

## Comparison of cost and treatment efficiency of solar assisted advance oxidation processes for textile dye bath effluent

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**Abstract**—The study investigated the efficiency and cost effectiveness of solar-assisted photochemical processes in comparison with advance oxidation processes (AOPs) for the textile effluents treatment. Efficiency of UV irradiation alone for one hour in removing color was almost double in comparison to solar radiation alone for effluents of different dye concentrations ( $E_1 > E_2 > E_3$ ). For coupled UV/H<sub>2</sub>O<sub>2</sub> process, there was higher color removal efficiency obtained for effluent E<sub>3</sub> (85%) as compared to E<sub>2</sub> (70%) and E<sub>1</sub> (57%), while E<sub>1</sub> showed higher COD removal efficiency (70%) as compared to E<sub>2</sub> (50%) and E<sub>3</sub> (62%). However, the efficiency of solar/H<sub>2</sub>O<sub>2</sub> for COD removal was comparable to UV/ H<sub>2</sub>O<sub>2</sub>, i.e., E<sub>2</sub> (57%) and E<sub>3</sub> (53%). In the case of UV and solar-assisted photo-Fenton processes, removal efficiency of the UV process was further increased as approached to almost 90% removal for E<sub>1</sub>; on the other hand, the solar-assisted process efficiency remained the same. The relative efficiencies of AOPs were found to be in the order of UV assisted photo-Fenton process > UV/H<sub>2</sub>O<sub>2</sub> > UV alone. Although, solar-assisted Fenton treatments were relatively low and slow but without any energy consumption in comparison to high energy consumption of UV. Among the UV processes, UV assisted photo-Fenton treatment appeared to have better color removal efficiency with energy requirements of 5 kWh/m<sup>3</sup>, 8 kWh/m<sup>3</sup> and 3 kWh/m<sup>3</sup> for E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, respectively.

Key words: Advance Oxidation Processes (AOPs), Removal Efficiency, Textile Effluent, Cost Efficiency, COD (Chemical Oxygen Demand)

### INTRODUCTION

Fresh water is essential for all activities of living organisms. In the recent century this natural source is being contaminated by different anthropogenic activities. Water-pollution control, wastewater treatment and conservation of water bodies have become an area of major concern for scientific society. Discharging untreated sewage and industrial wastewater and moreover excessive use of pesticides for agriculture has increased this pollution load into the major fresh water resources, which in turn has proved to be harmful for the health of living organisms and their surrounding environment [1].

The textile industry is the top ranked among the most water consuming industries around the world. It produces 50-100 liter wastewater per Kg of finished goods [2]. A total of 15% of the world production of dyes has been wasted in dyeing units and has added the pollution load in wastewater. Various environmental hazards are associated particularly with the intense nature of chemicals used in textile dyeing process (dyestuffs, surfactants, dispersing agents and other additives which are normally complex organic substances etc.), which in turn produces effluent that contains toxic contents of dye bath auxiliaries and unfixed dye material [3]. These chemicals are of recalcitrant nature: resistant to biodegradation and most physiochemical remediation methods such as precipitation and adsorption, and causes variations in the wastewater characteristics like chemical oxygen demand (COD), biological oxygen demand (BOD), Color,

total suspended solids (TSS), total dissolved solids (TDS), pH and heavy metals. Many studies have highlighted the mutagenic and carcinogenic nature of these dyes which are used in the textile industry. An understanding of the textile effluent is fundamental for the design of wastewater treatment plants and application of appropriate treatment technology. Textile effluent generally contains waste materials such as hard wastes, highly toxic waste with numerous pathogenic microorganisms, refractory organics, high volume wastes and dispersible wastes. The wastewater treatment process involves many steps such as primary, secondary and tertiary treatment steps. Several physio-chemical decolorizing techniques in combination with biological methods are used for treating textile effluent according to the pollution load, which includes physio-chemical flocculation combined with flotation, chemical coagulation, membrane technologies, adsorption, photo catalytic degradation, ion-exchange, irradiation and ozonation [4].

