

Statistical analysis of the effect of aromatic, azo and sulphonic acid groups on decolouration of acid dye effluents using advanced oxidation processes

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Abstract

In the present study, the effect of advanced oxidation processes such as ozone/UV, ozone/H₂O₂ and ozone/UV/H₂O₂ on decolouration of Acid Red 88, Acid Orange 7, Acid Orange 10 and Acid Red 73 dye effluents in the presence of sodium sulphate salt were considered. Studies were carried out to analyse and compare the effect of aromatic, azo and sulphonic acid groups on decolouration of acid dye effluents. Among the advanced oxidation processes, ozone/UV/H₂O₂ treatment is more efficient for decolouration than other treatments in all the dye effluents except in Acid Red 88, where ozone/UV treatment shows better decolouration than the other processes. Acid dyes possessing only naphthalene rings in its structure undergo faster decolouration than the dyes with the combination of benzene and naphthalene rings. Among the dyes studied, those with higher number of sulphonic acid groups in its structure are easier to decolour. But on increasing the azo groups in its structure, increasing decolouration time was observed. It was also found that acidic pH and lower salt concentration in the effluents are more efficient for decolouration in all the treatment processes.

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Keywords: Advanced oxidation process; Acid dyes; Colour removal; COD removal; Design experiment

1. Introduction

Ozone is a powerful oxidizing agent which on dissolution in an aqueous medium can react with a variety of organic molecules to cause partial oxidation or complete mineralisation, i.e. degradation to CO₂ and water. The activation of ozone to create even more powerful oxidizing hydroxyl (OH[•]) radicals gives an added dimension to ozone-based effluent treatment. The production of radicals from ozone, commonly by the use of initiators such as photon energy from ultraviolet light (UV) at a wavelength of 253.7 nm or by hydrogen peroxide (H₂O₂), is widely known as advanced oxidation

process [1]. Hydrogen peroxide and UV radiation are used to induce decomposition of ozone in water, generating highly reactive hydroxyl radicals. These hydroxyl radicals having a redox potential of 2.8 V are sufficiently reactive to permit the complete oxidation of organic molecules with relatively short contact time [2].

Many studies were carried out on different types of wastewater using advanced oxidation processes [3–7]. The outcome of these studies is that in most of the wastewater treatments, advanced oxidation processes are reported to be better than ozonation and in the rest it is otherwise. Among the different advanced oxidation processes reported, the efficiency of a particular process depends on the initiator used along with ozone.

In the present investigation, the effect of advanced oxidation processes such as ozone/UV, ozone/H₂O₂ and ozone/UV/H₂O₂ on decolouration of Acid Red 88, Acid

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Orange 7, Acid Orange 10 and Acid Red 73 dye effluents were carried out in the presence of sodium sulphate salt. These studies were conducted with a view to analyse and to compare the effect of aromatic, azo and sulphonic acid groups on decolouration of acid dye effluents using Box and Hunter central composite design experiments. Ozone/UV process was carried out with acid dye effluents prepared from dyes namely Acid Red 88, Acid Orange 7, Acid Orange 10, and Acid Red 73 and ozone/ H_2O_2 and ozone/UV/ H_2O_2 processes were carried out for all the above said acid dye effluents except Acid Red 73.

2. Materials and methods

2.1. Materials

Acid dye possessing mono and diazo groups (Atul Ltd., India) are used for the experiments. The properties and chemical structures of the dyes are given in Table 1 and Fig. 1, respectively. The sodium sulphate salt used is of analytical grade (Qualigens fine chemicals, India).

2.2. Experimental set-up

The experimental set-up consisted of an oxygen concentrator (Sim O₂ plus, Italy), ozone generator (Ozonetek Ltd., India), ozonation chamber and ozone destructor (Ozonetek Ltd., India). A controlled flow rate of 2 l/min of oxygen was used to produce 2 g/h of ozone. The concentration of ozone was analysed using an ozone analyser (BMT 201, Berlin). The ozonation chamber consists of an 850 mm glass column with 50 mm inner diameter having a capacity to hold 1500 ml of effluent. It was provided with a sample port at various points, an ozone gas inlet at the bottom with a ceramic diffuser over the inlet port to diffuse the oxygen/ozone gas mixture through the column and a closed top with a collection port to collect the unreacted ozone gas for analysis and a thermal vent leading to the ozone destructor before venting it out. A PTFE tube was used for connecting the ozone outlet port from the ozone generator to the ozone reaction chamber. To conduct advanced oxidation experiments, an 8 W low-pressure mercury vapour UV light source housed inside a quartz

envelope was mounted co-axially in the center of the ozonation chamber. The intensity of the light source was determined using ferrioxalate actinometry procedure adopted from the work of Hatchard and Parker [8]. The intensity of the light source was found to be $5.7 \pm 0.1 \times 10^{19}$ quanta/s. The quantity of hydrogen peroxide used in each experiment was 0.5 ml/l of 30% w/v.

