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Photocatalytic-Ozonation of Textile Dyeing Waste water using Fixed Catalyst System

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Abstract: Textile dyeing industries are one of the major polluting industries that generate highly coloured wastewater containing exhausted dyestuffs. These unfixed dyes are in general refractory in nature and difficult to treat effectively by the existing conventional methods. In the present work, decolourisation and degradation of six real textile dyeing wastewater were experimented using fixed catalyst mode Photocatalytic-Ozonation ($UV/TiO_2/O_3$) processes. The experiments were carried out in a reactor of 15 L capacity. All the wastewaters were highly coloured with Chemical Oxygen Demand (COD) ranging from 760 to 2080 mg/L and Total Organic Carbon (TOC) from 210 to 458 mg/L. The low biodegradability ratio indicated that the wastewater samples were less biodegradable. The coupled photocatalytic-ozonation yielded complete colour removal with 64 % COD removal after 30 minutes of treatment. It was also observed that the maximum oxidation and biodegradability improvement occurred in coupled photocatalytic-ozonation process. The reaction kinetics followed pseudo-first order. The immobilized catalyst system developed was found to be stable for 10 consecutive runs.

Keywords: Photocatalytic-Ozonation, AOP, fixed-catalyst, biodegradability.

I. INTRODUCTION

Textile industries consume large quantity of water and their effluents contain a wide range of Contaminants. Environmentally, these contaminants mean suspended solids, COD, BOD, as well as high pH and strong colour [1]. The removal of colour and organics from textile dyeing wastewater is one of the main problems of textile industry [2]. The colour and toxicity of dyes impart to water bodies are very undesirable and harmful to the water users for aesthetic and environmental reasons. The main sources of contamination in textile wastewater are the dyeing and finishing processes, because they require the addition of a wide variety of dyes and chemical compounds which are generally organic and have a complex structure [3]. Hence these mills are mandated to provide zero liquid discharge (ZLD) treatment systems by the regulatory authorities. The conventional physico-chemical method results in the transfer of pollutant from one phase to another phase while biological treatment alone is not sufficient in degrading the organic matter in wastewater [4, 5, 6]. Since the conventional treatment methods have lot of limitations, these units are in need of an environmentally friendly and cleaner wastewater treatment technology.

The advanced oxidation processes (AOPs), are currently considered to be a potential treatment method for the removal of colour which are characterized by production of the hydroxyl radical ($OH^{\cdot}$) as a primary oxidant. Hydroxyl radicals are highly reactive electrophiles (electron seeking) effective in destroying organic chemicals rapidly and non-selectively with nearly all electron-rich organic compounds [7]. Ozonation is well established technology used to decolourise the dyes effectively. The hydroxyl radical is a powerful and non-selective oxidant that can react through the possible mechanisms like hydrogen abstraction and electron transfer or radical addition [8].

It has also been demonstrated that textile biocides being frequently used in the fabric finishing process and known for their recalcitrance and toxicity, can be effectively degraded and detoxified, accompanied with partial oxidation (COD removal) and mineralization (TOC removal), using AOPs and ozone. The presence of UV and TiO_2 can accelerate the formation of hydroxyl radical through decomposition of Ozone [9]. In the last decade most attention has been given to TiO_2 due to its low cost, high photocatalytic activity and non-toxicity [10].

Heterogeneous photocatalytic oxidation can produce synergistic effect that can significantly reduce reaction time. But most of the lab scale studies were conducted with simulated dyeing wastewater. The real textile dyeing wastewater differs significantly from that of the simulated wastewaters as it contains mixture of dyes in addition to the salts.

In this work photocatalytic-ozonation process was employed to treat the real textile dyeing wastewater containing reactive dyes in bench-scale level. Most of the studies were conducted in slurry mode only, wherein the recovery and reuse of catalyst is difficult.

