anisaldehyde and dimethylsulphoxide degradation in the combined wastewater at optimum  $[Fe^{2+}]$  and time by UV/Fenton oxidation process

Parameter	p-anisaldehyde and dimethylsulphoxide combined wastewater					
Initial concentration	1:10000 dilution					
Optimum pH	3					
	% COD reduction			% compound degradation		
Time (hr)	3	5	8	3	5	8
FeSO <sub>4</sub> dosages (mg/L)						
10	20	34.5	48	20	30.3	50
25	30	38	56	28	40.6	60
50	35	56	68	32	50.6	70
75	30	40.2	50	30.2	39.6	55
100	15	25.8	35	15.3	28	40

**Table 8.** Comparison of relative performance of AOPs for percentage degradation of compounds and COD reduction of combined wastewater

Parameter	Combined wastewater (1:10000 dilution)		
Concentration	Combined wastewater (1:10000 dilution)		
AOP treatment method	H <sub>2</sub> O <sub>2</sub> /UV	Fenton/UV	TiO <sub>2</sub> /UV
	H <sub>2</sub> O <sub>2</sub> 500 ppm	H <sub>2</sub> O <sub>2</sub> 200 ppm	TiO <sub>2</sub> : 250 mg/L
Optimum pH	7	3	7
Optimum irradiation time	8	8	8
% Compound degradation	70.2	70	80
% COD reduction	53.8	68	77

anisaldehyde and dimethylsulphoxide was evaluated by measuring the absorbance by using UV-visible spectrophotometer (ECIL,GS 5703 At,India). The COD reduction wastewater was observed by analyzing COD before and after the irradiation and treatment and at varying pH using Hach COD digester. The concentration of compound *p*-anisaldehyde and dimethylsulphoxide were measured at 215 nm before and after the treatment. The pH was measured using digital pH meter (MKVI, Systronics). Before analysis, a small quantity of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (Merck) was added to sample solution to destroy any residual H<sub>2</sub>O<sub>2</sub>. The samples of UV/TiO<sub>2</sub> treated samples were analyzed after separation (Remi Research R 24 centrifuge) of TiO<sub>2</sub> at 8000 RPM by a 0.2 μm (Mdi, India) nylon

66 membrane syringe filters.

#### GC analysis

The extent of decomposition of studied compounds in wastewater after treatment was determined by GC analysis using GC instrument (Shimadzu, model GC-17A with head space AOC-5000, auto injector and GC solution software version 2.10.00Su3).

#### RESULT AND DISCUSSION

##### Effect of H<sub>2</sub>O<sub>2</sub> concentration and UV irradiation time exposure

The optimized conditions were established for achieving higher degradation efficiency by varying different parameters, like initial concentrations of the compound, initial pH

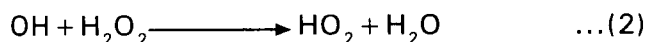
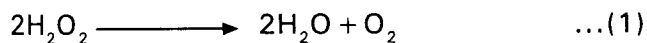
**Table 9.** Effect of optimum dosages of TiO<sub>2</sub> and irradiation time on percentage p-anisaldehyde and dimethylsulphoxide degradation and COD removal in combined wastewater (1: 10000 dilution)

Name of the compound	p-anisaldehyde and dimethylsulphoxide combined wastewater	
Initial concentration	1:10000 dilution	
Optimum pH	7	
Optimum dosage of TiO <sub>2</sub>	250 mg/L	
Irradiation time (hr)	3	8
% compound degradation	45	80*
% COD removal	32	77*

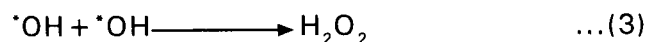
\*Optimum dosage of TiO<sub>2</sub> for maximum percent p-anisaldehyde and dimethylsulphoxide degradation in combined wastewater and COD reduction in wastewater by UV/TiO<sub>2</sub> oxidation process

of combined wastewater and irradiation time. The UV/H<sub>2</sub>O<sub>2</sub> treatment produced substantial decrease in the COD (53%) and degradation of compound (70%) at optimum irradiation time 8 hr and pH, at 500 ppm of H<sub>2</sub>O<sub>2</sub> dosage (Table 2, Figures 2 and 3). When the H<sub>2</sub>O<sub>2</sub> dosages were increased to 1000 ppm, there was a decrease in compound degradation efficiency from 70% to 50% and COD reduction from 53% to 40% (Table 2, Figures 2 and 3).