2.3. Experimental design

A class of five level central composite design for the estimation of parameters in a second order model was developed by Box–Hunter [9–11]. The experimental design in coded values and their actual values for the process variables used namely, salt concentration (X_1), pH (X_2) and treatment time (X_3) are given in Tables 2 and 3, respectively. The maximum time used for the treatment of effluents was selected to ensure complete decolouration of these treatments. The regression equations of the response, i.e. percentage of colour removal (Y) for the various dyes were calculated using a second order polynomial equation (1),

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

where Y is the predicted response, β_0 the constant, β_1 , β_2 , and β_3 the linear coefficients, β_{11} , β_{22} , and β_{33} the quadratic coefficients, β_{12} , β_{13} , and β_{23} the cross product coefficients.

To test the estimated regression equation for the goodness of fit, Fisher's F -test was employed and the multiple correlation coefficient R^2 was calculated. When the calculated R^2 value lies between 0.85 and 0.99, the fitted regression equation was considered to be a good fit of the model.

2.4. Parameters analysed

Five hundred millilitres of effluent having a concentration of 500 μM of dye was used. Effluent was subjected to decolouration in the ozonation chamber and it was determined through absorbance at maximum wavelength (λ_{max}) of the dye by using Hitachi UV–visible spectrophotometer (U-3210), Japan. The pH of the effluent was determined before and after treatment by using a pH meter (Systronics- μ pH system 361, India). Chemical oxygen demand (COD) was analysed by open reflux method using the standard method for wastewater analysis [12]. The COD reduction was determined only for the samples, which were treated with optimized conditions for complete colour removal.

Table 1
Properties of the dyes

S. no.	C.I. name	Molecular weight	λ_{max} (nm)	Chemical nature
1	Acid Red 88	400	505.2	Monoazo, monosulphonic
2	Acid Orange 7	350	485.6	Monoazo, monosulphonic
3	Acid Orange 10	452	479.2	Monoazo, disulphonic
4	Acid Red 73	556	509.6	Diazo, disulphonic

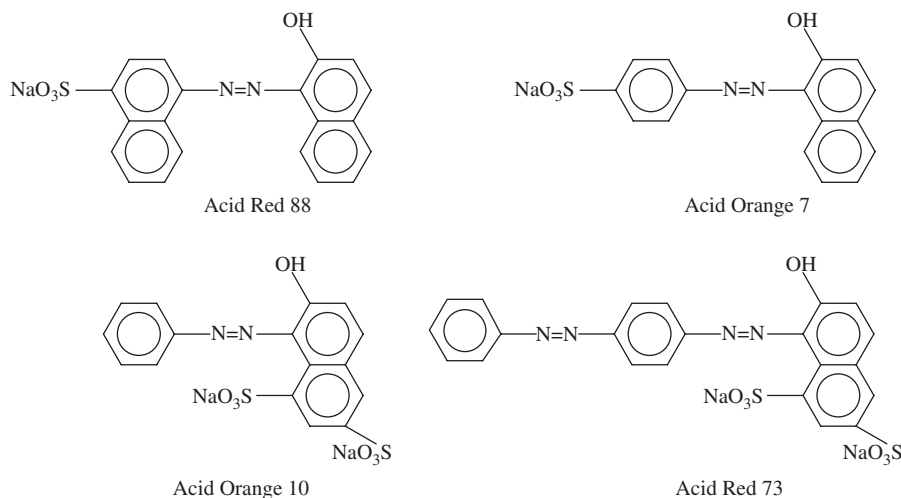


Fig. 1. Chemical structure of the dyes used.