The experiments reported in [11] and [12] reveal that stainless steel could be a stable substrate for TiO_2 coating. Hence in this study the effect of photocatalyst coated on stainless steel sheet was investigated for the coupled photocatalytic-ozonation process.

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II. MATERIALS AND METHODS

A. Experiment

The real textile dyeing wastewater samples (IWW1-IWW6) were obtained as required from the study unit which is a textile dyeing industry located in Erode district of Tamilnadu. Commercially available nano Titanium dioxide (TiO_2) powder (Particle size-68 nm and surface area-20 m^2/g) was procured from Tianan Chemicals, China. The bench-scale set-up consisted of ozone generator (Faraday Ozone L20 G, supplied by M/s Faraday Ozone Ltd.) which was fed with liquid oxygen and an immersion type reactor of volume 15 L. The reactor was made of acrylic material with 20 cm diameter and 60 cm height and an UV lamp (40 W, 254 nm) immersed at the centre of the reactor using Quartz tube. An ozone trap which was a bubble column setup containing potassium iodide solution was connected at the top of the reactor to collect all the remaining ozone gas exiting from the reactor. The TiO_2 catalyst was coated on a flexible stainless steel sheet of size 60 x 60 cm and inserted into the reactor. The experiments were conducted with an optimized ozone dose of 8.85g/h for a period of 30 minutes in the bench-scale reactor and the experiment was repeated 10 times for the same effluent using the same coated plate. The influence of inorganic ion concentration was examined using Glauber's salt (decahydrate sodium sulfate) and soda ash (sodium carbonate) since they are widely used in textile dyeing processes.

B. Catalyst Coating

The viscous mixture of TiO_2 was prepared using 20 g of TiO_2 powder and 10% PVA (Poly Vinyl Alcohol) solution. This mixture was then sprayed over the acid-cleaned stainless steel sheet using a spray gun and dried in hot-air oven at 300°C for 3 hours. The dry film thinckness was measured using Elecoat 6103 instrument and it was found to be 2 mm. The catalyst coated stainless steel sheet was introduced into the reactor in such a way that it fits the cylindrical shape of the reactor.

C. Analysis

The samples were analysed as per the standard methods [13]. Digital pH meter was used to measure the pH for raw wastewater sample. The chemical oxygen demand was calculated by open reflux method using COD digester. The TOC analysis was carried out using TOC analyzer micro N/C model 1997 manufactured by Analytica Jena (Germany). The absorbance spectra of the sample were recorded using CHEMLINE CL-310 spectrophotometer; recording the absorption coefficient at 436, 525 and 620 nm for each wastewater samples. Percentage of colour/COD removal was calculated using Equation 1.

$$\eta = ((A_o - A_1)/A_o) \times 100 \qquad (1)$$

where, A_o= Absorbance/COD of sample before treatment
A_1 = Absorbance/COD of sample after treatment

The rate constant derived from the pseudo first-order kinetics for decolourisation (Equation 2) and degradation (Equation 3) of textile dyeing wastewaters was used to compare the effect of AOPs viz., Ozonation, UV/O_3, $UVTiO_2$, and $UV/TiO_2/O_3$ process.

$$\ln(A/A_0) = -k_1 t \qquad (2)$$
$$\ln(C/C_0) = -k_2 t \qquad (3)$$

where k_1 and k_2 are decolourisation and degradation kinetic rate constants ($min.^{-1}$) respectively, A_0 is the initial absorbance coefficient, A is the absorbance coefficient at time t, C_0 is the initial COD (mg/L), C is the COD at time t (mg/L) and t is the contact time (minutes).

III. METHODOLOGY

The real textile dyeing wastewaters obtained from the study unit were characterized and all the experiments were carried at room temperature. The coupled $UV/TiO_2/O_3$processes were adopted for treatment of wastewater samples. The working volume of reactor and contact time were maintained at 15 L and 30 minutes, respectively. For the optimization studies Ozone dosage of 8.85 g/h and TiO2 concentration of 5 mg/cm^2 were maintained. Treated samples were taken for analysis of colour and organics. The TiO_2 coat was reused without any modification and all experiments were conducted at the actual pH of the dyeing wastewater which was around pH 10.