Biological method is promising in reducing organic content and nutrient content of municipal wastewater, but in case of biologically resistant dyestuffs of textile dye baths, the biological treatment does not produce effective results. Advanced oxidation processes (AOPs) have been widely used in removing organic and inorganic contaminants from textile wastewater, as various physiochemical technologies such as membrane filtration or activated carbon adsorption and conventional chemical oxidation processes have some limitations [5-13]. Venkatadri et al. (2009) reported application of three chemical treatment methods such as UV/H<sub>2</sub>O<sub>2</sub> process, Fenton's reagent treatment and titanium dioxide-assisted photo catalytic degradation [14]. Photo-assisted Fenton's system is one of the best technologies used for degrading water-soluble organic contaminants

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present in wastewater. Fenton reagent is very helpful in extracting the low energy photons from the spectrum of visible light [15]. Use of solar radiation for photolytic advanced process is a very fascinating and fast developing area and has been applied in many fields to treat the waste [16]. The ultraviolet light or near UV light reacts with photo catalyst to produce hydroxyl radicals that rapidly destroy the chemical bonds of the contaminants [17]. AOPs have great strength to break the aromatic structures of organic compounds, which in turn improves its biodegradability and the chromophoric group of the dye which leads to complete decolorization [18]. The use of solar radiation in ambient conditions makes the AOPs more cost effective, especially in the countries where availability and duration of solar light is in excess. Solar light and UV radiation can provide successful treatment of textile dyes and commercial surfactants [19]. After its application, treated waste water can be reused after small disinfection. Advance oxidation processes (AOPs) have provided a good substitute for protecting the environment by eliminating waste from wastewater [20], and have proven to be disinfectant against pathogens in order to ensure quality of treated waste water and completely oxidize and mineralize the textile effluent into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  with almost no sludge [21]. This study was aimed to evaluate the efficiency of advance oxidation processes for decolorizing and removing COD from the textile dye bath effluent, to study the solar light as a source of UV radiation for reducing color and COD of dye bath effluent, and to determine the cost effectiveness and reduction in energy consumption of advance oxidation processes by using sunlight in replacement of UV.

## METHODOLOGY

### 1. Sampling of Textile Wastewater

The textile waste water was sampled according to APHA protocols [22]. The wastewater sample was a dye bath effluent taken from the wastewater treatment plant of the textile industry (AZGARD 9). The raw water sample taken from the plant inlet was labeled as  $E_1$ ; a second sample was collected from equalization tank after flow equalization and labeled as  $E_2$ , and third from primary treatment clarifier as  $E_3$ . Initial COD and color were measured according to standard methods for examination of water and wastewater (Table 1) [22].

### 2. Preparation of Chemicals

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ; 35%) of analytical grade and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Ferrous Sulfate Heptahydrate) from Merck Germany were used. For the determination of COD  $\text{H}_2\text{SO}_4$  (conc.), FAS (Ferrous Ammonium Sulfate) of 0.1 N and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) of 0.25 N were used. De-ionized distilled water was used to prepare all the reagent solution. The absorbance of color was determined by using a spectrophotometer (Spectro Scan 80D-UV-VIS Spectrophotometer) to find the initial and final concentration of dye color, while COD of the samples was measured by applying close

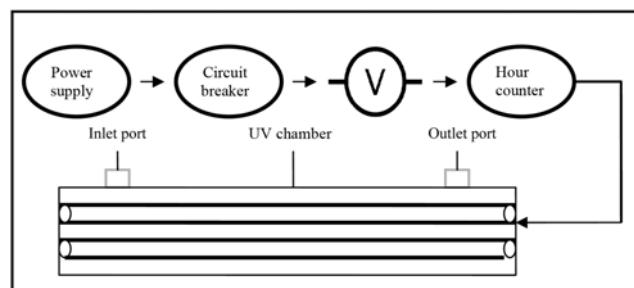


Fig. 1. The schematic for UV setup (UV,  $\text{UV}/\text{H}_2\text{O}_2$ ,  $\text{UV}/\text{FeSO}_4$ ).

reflux method.

### 3. Determination of Lambda Max

Lambda max was measured by recording the absorbance by varying the wavelength and a point was selected where the value of absorbance was found to be maximum; it was clearly identified that before and after that value the absorbance reduced. The lambda max for the dye bath samples was calculated and it was found at wavelength 662 nm. Beer Lambert's law ( $A = l \times c \times \epsilon C$ ; where  $A$ =absorbance,  $c$ =molar concentration,  $l$ =optical path length) was applied for finding the concentration of remnants of dyes in samples.

### 4. UV-reactor Design

UV-Reactor was designed for laboratory scale experiment to study the effect of UV irradiation on wastewater samples. The reactor consisted of two major parts: external and internal. External portion of the reactor was a powder coated iron box (with dimensions of height: 6.5", length: 42" and width: 12"). The schematic of the UV reactor is shown in Fig. 1. A voltmeter and an hour meter were attached on its front side, while two openings on the lateral side of the box were internally connected with the UV chamber inside the box for loading and unloading of the sample. Second major part of the reactor was the UV chamber (a long stainless steel column with dimensions  $l=32"$  and  $d=3"$  and capacity: 5 L sample) fixed inside the iron box. Two UV lamps (low pressure mercury vapor lamp of 36 W with  $\lambda=254$  nm) were wrapped in a Pyrex tube (high silica quartz) to be placed inside the UV chamber for power requirement of 72 W.