3. Results and discussion

Response surface methodology is an empirical modeling technique, which is used to evaluate the relationship between a set of controllable experimental factors and observed results [13]. Several factors influence colour removal of acid dye effluents of which, salt concentration, pH and treatment time play a vital role. In order to study the effect of these variables central composite design was used. Treatments were carried out in triplicate based on the design experiment given in Table 2. The regression equations obtained using the analysis of variance that gives the level of

percent colour removal along with R^2 values are given in Table 4. The R^2 values of above 0.94 show that the regression equations are a good fit of the model. The time required for complete decolouration of the effluents was found out by determining X_3 from the regression equations by substituting $Y = 100\%$ for different values of X_1 and X_2 .

3.1. Decolouration of acid dye effluents

3.1.1. Effect of advanced oxidation processes on complete decolouration

Table 5 shows the time taken for complete decolouration of acid dye effluents using ozone/UV treatment. UV light acts by providing energy to disrupt chemical bonds, since the energy of UV light is of the same order as that of covalent bonds. When a chemical bond is cleaved by UV light, the remaining fragments are often more susceptible to ozone attack. Also, these fragmented by-products themselves can be reactive and degrade further. The mechanism involved in this process is ozone in gaseous phase enriched with water vapour undergoes photolysis to release an oxygen molecule and an atomic oxygen [14]. The latter may react with water to produce hydroxyl radicals.

Table 2
Experimental design in coded values

Expt. no.	Coded values of the variables		
	X_1	X_2	X_3
1	−1	−1	−1
2	+1	−1	−1
3	−1	+1	−1
4	+1	+1	−1
5	−1	−1	+1
6	+1	−1	+1
7	−1	+1	+1
8	+1	+1	+1
9	−1.682	0	0
10	+1.682	0	0
11	0	−1.682	0
12	0	+1.682	0
13	0	0	−1.682
14	0	0	+1.682
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

Table 3
Actual values of the variables for the coded values

Variables	Actual values for the coded values				
	−1.682	−1.000	0	+1.000	+1.682
Salt conc., g/l (X_1)	5	7	10	13	15
pH (X_2)	3	4.6	7	9.4	11
Time (s) (X_3)	30	97	195	293	360
Acid Red 88	30	133	285	437	540
Acid Orange 7	30	133	285	437	540
Acid Orange 10	30	133	285	437	540
Acid Red 73	30	170	375	580	720

Table 4

Regression equations obtained for percent colour removal from the acid dye effluents using advanced oxidation processes

Name of the dyes used	Regression equations	R ² value
<i>Ozone/UV process</i>		
Acid Red 88	$Y = 96.7795 - 0.7466X_1 - 0.0425X_2 + 21.1613X_3 - 0.6504X_1^2 - 0.0053X_2^2 - 14.2518X_3^2 + 0.3987X_1X_2 + 0.6037X_1X_3 + 0.1037X_2X_3$	0.98
Acid Orange 7	$Y = 95.0498 - 0.9529X_1 + 0.4003X_2 + 22.1254X_3 - 0.384X_1^2 + 0.8494X_2^2 + 0.3880X_1X_2 + 1.3855X_1X_3 - 0.9725X_2X_3$	0.98
Acid Orange 10	$Y = 94.2256 - 0.1638X_1 - 0.2357X_2 + 18.4318X_3 + 0.9458X_1^2 + 1.2060X_2^2 - 12.1375X_3^2 - 0.0851X_1X_2 + 0.4628X_1X_3 - 0.0298X_2X_3$	0.95
Acid Red 73	$Y = 90.1269 - 0.5754X_1 - 0.8764X_2 + 20.3682X_3 + 0.3815X_1^2 + 2.0852X_2^2 - 11.7388X_3^2 - 0.1525X_1X_2 + 0.55X_1X_3 + 0.6X_2X_3$	0.94
<i>Ozone/H₂O₂ process</i>		
Acid Red 88	$Y = 94.6916 - 0.3655X_1 - 0.8057X_2 + 22.2426X_3 - 0.5792X_1^2 - 0.0402X_2^2 - 14.1629X_3^2 + 0.1075X_1X_2 + 0.5X_1X_3 + 0.53X_2X_3$	0.98
Acid Orange 7	$Y = 93.4494 - 0.4878X_1 - 0.5275X_2 + 22.8257X_3 - 0.7166X_1^2 + 0.0824X_2^2 - 14.264X_3^2 - 0.0815X_1X_2 + 0.6627X_1X_3 + 0.1922X_2X_3$	0.98
Acid Orange 10	$Y = 92.4815 - 0.5590X_1 - 0.2647X_2 + 18.8132X_3 + 0.9245X_1^2 + 1.3540X_2^2 - 11.6911X_3^2 + 0.0885X_1X_2 - 0.1415X_1X_3 - 0.7702X_2X_3$	0.95
<i>Ozone/UV/H₂O₂ process</i>		
Acid Red 88	$Y = 96.7115 - 0.3859X_1 - 0.2146X_2 + 21.1996X_3 - 0.8292X_1^2 + 0.2205X_2^2 - 13.8155X_3^2 + 0.0175X_1X_2 + 0.7225X_1X_3 + 0.27X_2X_3$	0.98
Acid Orange 7	$Y = 95.2311 - 0.3742X_1 - 1.3986X_2 + 20.9837X_3 + 0.1887X_1^2 + 0.8969X_2^2 - 13.8159X_3^2 + 0.1661X_1X_2 + 0.3373X_1X_3 + 2.2138X_2X_3$	0.98
Acid Orange 10	$Y = 96.7273 - 0.6006X_1 - 0.2451X_2 + 17.7135X_3 + 0.5047X_1^2 + 0.4591X_2^2 - 12.3053X_3^2 - 0.1492X_1X_2 + 0.4680X_1X_3 + 0.5112X_2X_3$	0.95