IV. RESULTS AND DISCUSSIONS

All experiments were carried out at actual pH of wastewater. The initial characteristics of IWWs are presented in Table I. The samples were of various colour with absorbance values ranging between 64.3 and 92.2 m^{-1} at 436 nm, 13.5 and 98.1 m^{-1} at 525 nm and 3.6 and 38.6 m^{-1} at 620 nm respectively. The COD was in the range between 760 and 2080 mg/L and TOC between 210 and 458 mg/L.

Table I Characteristics of Simulated textile Dyeing Wastewaters (n=3)

PARAMETER		**IWW 1**	**IWW 2**	**IWW 3**	**IWW 4**	**IWW 5**	**IWW 6**
Colour		Mustard Yellow	Burgundy Red	Charcoal	Rosrod	Elephant	Hot coral
Colour Absorbance (m^{-1})	**436 nm**	64.3	82.6	67.3	92.2	75.2	82.5
	525 nm	13.5	71.6	35.5	98.1	41.5	43.1
	620 nm	3.6	9.5	28.4	12.3	38.6	22.2
pH		10.4	10.4	10.7	10.5	10.4	10.3

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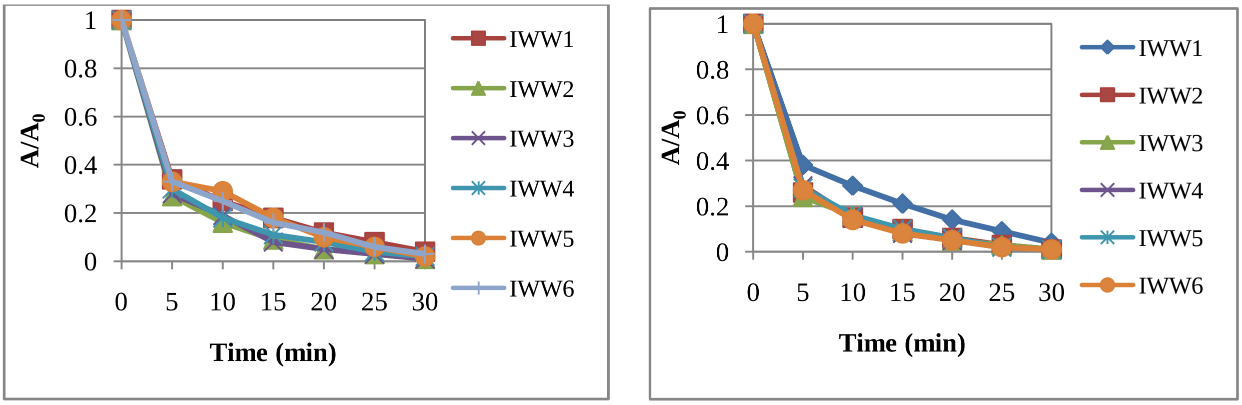
BOD_3 (mg/L)	130	102	98	154	100	130
COD (mg/L)	1520	1040	760	2080	960	1880
BOD_3/COD	0.08	0.09	0.13	0.07	0.10	0.07
TOC (mg/L)	402	289	210	458	265	411
TDS (mg/L)	6990	6700	6200	7360	6760	6280
TSS (mg/L)	110	150	205	135	168	189
Sulphate (mg/L)	2250	2300	2450	2300	2300	2350

BOD_3 of the wastewaters was varying from 98 to 130 mg/L and their biodegradability i.e., BOD_3/COD was between 0.07 and 0.13. The TDS of the samples were high ranging from 6200 to 7360 mg/L due to the addition of salt in dyeing process. The addition of Glauber's salt in dyeing, contributed to sulphate whose concentration was ranging from 2250 to 2450 mg/L. The IWWs were highly alkaline with pH value greater than 10.