This was attributed to the reaction of excess quantity of H<sub>2</sub>O<sub>2</sub> with the <sup>•</sup>OH radicals to produce perhydroxyl radical HO<sub>2</sub><sup>•</sup> which has low oxidation potential than <sup>•</sup>OH radicals (equation 1 and 2) :



In addition, <sup>•</sup>OH radicals generated at high local concentration would readily dimerise to H<sub>2</sub>O<sub>2</sub> (equation 3) :



Thus, if H<sub>2</sub>O<sub>2</sub> dosage is increased above the limiting value of 500 ppm, competition for <sup>•</sup>OH radicals could be anticipated.

### Effect of Fe<sup>+2</sup> and H<sub>2</sub>O<sub>2</sub> dosages in Fenton oxidation process

At optimum 50 mg/L Fe<sup>+2</sup> dosage, the percentage compound degradation was 45% and COD reduction was 21%. Above 50 mg/L of FeSO<sub>4</sub> dosage, a decrease in degradation efficiency was observed (Table 3, Figures 4 and 5). The H<sub>2</sub>O<sub>2</sub> concentration of 200 ppm was effective degrading 43.5% compound and 43.5% COD reduction after 8 hr of irradiation at optimum pH of 3. (Table 4, Figures 6 and 7). Hydrogen peroxide is considered the limiting reagent in UV/Fenton process. At a higher concentrations (more than 200 ppm H<sub>2</sub>O<sub>2</sub>) led to saturation in the compound removal rate. It suggests that the compound degradation rate becomes insensitive to H<sub>2</sub>O<sub>2</sub> concentration due to <sup>•</sup>OH radical decay.

### Effect of pH in Fenton chemical oxidation process and UV/Fenton advanced oxidation processes

At optimum Fenton dosages in Fenton reaction, 21.4% COD reduction and 40.2% compound degradation was observed (Table 6). At optimum condition, about 89% compound degradation and 70% COD reduction (Table 5) was observed at optimum pH of 3 by UV/Fenton oxidation process. The concentration of Fe<sup>2+</sup> in solution in relation to pH at 25°C was studied by some authors. It was observed that the solubility of Fe<sup>2+</sup> is very high for a pH lower than 2 and too small for a pH higher than 3.2. Therefore, in Fenton conditions (pH 2.4 to 3.2), the Fe<sup>2+</sup> would be in solution, if pH is maintained around 3.0. However, at higher pH, ferric ions would begin to precipitate as hydroxide and retard the degradation rate. These results are in line with the results reported by Miguel Rodriguez (2003) for the studies on Fenton/UV based oxidation processes for the treatment of nitroamines, phenols and chlorinated ethers in wastewater treatment. It has been also reported that for pH values above 4, the degradation efficiency strongly

**Table 10.** Optimization studies of *p*-anisaldehyde and dimethylsulphoxide degradation in the combined wastewater at optimum  $TiO_2$  dosages and varying pH and time by UV/ $TiO_2$  oxidation process

Parameter	p-anisaldehyde & dimethylsulphoxide combined wastewater					
Initial concentration	1:10000 dilution					
Optimum $TiO_2$ dosages (mg/L)	250					
	% COD reduction			% compound degradation		
Time (hr)	3	5	8	3	5	8
pH						
5	21	25	50	32	62	70
6	25	42	60	38	67	75
7	31.2	56.4	76.4	60	76.4	98.5
8	22	42	60	40.2	60.8	78