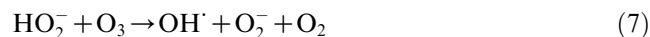
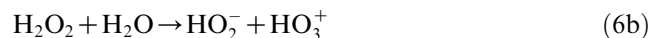
The direct production of H₂O₂ by the following reaction is also possible [15]



The hydrogen peroxide formed in this manner would undergo either (i) photolysis reaction with UV or (ii) decomposition reaction with ozone as shown below,



or



The rate of production of OH[•] from H₂O₂ through ozone decomposition reaction is greater than that of the photolysis reaction [16]. The decomposition of H₂O₂ increases with increase in pH. Decomposition initiated by hydroperoxide anion (HO₂[•]) is vastly superior to that of ozone decomposition initiated by hydroxide ion (OH[•]). The hydroxyl radicals are known to be the most powerful oxidizing agents to oxidize organic compounds and colour bearing compounds at a higher reaction rate than ozone itself.

There is also a possibility of the production of OH[•] during the ozone reaction with organic moieties in aqueous solution, which would further undergo ozone decomposition reactions as given in Eqs. (7)–(11) [17].

Table 6 shows the time taken for complete decolouration of acid dye effluents using ozone/H₂O₂ treatment. Hydrogen peroxide can decompose into the hydroxyl radical (OH[•]), and H₂O₂ can be thought of as a source of this highly reactive free radical. This conversion

Table 5
Time taken for 100% decolouration of acid dye effluents by ozone/UV treatment

Salt conc. (g/l)	Time (s)																			
	pH (Acid Red 88)					pH (Acid Orange 7)					pH (Acid Orange 10)					pH (Acid Red 73)				
	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11
5	214	216	218	218	216	297	316	328	326	308	279	303	313	304	281	385	460	516	473	408
7	209	212	213	213	212	299	316	324	319	302	294	322	336	326	299	396	481	520	501	423
10	209	211	212	212	211	308	322	326	319	300	302	334	352	341	311	404	497	556	535	438
13	215	217	218	217	216	321	334	336	325	304	294	323	336	328	304	402	489	535	528	442
15	223	225	226	225	223	335	347	348	334	311	280	304	316	310	290	396	475	520	509	438

occurs slowly under cold, dark conditions, but is facile in the presence of UV–vis light or at high temperatures. Free radicals, being oxidants, are capable of withdrawing atoms (often hydrogen) from a substrate, while turning the substrate into an unstable free radical. The resulting free radical based substrate is highly reactive, and may undergo internal reactions that form functionality on the substrate that is susceptible to attack by ozone. Consequently, the role of hydrogen peroxide in advanced oxidation processes is probably to make the pollutant more susceptible to ozone attack (major effect), and also to aid in the overall oxidation (minor effect). The mechanisms involved in ozone/H₂O₂ process are clearly discussed in Eqs. (6)–(11).

Table 7 shows the time taken for complete decolouration of acid dye effluents using ozone/UV/H₂O₂ treatment. Among the advanced oxidation processes, ozone/UV/H₂O₂ treatment was more efficient for decolouration than other treatments in all the dye effluents except in Acid Red 88. In case of Acid Red 88, ozone/UV treatment gives better results.