A. Effect of Photocatalytic-ozonation

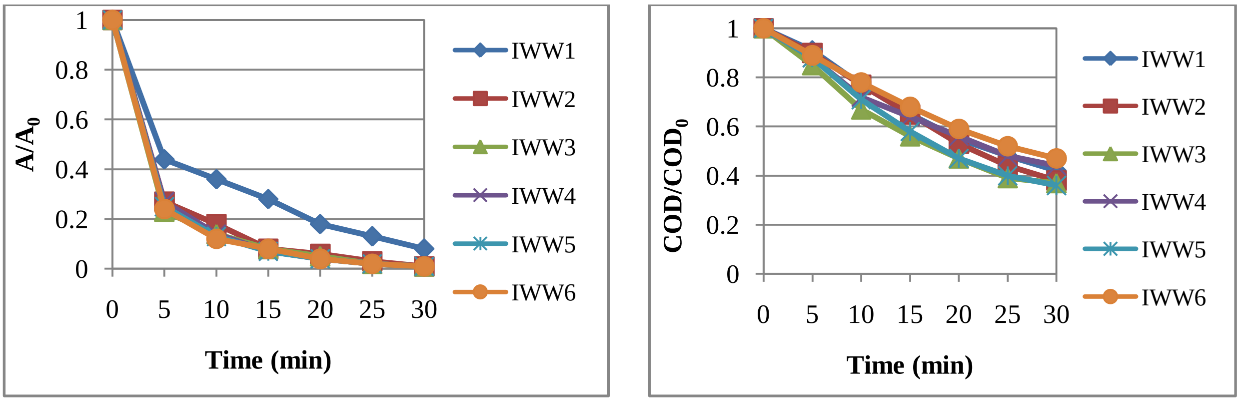
The photocatalytic-ozonation batch experiments were conducted with immobilized TiO_2 catalyst and an optimum ozone dose of 8.85 g/h. The decolourisation and degradation pattern are illustrated in Figure 1. Complete decolourisation was observed in all the samples after 30 minutes of treatment with nearly 60 % colour removal within first5minutes of the experiments. The rapid decolourisation is due to the oxidative attack on the chromophoric group in dyes. Although colour removal was high, the degradation rate measured in terms of COD removal indicated that the intermediate compounds formed during the experiment were still contributing to organics. COD removal a maximum of 64 % obtained after 30 minutes treatment. It can be noted from the pseudo-first order kinetic constants presented in Table II that colour removal was significantly faster than the CODremoval. The fastest kinetics was observed in sample viz., IWW3 with decolourisation rate constants of 0.1523, 0.1527 and 0.1586 min^{-1} at 436, 525 and 620 nm, respectively and degradation constant of 0.036 min^{-1}.

The recombination of electrons formed on TiO_2 surface with positive holes is reduced in the coupled photocatalytic-ozonation process as the dissolved ozone can easily accept electrons [14]. Although the pH of wastewaters were alkaline the performance of photocatalytic-ozonation was high which can be attributed to the increase in the concentration of hydroxyl radical in alkaline pH [15]. In the combined process the hydroxyl radical and hydrogen peroxide are produced through more than one parallel pathway [16]. The control experiments were conducted in the presence and absence of catalyst and ozone. The dark adsorption observed to be inefficient while the UV/TiO_2 process in the absence of ozone was slow and yielded less than 20 % colour and COD removal akin to that reported in [17]. The Ozonation yielded almost complete colour removal both in the presence and absence UV irradiation. Nevertheless, the COD removal was less than 50 % after the same 30 minutes of treatment.The increased performance could also be attributed to the production of more hydroxyl radical when ozone coupled with UV wherein one molecule of ozone would give rise to two molecules of hydroxyl radical [18]. Further, the presence of UV in Ozonation process can also enhance the degradation of intermediates that resist oxidation by ozone [19]. Since ozone absorbs radiation at 260 nm strongly the integration of UV-C in an ozonation system significantly increases the degradation of organic pollutants in it [20].