**Table 11.** Details of GC headspace chromatograms for *p*-anisaldehyde and dimethylsulphoxide in the combined wastewater

Chromatograph figure no.	Description of GC chromatograms of 2-aminothiophenol wastewater treated with advanced oxidation processes						
	Concentration	Peak at retention time in min	AOP treatment method	Optimum Dosages	pH	Irradiation time, hr	
12	1:10000 dilutions	13.589	5.830	—	—	—	
13	1:10000 dilutions	Absent	5.760	UV/ $H_2O_2$	500 ppm $H_2O_2$	7	3
14	1:10000 dilutions	Absent	Absent	UV/Fenton	50 mg/L $FeSO_4$ 200 ppm $H_2O_2$	3	3
15	1:10000 dilutions	Absent	Absent	UV/Fenton	50 mg/L $FeSO_4$ 200 ppm $H_2O_2$	3	5
16	1:10000 dilutions	Absent	5.684	UV/ $TiO_2$	$TiO_2$ 250 mg/L	7	3
17	1:10000 dilutions	Absent	Absent	UV/ $TiO_2$	$TiO_2$ 250 mg/L	7	5

decreases since iron precipitates as hydroxide derivative, reducing the  $Fe^{2+}$  availability and the oxidation transmission (Karpel *et al.*, 1997; Alton *et al.*, 2002).

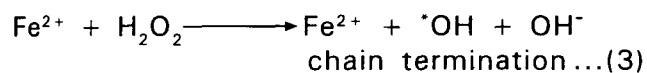
#### Effect of $Fe^{+2}$ and $H_2O_2$ dosages in UV/Fenton advanced oxidation process

The key features of the Fenton reaction are believed to be its reagent conditions, that is  $Fe^{+2}$  and  $H_2O_2$  concentration, and the re-

action characteristics (pH and the quantity of organic contaminants). At 50 mg/L Fenton dosage, 70% compound degradation and 68% COD reduction was effected at optimized conditions (irradiation time 8 hr and pH 3) (Table 7, Figures 8 and 9).

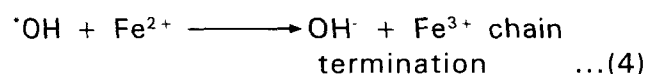
At 200 ppm  $H_2O_2$  dosage, 70% compound degradation and 68% COD reduction was observed at optimized condition (Table 8). The figures 8 and 9 have established the

stoichiometric relationship between  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$  and organic contaminant (p-anisaldehyde and dimethylsulphoxide) to maximize the efficiency of degradation process. A high ratio of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentration was needed for chain initiation (Regg *et al.*, 1954) (equation 3)



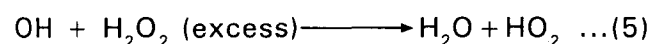
$$k_1 \simeq 70 \text{ m}^{-1} \text{ S}^{-1}$$

At low  $\text{H}_2\text{O}_2$  concentration, the radical chain reactions are quickly terminated. This is due to the reason that the  $\cdot\text{OH}$  radicals produced mainly react with the ferrous ions & not with hydrogen peroxide (Buxton and Greenstock, 1998) (equation 4) :



$$k_2 \simeq 3.2 \times 10^8 \text{ m}^{-1} \text{ S}^{-1}$$

Whereas excess of  $\text{H}_2\text{O}_2$  concentration reacts with  $\cdot\text{OH}$  competing with organic contaminants and consequently reducing the efficiency of the treatment (equation 5) due to production of perhydroxyl radicals  $\text{HO}_2^{\cdot}$  which has less oxidation potential :



### Effect of $\text{TiO}_2$ dosages

The experiment results revealed that 80% compound degradation and 77% COD reduction was effected with 250 mg/L of catalyst  $\text{TiO}_2$  at optimized conditions (pH7, irradiation time 8 hr). The degradation rate decreased beyond 250 mg/L  $\text{TiO}_2$  dosage. (Table 9, Figures 10 and 11). This may be due to the aggregation of  $\text{TiO}_2$  particles at high concentration, causing a decrease in the number of surface active sites. Several authors relate this to the light scattering and consequent reduction in light penetration through the solution induced by light proof suspended catalyst. The optimal catalyst  $\text{TiO}_2$  concentration that ensures a total adsorption of efficient photons range from 0.1 to 5.08 g/L (Androcuzzi *et al.*, 1989; Bauer *et al.*, 1999; Yue and Legrini, 1992).