### 5. Experimental Procedures

In first step, optimization of hydrogen peroxide and ferrous sulfate was made for various samples of wastewater, and then the optimal doses were used in different experiments. The whole experimental procedure is shown in Fig. 2.

### 6. Calculation of Energy Requirement for AOPs

A very strong scale-up parameter EE/O (electrical energy per order requirement to reduce a pollutant or contaminant by logarithmic scale (one order of magnitude) in  $1 \text{ m}^3$  of any water sample) was used to compare the color removal efficiencies of different processes. The value of parameter (EE/O) does not depend upon the nature of the system. It determined the direct relationship between electrical energy efficiency of advance oxidation processes (AOPs) and gave the comparative values as well. The following empirical relationship (Eq. (1)) was used to calculate EE/O.

$$\frac{EE}{O} = \frac{P(\text{kW}) \times t(\text{min}) \times 1000}{V(\text{L}) \times 60 \times \log(C_o/C_f)} \quad (1)$$

where  $P$ =the power input of the UV-lamp in kW;  $t$ =oxidation time in minutes;  $V$ =the volume of the sample in liter;  $C_o$ =initial value

Table 1. Characterization of the untreated samples

Sample	COD	Color
$E_1$	243	0.738
$E_2$	125	0.322
$E_3$	52	0.128

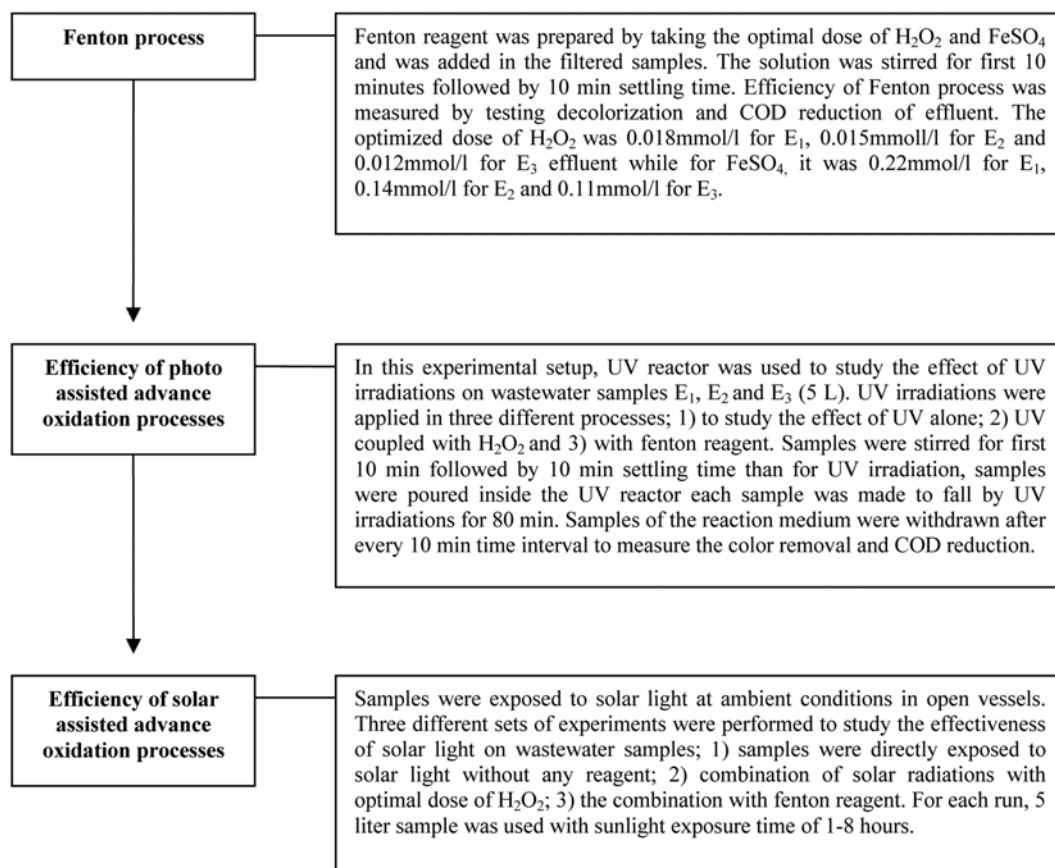


Fig. 2. Experimental procedure.