(a)

(b)



(c) (d)

Figure 1 Decolourisation and Degradation by Photocatalytic-ozonation (a) Colour removal at 436 nm (b) Colour removal at 525 nm (c) Colour removal at 620 nm and (d) COD removal

Table II Kinetic Constants

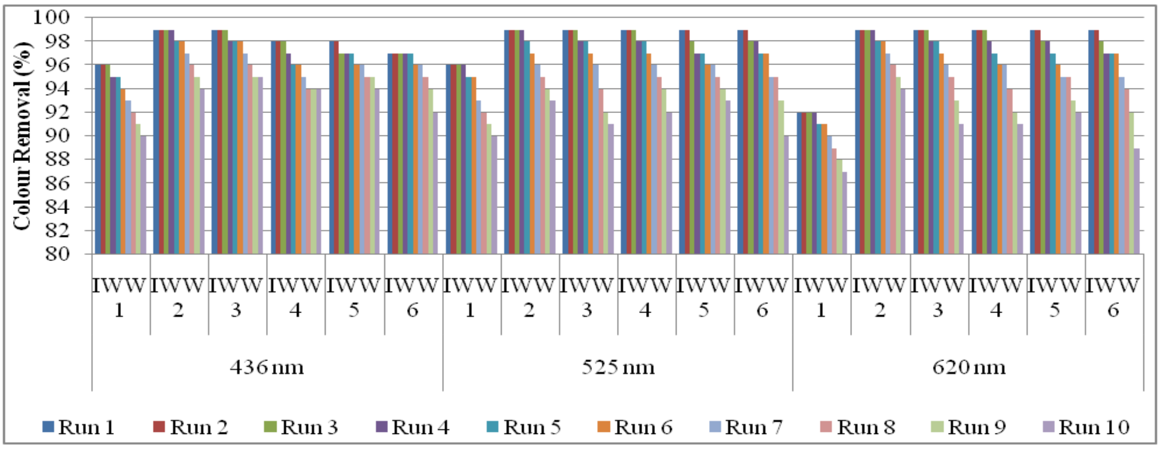
Sample	Colour Removal (k, min^{-1})			COD Removal (k, min^{-1})
	436 nm	525 nm	620 nm	
IWW1	0.1086	0.1040	0.0855	0.029
IWW2	0.1524	0.1505	0.1511	0.032
IWW3	0.1523	0.1527	0.1586	0.036
IWW4	0.1339	0.1578	0.1611	0.029
IWW5	0.1219	0.1545	0.1616	0.036
IWW6	0.1164	0.1582	0.1608	0.026