### Effect of pH in UV/ $\text{TiO}_2$ process

From table 10, it is evident that the zero point charge or pH at which the surface of an oxide is uncharged for  $\text{TiO}_2$  is around 7; where maximum compound degradation (98%) and COD reduction (76.4%) was effected. This could be explained by the fact that the pH of aqueous solutions significantly affects the particle size, the surface charge and the band edge positions of the  $\text{TiO}_2$  due to its amphoteric character (Beltran-Heredia *et al.*, 2001).

### G.C. evaluation of effectiveness of AOPs

The G.C. chromatograms suggested that UV/Fenton process was effective in the degradation of compounds as well as other volatile organics in wastewater (Table 11, Figures 12,13, 14, 15). From the GC headspace chromatograms (Figure 12), it was evident from the presence of other peaks that there are volatile organics other than p-anisaldehyde and dimethylsulphoxide. These other volatile organics also got degraded by UV/ $\text{H}_2\text{O}_2$ , UV/Fenton and UV/ $\text{TiO}_2$  advanced oxidation processes at the end of 5 hr, which was evident from the reduction of number of peaks in chromatograms nos. 13, 14 and 15. Similarly, the degradation of p-anisaldehyde and dimethylsulphoxide was 100% at the end of 5 hr of irradiation time for UV/ $\text{H}_2\text{O}_2$ , UV/Fenton and UV/ $\text{TiO}_2$  processes.

### Effects of biological pretreatment of oxidized wastewater

The biological pretreatment of oxidized wastewater samples produced a marked increase in biodegradability. The BOD/COD ratio was found to be between 0.6 to 0.7. This was then subjected to biological treatment. The MLSS was found to be 3500 mg/L when the photo Fenton oxidized wastewater was treated biologically. Figure 16 indicates a proposed process flow diagram for combined UV/Fenton and biological treatment process.

### CONCLUSION

The degradation process by  $\text{H}_2\text{O}_2$  only or

Fenton only is less effective since only about 50% compound degradation and 35% COD reduction was effected after 8 hr of treatment. With UV/H<sub>2</sub>O<sub>2</sub> oxidation process, 70% compound degradation and 50% COD reduction was observed of 500 ppm H<sub>2</sub>O<sub>2</sub> dosage at optimized conditions. Whereas UV/Fenton oxidation process resulted a degradation of 70% compound and 76% COD reduction at optimum pH 3 after 8 hr of treatment. A dose of 250 mg of TiO<sub>2</sub> degraded about 98% compound and 76% COD reduction at optimized conditions of pH 7 and 8 hr of treatment by UV/TiO<sub>2</sub> heterogenous photo oxidation process. Moreover, all the above processes resulted in the degradation of other volatile organics to the extent of about 99%. The photo degradation rate of the studied refractory toxic organics is affected by pH, Fenton dosages and irradiation time. Therefore, UV/Fenton oxidation process was found to be cost effective treatment as pre-treatment method for the treatment of selected compounds in wastewater produced by bulk drugs manufacturing processes. The treatability of oxidized effluent improved to 0.6 to 0.7 post UV/Fenton treatment. Therefore, UV/Fenton oxidation process coupled with the biological treatment process is most suitable and cost effective for the treatment of the industrial wastewater intended for reuse. The pH of solutions and irradiation time also effect the extent of degradation in all these systems of the optimum conditions.

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