(concentration) of contaminant and  $C_f$ =final value (concentration) of contaminant.

## RESULTS AND DISCUSSION

### 1. Efficiency of UV and Solar-assisted Advanced Oxidation Processes

The experimental results described the efficiency of UV and solar-assisted photo-Fenton processes on color and COD removal for raw water sample ( $E_1$ ), sample after equalization process ( $E_2$ ) and after pretreatment process ( $E_3$ ) of wastewater treatment plant. With an

increase in UV exposure time, a gradual increase in color and COD removal efficiency was observed for all the effluents (Table 2(a)), and a decreasing trend was followed by the increase in dye concentration in samples as UV radiation penetrates low in high dye concentration. Raw water sample ( $E_1$ ) with higher dye concentration (0.738 mg/l) showed a decrease in the rate of decolorization as compared to the other two samples  $E_2$  (0.322 mg/l) and  $E_3$  (0.128 mg/l). The optimal dose for color and COD removal was found to be 60 minutes for all dye concentrations, but removal efficiency (%) was higher for low initial dye concentration. For sample  $E_1$ , removal efficiency for color and COD was 41% and 17%, respec-

Table 2. (a) Effect of UV irradiation with time on color and COD removal (absolute and %) of various samples ( $E_1$ ,  $E_2$ ,  $E_3$ )

UV time (minutes)	$E_1$				$E_2$				$E_3$			
	Color		COD		Color		COD		Color		COD	
	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency
10	0.686	7	233	4	0.293	9	119	5	0.108	16	47	10
20	0.620	16	216	11	0.267	17	114	9	0.099	23	46	11
30	0.583	21	211	13	0.245	24	98	22	0.087	32	40	23
40	0.531	28	211	13	0.219	32	91	27	0.076	41	35	33
50	0.487	34	211	13	0.200	38	85	32	0.067	48	31	41
60	0.435	41	202	17	0.174	46	75	40	0.060	53	31	41
70	0.435	41	202	17	0.174	46	75	40	0.058	55	31	40
80	0.428	42	199	18	0.174	46	75	40	0.051	60	31	41

**Table 2. (b) Effect of solar Irradiation with time on color and COD removal (absolute and %) of various samples (E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>)**

Solar irradiation (hours)	E <sub>1</sub>				E <sub>2</sub>				E <sub>3</sub>			
	Color		COD		Color		COD		Color		COD	
	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency
1	0.694	6	219	10	0.293	9	113	10	0.111	13	49	6
2	0.686	7	211	13	0.287	11	106	15	0.109	15	47	10
3	0.672	9	202	17	0.277	14	100	20	0.105	18	45	14
4	0.642	13	197	19	0.277	14	95	24	0.102	20	44	16
5	0.642	13	194	20	0.267	17	91	27	0.097	24	42	19
6	0.620	16	190	22	0.264	18	88	30	0.087	32	39	25
7	0.590	20	182	25	0.242	25	88	30	0.082	36	37	28
8	0.576	22	180	26	0.232	28	88	30	0.081	37	36	30

tively, which reached to 46% and 40% for sample E<sub>2</sub> and further increased to 53% and 41% for sample E<sub>3</sub> (Table 2(a)). It appeared that UV alone was not providing an effective solution for treating dye bath sample as E<sub>1</sub> having high concentration of dye in it which seemed to be photolytically stable and had taken longer time duration for treatment and giving poor results [23]. The efficiency of solar light was also low and maximum color and COD removal of samples after 8 hours exposure to sunlight was 20%, 26%; 28%, 30% and 37%, 30% for effluents E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, respectively (Table

2(b)).

The efficiency of coupled UV/H<sub>2</sub>O<sub>2</sub> process (Table 3(a)), carried out at optimal doses of H<sub>2</sub>O<sub>2</sub> (0.018, 0.015 and 0.012 mmol/l for E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub> respectively), proved that the process had improved COD and color removal (%) to some extent as the combination of UV with H<sub>2</sub>O<sub>2</sub> increased its rate of decomposition, which in turn produced more hydroxyl radicals for dye oxidation [24]. With the UV/H<sub>2</sub>O<sub>2</sub> exposure time of 60 minutes, the color removal for effluent E<sub>3</sub> was high (74%) as compared to effluents E<sub>2</sub> (59%) and E<sub>1</sub>

**Table 3. (a) Effect of UV/H<sub>2</sub>O<sub>2</sub> process with time on color and COD removal (absolute and %) of various samples (E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>)**