B. Effect of Catalyst Reuse

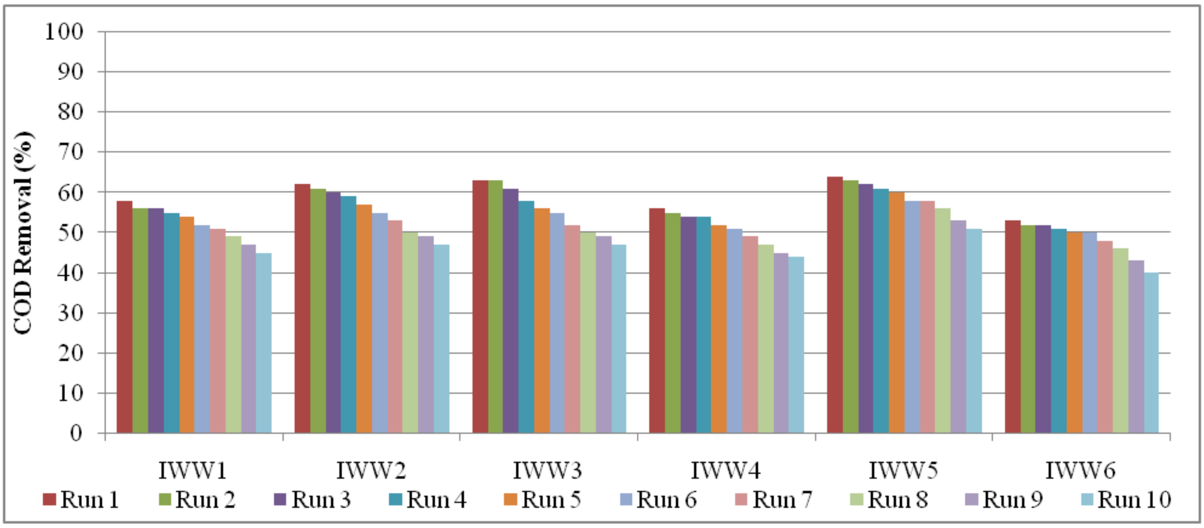
In order to study the reusability of catalyst the photocatalytic-ozonation experiments were carried with the immobilized catalyst without any modification continuously for 10 runs. It could be deciphered from the results depicted in Figure 2 that the decolourisation and degradation efficiency decreased with reuse of catalyst. However, colour and COD removal of about 90 and 50 %, respectively were observed upto 8 runs which plummeted to 86 and 40 %, respectively after 10th run. The catalyst immobilization was stable even after 10 runs but the decrease in process efficiency could be due to the poisoning of catalyst surface by the intermediate dye compounds. The disintegration of catalyst coat caused by the movement of liquid inside the reactor was visible after 10th run. The decrease in photocatalytic-ozonation efficiency with catalyst reuse is also reported elsewhere [21].

C. Effect on TOC and Biodegradability

The effect of fixed catalyst on TOC and biodegradability ratio is illustrated in Figure 3. The mineralization was low compared to COD removal as less than 20 % TOC removal only was observed in all samples. However, the increase in biodegradability measured in terms of BOD_3/COD value was significant with maximum increase observed in sample viz., IWW3. Addition of Ozone reportedly enhances the biodegradability of wastewater containing organic pollutants [22, 23]. Although the TOC removal and improvement in biodegradability decreased with increase in catalyst reuse, the difference in process efficiency was less significant.

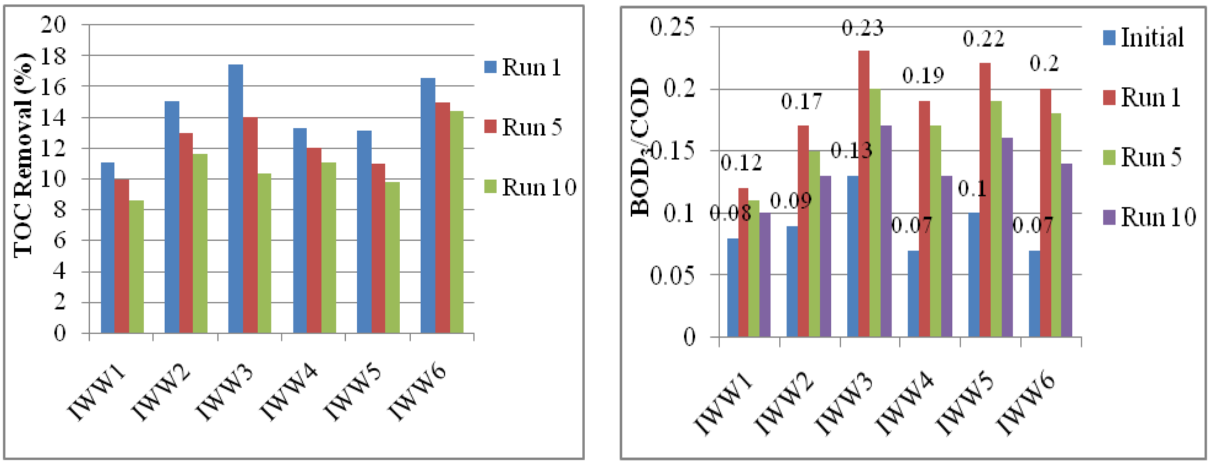


(a)