3.2. Effects of azo and sulphonic groups on complete decolouration

It was observed from the results given in Table 5 that the diazo dyes take longer time for complete decolouration than mono azo dyes at any given treatment condition. Shu and Huang [6] reported such behavior in the treatment of effluents containing the dyes such as Acid Black 1, Direct Yellow 4, Acid Red 1 and Acid Orange 10 using ozone. Muthukumar and Selvakumar

[18] also reported that increasing the azo groups in the dye structure increases the decolouration time. It can also be seen from Tables 5–7 that, under any given conditions, the time taken for decolouration is not the same for all the monoazo dyes chosen. This reveals that the decolouration depends not only on the azo groups but also on the other structural features present in the dyes. Acid Red 88 containing two naphthalene rings are decoloured faster than the Acid Orange 7 and Acid Orange 10 containing a benzene ring and a naphthalene ring. The reason for this trend is probably due to the higher rate constant of the reaction of ozone with naphthalene than that of benzene. This observation is further proved by the kinetics and mechanism of the reaction of ozone with aromatic compounds [19] and the susceptibility of electron rich naphthalene moieties to rapid attack by ozone [7]. Moreover it can also be seen from the results that the diazo dye with certain number of sulphonic acid groups take longer time for decolouration than mono azo dyes with the same number of sulphonic acid groups.

It was also observed from Tables 5–7 that the decolouration time for the monosulphonic dye is more when compared with those of dyes having higher number of sulphonic acid groups in all the processes except in ozone/H₂O₂ process. Hence, it can be said that the higher the number of sulphonic acid groups in the dye structure, the lower is the decolouration time. This is because of the increased solubility rendered by the higher number of sulphonic acid groups, which in turn results in better interaction between the dye molecules with either ozone or secondary free radicals produced

Table 6
Time taken for 100% decolouration of acid dye effluents by ozone/H₂O₂ treatment

Salt conc. (g/l)	Time (s)														
	pH (Acid Red 88)					pH (Acid Orange 7)					pH (Acid Orange 10)				
	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11
5	224	229	235	242	251	356	364	372	377	379	281	307	322	317	292
7	218	222	227	232	238	337	343	348	352	354	298	330	351	344	312
10	217	220	224	228	233	330	336	342	346	349	312	352	391	380	329
13	224	226	230	233	237	340	347	354	360	364	310	349	382	367	323
15	234	237	240	243	247	358	369	380	392	406	300	331	351	340	306

Table 7
Time taken for 100% decolouration of acid dye effluents by ozone/UV/H₂O₂ treatment

Salt conc. (g/l)	Time (s)														
	pH (Acid Red 88)					pH (Acid Orange 7)					pH (Acid Orange 10)				
	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11
5	219	224	226	226	224	270	299	316	320	312	281	290	293	290	281
7	210	214	216	216	214	277	305	322	324	315	292	302	306	303	294
10	207	210	212	212	210	284	312	327	327	317	300	313	318	316	306
13	213	217	219	219	216	288	315	328	327	316	298	311	318	317	309
15	224	229	230	230	227	289	314	327	325	313	291	304	311	312	305

from it. The results justify the belief that the rate of dye decomposition by advanced oxidation processes strongly depends upon the solubility of the dyes. Shu and Huang [6] reported such behavior in the treatment of effluents containing the dyes such as Acid Black 1, Direct Yellow 4, Acid Red 1 and Acid Orange 10 using ozone.

3.3. Effect of pH and salt concentration on complete decolouration time

The influence of pH is the result of the relationship between oxidation potential and decomposition behavior of ozone. In acidic pH, the ozone is available as molecular ozone and in alkaline pH it decomposes into secondary free radicals such as OH[•], HO₂[•], HO₃[•] and HO₄[•]. Among the radicals produced, OH[•] is important and has the highest oxidation potential of 2.8 V. Even though hydroxyl radical has a higher oxidation potential than ozone, its selectivity is very less [20]. The oxidizing potential of ozone decreases from 2.08 V in acidic pH to 1.4 V in alkaline solutions [21]. This indicates that as the ozone stability decreases with increasing pH it results in the generation of secondary free radicals.