UV time (minutes)	E <sub>1</sub>				E <sub>2</sub>				E <sub>3</sub>			
	Color		COD		Color		COD		Color		COD	
	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency
10	0.649	12	204	16	0.264	18	98	22	0.097	24	39	25
20	0.613	17	175	28	0.235	27	90	28	0.081	37	37	28
30	0.554	25	156	36	0.209	35	88	30	0.067	48	33	36
40	0.502	32	141	42	0.187	42	79	37	0.055	57	30	43
50	0.450	39	129	47	0.145	55	73	42	0.045	65	27	49
60	0.384	48	102	58	0.132	59	64	49	0.033	74	23	56
70	0.339	54	87	64	0.116	64	63	50	0.026	80	21	59
80	0.317	57	73	70	0.097	70	63	50	0.019	85	20	62

**Table 3. (b) Effect of solar/H<sub>2</sub>O<sub>2</sub> process with time on color and COD removal (absolute and %) of various samples (E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>)**

Solar irradiation (hours)	E <sub>1</sub>				E <sub>2</sub>				E <sub>3</sub>			
	Color		COD		Color		COD		Color		COD	
	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency
1	0.672	9	219	10	0.274	15	105	16	0.108	16	44	16
2	0.642	13	209	14	0.264	18	90	28	0.105	18	41	21
3	0.627	15	199	18	0.248	23	80	36	0.095	26	38	26
4	0.590	20	182	25	0.238	26	73	42	0.087	32	35	32
5	0.576	22	180	26	0.225	30	68	46	0.079	38	33	37
6	0.554	25	170	30	0.219	32	68	46	0.077	40	28	46
7	0.554	25	160	34	0.187	42	63	50	0.070	45	24	53
8	0.517	30	146	40	0.184	43	54	57	0.064	50	24	53

(48%). On the contrary, COD reduction for effluent E<sub>1</sub> with the same UV exposure time was comparatively low as 58%, which was further decreased to 49% for effluent E<sub>2</sub> followed by the low COD removal efficiency (49%) of effluent E<sub>1</sub>. It is evident that addition of H<sub>2</sub>O<sub>2</sub> in sample solutions with UV exposure proved to be significant for improving color and COD removal efficiency upto 10 to 15% for all samples. On the other hand, Solar/H<sub>2</sub>O<sub>2</sub> was unable to furnish any significant change and the maximum color and COD removal of the samples after 8 hours exposure to sunlight was 30%, 40% (E<sub>1</sub>); 42%, 50% (E<sub>2</sub>) and 45%, 53% (E<sub>3</sub>), respectively (Table 3(b)).

The treatment efficiency was further enhanced by photo-Fenton process. Experimental results showed the dramatic increase in the color and COD removal efficiency through UV assisted photo-Fenton process (Table 4(a)). The concentration of Fe<sup>2+</sup> (ferrous ion) is one of the main factors that influence the photo-Fenton reaction [25]. The optimal dosage of Fenton reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) used for E<sub>1</sub> was (0.22/0.018 mmol/l), E<sub>2</sub> (0.14/0.015 mmol/l) and E<sub>3</sub> (0.11/0.012 mmol/l) samples, respectively. There was substantial improvement in the efficiency of color and COD removal (%) between 50 to 80 min of UV irradiation time. Sample (E<sub>1</sub>) showed 75%, 90% color and COD removal while E<sub>2</sub> and E<sub>3</sub> had 44%, 51% and 72%, 51% color and COD removal (%), respectively. Results (Table 4(b)) showed the color and COD removal (%) of solar-assisted Fenton process. Exposure to solar light for 6 to 8 hours showed substantial color and COD reduction. The color removal was 48%, 37% and 54% while COD

reduction was 49% and 52% and 56% for effluents E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, respectively, as the process proved to be more appropriate. Solar-assisted photo-Fenton process increases the treatment efficiency and reduces the amount of Fe<sup>3+</sup> containing sludge. The photo-Fenton process starts with the combination of H<sub>2</sub>O<sub>2</sub> with Fe<sup>2+</sup> utilizing the part of solar radiations with  $\lambda < 450$  nm, which reduces the ferrous ions generated as the process generates more hydroxyl radicals leading to the high rate of degradation of organic pollutants coupled with the enhancement of removal efficiency due to iron salt solubility [4,25].

## 2. Kinetics

Decolorization of a dye sample is a combination of different processes and complicated, so it is difficult to study the reaction kinetics singly. For this assumed reaction kinetics can be predicted [26]. A graph was plotted between  $-\ln C_0/C_t$  and time for color removal of wastewater samples by different AOPs and a typical plot of linear regression was obtained (Fig. 3 and 4).