(b)

Figure 2 Effect of Catalyst Reuse in (a) Decolourisation and (b) Degradation



(a) (b)

Figure 3Effects of Fixed Catalyst on (a) TOC and (b) biodegradability

D. Effect of Inorganic Salts

In order to study the influence of inorganic ion concentration in decolourisation and degradation of textile dyeing wastewater, sample viz., IWW3 was simulated and the experiment was carried by varying the concentrations of Glauber's salt and soda ash from 20 – 80 g/L and 5 – 20 g/L, respectively. The results are presented in Tables III and IV. The maximum COD removal of 66% was obtained at a salt and soda concentration of 40 g/L and 10 g/L, respectively. The efficiency of the coupled process decreased with the increase in salt and soda concentration due to the scavenging of hydroxyl radical at higher salt concentration [24]. It is also reported that the presence of sodium sulphate can enhance the process efficiency through formation of sulphate radical at alkaline pH [25].

Table III Effect of Salt Concentration in Photocatalytic-Ozonation

Time (minutes)	Color Removal (%) at Soda = 10 g/L												COD Removal (%)			
	Salt=20 g/L			Salt=40 g/L			Salt=60 g/L			Salt = 80 g/L			Salt 20 g/L	Salt 40 g/L	Salt 60 g/L	Salt 80 g/L
	436 nm	525 nm	620 nm	436 nm	525 nm	620 nm	436 nm	525 nm	620 nm	436 nm	525 nm	620 nm				
5	53	46	50	63	56	53	66	58	56	65	54	50	5	8	6	4
10	70	66	78	78	68	63	79	73	76	80	70	68	18	16	13	10
15	83	78	82	85	73	75	88	88	89	92	85	79	27	31	24	21
20	92	89	91	92	85	87	93	94	93	94	92	86	39	43	36	33
25	94	94	95	95	95	96	95	96	96	96	96	94	51	54	49	44
30	98	97	98	97	99	99	99	99	99	99	98	95	63	66	61	57

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Table IV Effect of Soda Concentration in Photocatalytic-Ozonation

Time (minutes)	Color Removal (%) at Salt = 40 g/L												COD Removal (%)			
	Soda= 5 g/L			Soda= 10 g/L			Soda= 15g/L			Soda= 20 g/L			Soda 5 g/L	Soda 10 g/L	Soda 15 g/L	Soda 20 g/L
	436 nm	525 nm	620 nm	436 nm	525 nm	620 nm	436 nm	525 nm	620 nm	436 nm	525 nm	620 nm				
5	55	48	50	66	56	53	66	58	56	65	54	50	7	8	6	4
10	70	66	78	78	68	63	75	74	76	80	70	68	15	16	14	13
15	88	80	82	85	72	76	88	88	89	91	88	81	28	31	26	28
20	94	89	91	90	88	87	93	94	94	94	92	86	36	43	37	36
25	96	94	95	95	95	95	95	96	96	96	96	94	52	54	48	45
30	98	96	98	97	99	99	99	99	99	99	98	95	64	66	64	62

V. CONCLUSION

The treatment of real textile dyeing wastewater using immobilized catalyst in photocatalytic-ozonation system was found to be feasible. Complete decolourisation with 64 % COD reduction was observed after 30 minutes of treatment at alkaline pH. The decolourisation and degradation by followed pseudo-first order kinetics. The immobilized catalyst was found to be stable with almost 85 % colours and 40 % COD removal observed even after 10 runs. Hence the fixed catalyst developed for photocatalytic-ozonation process could be an efficient and economic system for treatment of textile dyeing wastewater.

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