It was observed from Tables 5–7 that the time taken for complete colour removal increases with increasing pH up to 7, beyond this level it decreases in all the cases. This clearly indicates that there are two different oxidizing mechanisms, i.e. in acidic pH molecular ozone remains as the main oxidant and at alkaline pH it decomposed to produce hydroxyl radical which acts as an oxidant. But in the case of ozone/H₂O₂ treatment, when the pH increases, the time taken for complete decolouration also increases. This may be due to the

hydroxyl ion, which reacts with ozone to form the hydroperoxide ion (HO₂[•]). It is the conjugate base of H₂O₂ and at a pH lower than 11.6 (which is the pK_a of H₂O₂) it will be predominantly converted to H₂O₂. Hence, the hydroxyl radicals catalyse the formation of hydrogen peroxide and the rate of decolouration reaction becomes slow in ozone/H₂O₂ treatments.

The overall observation made from this study on the effect of salt on complete decolouration time showed a mixed trend. In most of the cases, the effluent contains lower salt concentration and the treatment time required for complete decolouration is less irrespective of the treatment processes and pH used. The mechanism for the effect of salt concentration is not clear and has to be studied in detail.

3.4. Most suitable conditions for complete decolouration

It has been already seen that decolouration by advanced oxidation process is effective at higher levels of both acidic and alkaline conditions, whereas the decolouration time varies with the salt concentration. Hence, optimization of pH and salt concentration on decolouration are necessary for achieving maximum efficiency of the treatment processes. The most suitable conditions and the corresponding treatment time for complete colour removal, which are optimized from the results obtained from the regression equations are given in Table 8. From the table it is observed that for any given acid dye, the acidic pH with low salt concentration gives a better effect in most of the treatments except in ozone/H₂O₂ process where 10 g/l salt concentration gives a better result.

Table 8
Most suitable conditions for complete colour removal of acid dye effluents

Name of the dye used	Ozone/UV process			Ozone/H ₂ O ₂ process			Ozone/UV/H ₂ O ₂ process		
	Salt conc. (g/l)	pH	Time (s)	Salt conc. (g/l)	pH	Time (s)	Salt conc. (g/l)	pH	Time (s)
Acid Red 88	7	3	209	10	3	217	10	3	207
Acid Orange 7	5	3	297	10	3	330	5	3	270
Acid Orange 10	5	3	279	5	3	281	5	3	281
Acid Red 73	5	3	372	—	—	—	—	—	—

Table 9
Percent COD reduction of the most suitable conditions of advanced oxidation processes

Advanced oxidation process	% COD reduction			
	Acid Red 88	Acid Orange 7	Acid Orange 10	Acid Red 73
Ozone/UV	62	64	64	66
Ozone/H ₂ O ₂	60	67	29	—
Ozone/UV/H ₂ O ₂	65	63	42	—

3.5. Effect of advanced oxidation process on COD reduction

Table 9 shows the percent COD removal of acid dye effluents for the most suitable conditions as given in Table 8. In all the dye effluents, the reduction of COD shows that the advanced oxidation processes could eliminate the COD. The reduction of COD is due to the reduction of total organic carbon (TOC) and partial oxidation of organic substrates. Similar observations were made by Lopez et al. [22], who observed a reduction of COD in their study on ozone treatment of industrial textile effluents. Koynnchu and Afsar and Perkins et al. [23,24] also observed a similar trend in the treatment of reactive dye and acid dye effluents, respectively. The maximum removal of COD was obtained in Acid Orange 7 dye effluent by ozone/H₂O₂ treatment. The formation of by-products during the oxidation processes results in less reduction of COD in all the dye effluents studied.

4. Conclusions

Among the advanced oxidation processes, ozone/UV/H₂O₂ treatment is more efficient than other treatments in all the dye effluents except in Acid Red 88, where ozone/UV treatment gives a better result. Acid dyes possessing only naphthalene rings in its structure undergo faster decolouration than the dyes with the combination of benzene and naphthalene rings. Among the dyes studied, those having a higher number of sulphonic acid groups in their structure are easier to decolour. Increasing the azo group in its structure increases the decolouration time. It is also found that acidic pH and lower salt content in the effluents are more efficient for decolouration. The efficiency of advanced oxidation processes is slower at neutral pH for all the dyes studied and it is higher both at acidic and alkaline pH except in ozone/H₂O₂ process where increasing pH increases the complete decolouration time. The effect of salt concentration on complete decolouration time shows a mixed trend. The mechanism for the effect of salt concentration on decolouration is not clear and has to be studied in detail. Above

60% COD reduction is observed in all the dye effluents except in Acid Orange 10 where less than 45% COD reduction is observed in ozone/H₂O₂ and ozone/UV/H₂O₂ processes.

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