The solar-assisted processes mainly showed the pseudo-first-order kinetics, while UV/H<sub>2</sub>O<sub>2</sub> process showed the typical first-order reaction plot for all wastewater samples and the value of correlation coefficient R<sup>2</sup> was 0.99 (Fig. 4). The photo-Fenton process and UV alone (except for sample E<sub>2</sub>) showed pseudo-first-order plot. The value of R<sup>2</sup> was greater than 0.9 for all experiments, which shows the effectiveness of assumed kinetics for photo-assisted AOPs processes. The results described that rate of color removal was ini-

**Table 4. (a) Effect of time on UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> process for color and COD removal (absolute and %) of various samples (E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>)**

UV time (minutes)	E <sub>1</sub>				E <sub>2</sub>				E <sub>3</sub>			
	Color		COD		Color		COD		Color		COD	
	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency
10	0.561	24	158	35	0.238	26	95	24	0.095	26	38	27
20	0.472	36	126	48	0.203	37	81	35	0.083	35	37	29
30	0.384	48	109	55	0.167	48	75	40	0.069	46	35	33
40	0.325	56	97	60	0.113	65	61	51	0.054	58	33	37
50	0.236	68	61	75	0.155	52	56	55	0.019	85	18	65
60	0.185	75	27	89	0.129	60	54	57	0.019	85	23	55
70	0.133	82	32	87	0.100	69	51	59	0.013	90	18	65
80	0.089	88	27	89	0.077	76	50	60	0.008	94	17	68

**Table 4. (b) Effect of time on solar/ H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> process for color and COD removal (absolute and %) of various samples (E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>)**

Solar irradiation (hours)	E <sub>1</sub>				E <sub>2</sub>				E <sub>3</sub>			
	Color		COD		Color		COD		Color		COD	
	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency	Absolute value	%Age efficiency
1	0.657	11	199	18	0.274	15	99	21	0.110	14	41	22
2	0.605	18	194	20	0.274	15	95	24	0.102	20	37	28
3	0.546	26	180	26	0.261	19	89	29	0.092	28	35	32
4	0.502	32	175	28	0.251	22	79	37	0.084	34	33	37
5	0.443	40	156	36	0.238	26	75	40	0.074	42	31	40
6	0.406	45	148	39	0.180	44	68	46	0.064	50	28	46
7	0.384	48	124	49	0.161	50	60	52	0.059	54	23	56
8	0.354	52	124	49	0.161	50	57	54	0.054	58	22	57

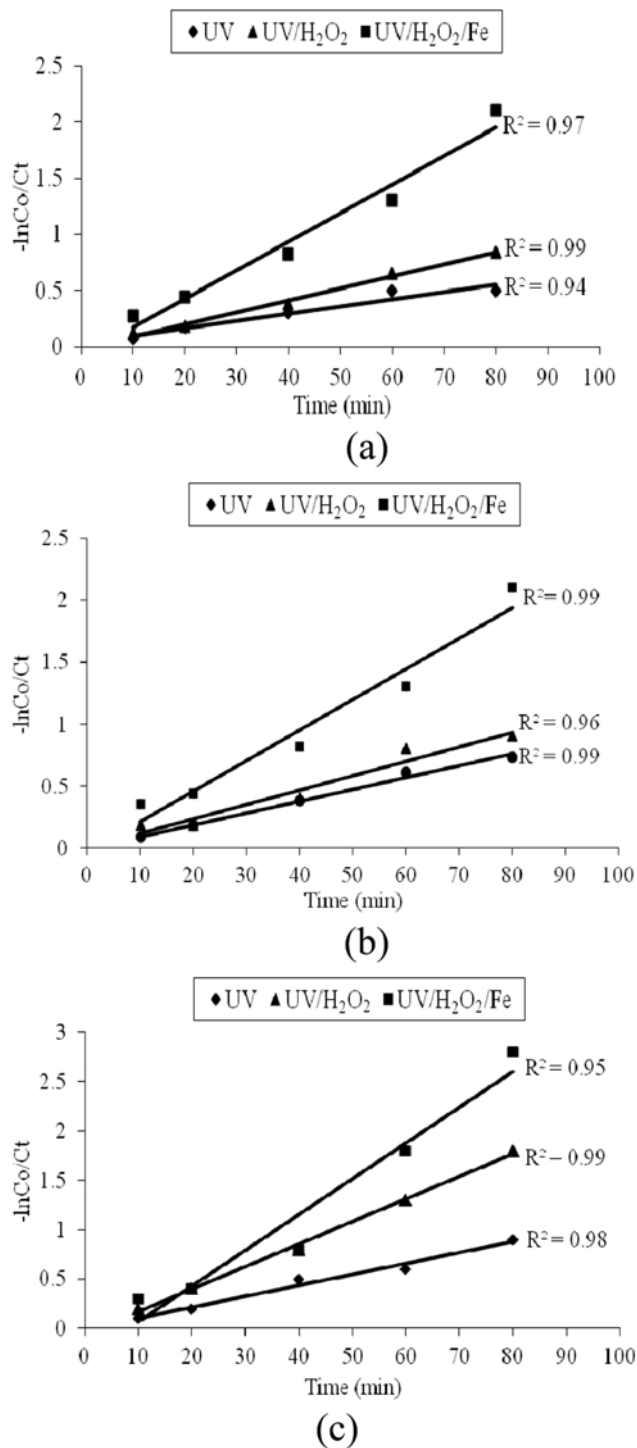


Fig. 3. Rate of decomposition of color versus time for various samples E<sub>1</sub> (a), E<sub>2</sub> (b) and E<sub>3</sub> (c) with UV source (UV lamp).

tially slow but showed gradual increasing trend. In the initial phase of the reaction, highly reactive hydroxyl radicals formed, which converted the substrate into the unstable intermediates [27]. In the second step, these intermediates were converted to stable end products, keeping the rates stable or increasing in the end.

### 3. Comparison of Energy Requirements for Color Removal (%) of Various Samples (E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>) with AOPs

To study the cost effectiveness and efficiency of the of the photo-

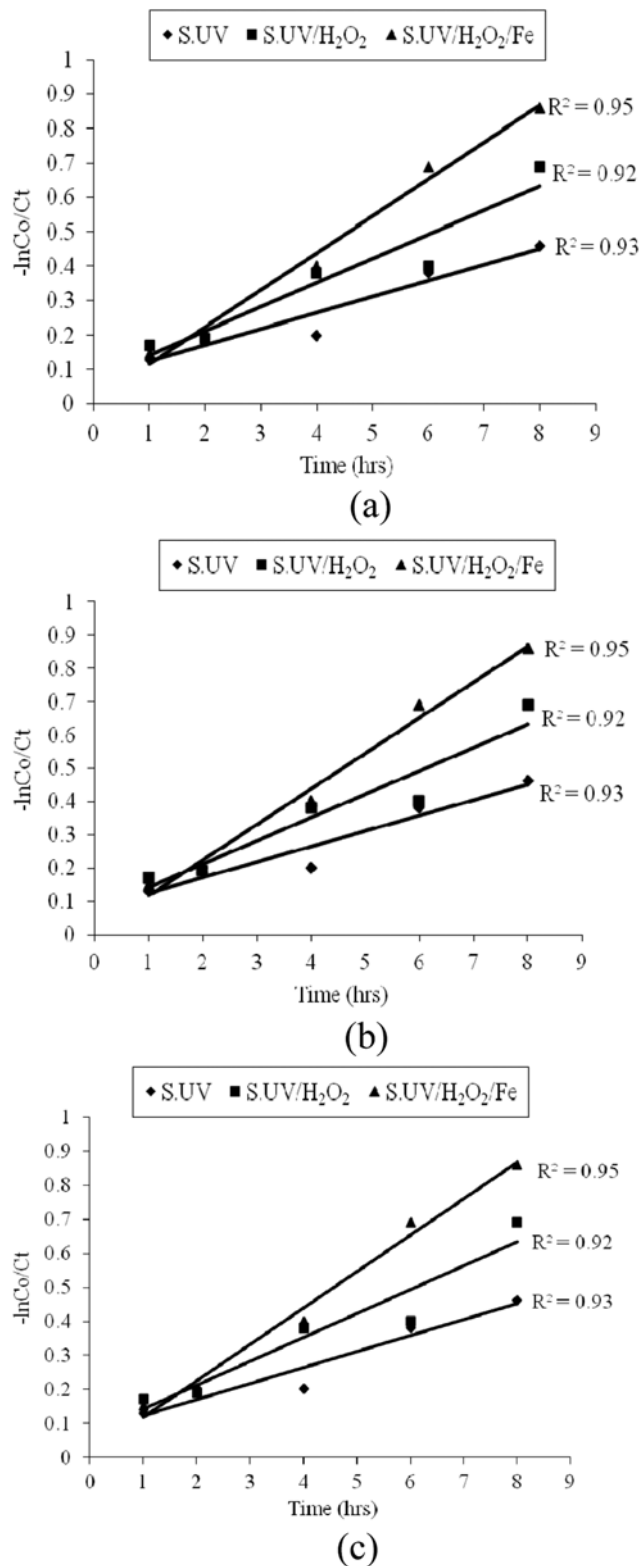


Fig. 4. Rate of decomposition of color versus time for various samples E<sub>1</sub> (a), E<sub>2</sub> (b) and E<sub>3</sub> (c) with solar light.

assisted advance oxidation processes, the electrical energy requirement for the processes was determined (Table 5) because a small value of energy consumption was directly associated with the low cost of the technique, which in turn proved the goodness and cost

**Table 5. Comparison of electrical energy requirements for color removal (%) of various samples (E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>)**

Processes	E <sub>1</sub>		E <sub>2</sub>		E <sub>3</sub>	
	Color removal	EE/O	Color removal	EE/O	Color removal	EE/O
	(% Age)	(kWh/m <sup>3</sup> )	(% Age)	(kWh/m <sup>3</sup> )	(% Age)	(kWh/m <sup>3</sup> )
UV	41	12	48	12	48	8
UV/ H <sub>2</sub> O <sub>2</sub>	48	10	42	12	65	4
Photo-fenton (UV lamp)	75	5	65	8	85	3
Solar alone	20	Nil	25	Nil	32	Nil
Solar/ H <sub>2</sub> O <sub>2</sub>	30	Nil	42	Nil	45	Nil
Photo-fenton solar	48	Nil	50	Nil	54	Nil

effectiveness of the AOPs. For this, the amount of consumed electrical energy was determined. It is apparent from the results that among all photochemical advance oxidation processes using a UV lamp, although photo-Fenton proved to be more promising as it consumed less energy as compared to the other processes, it still appeared to be energy intensive. On the other hand, solar-assisted Fenton process proved to be very economical due to the free availability of solar light with negligible electrical energy consumption and the color removal (%) of sample E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub> which was 52%, 50% and 58% just at exposure time of 8 hours in sunlight for solar-assisted Fenton process, while for solar/H<sub>2</sub>O<sub>2</sub> there was 30% color removal for sample E<sub>1</sub>, 43% for E<sub>2</sub> and 50% for E<sub>3</sub> at 8 hours exposure to sunlight (Table 5).

The electrical energy consumption was 12, 12 and 8 kWh/m<sup>3</sup> for UV alone at optimal value of time, that is 60, 70 and 50 minutes for samples E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, respectively, while for UV/H<sub>2</sub>O<sub>2</sub> process the optimal value of energy consumption for color removal (%) was noted 10, 12 and 4 kWh/m<sup>3</sup>, whereas the UV irradiation time was 60, 60 and 40 minutes for E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, respectively (Table 5). However, the photo-Fenton process among all AOPs proved to be better in terms of energy consumption and color reductions in dye bath sample. The energy requirement for this process was recorded as 5, 8 and 3 kWh/m<sup>3</sup> at 60, 40, 50 minutes time duration of UV exposure to samples E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, respectively.

### CONCLUSION

All AOPs used in this study appeared to be capable of decolorizing the dye and reducing the COD from wastewater samples except solar alone. Among all AOPs the photo-assisted Fenton process H<sub>2</sub>O<sub>2</sub>/Fe/UV appeared to be more suitable and faster as compared to H<sub>2</sub>O<sub>2</sub>/UV and UV alone. The optimal value for color removal (%) for photo-Fenton process was 75%, 65% and 85% in 50 to 60 min time duration for samples E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, respectively, and COD removal (%) was 89%, 51% and 51% for wastewater sample E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, respectively.

However, the solar-assisted Fenton reaction proved to be more promising in its efficiency in terms of its cost effectiveness and performance in decolorizing dye as compared to photo-Fenton processes using UV lamp for irradiation. In this case there was 52%, 50% and 58% color removal for 8 hours sunlight exposure time for samples E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, respectively. Electrical energy consumption for this process was negligible.

For all solar-assisted advance oxidation, the disappearance of dye

was described as pseudo-first-order kinetics and the value of R<sup>2</sup> was 0.92 except for the solar-assisted Fenton process for which it was 0.95. The R<sup>2</sup> value was <0.99 for all photo-assisted advance oxidation processes applied for samples E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub>, except UV/H<sub>2</sub>O<sub>2</sub> process for which R<sup>2</sup> value was 0.99 and depicted that reaction showed first-order kinetics.

All the UV based processes appeared to be energy intensive; however, the electrical energy consumption for the photo-Fenton process was low, and it was 5 kWh/m<sup>3</sup>, 8 kWh/m<sup>3</sup> and 3 kWh/m<sup>3</sup> for E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub> samples, respectively. On the other hand, for all solar-assisted reactions energy consumption was negligible.

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