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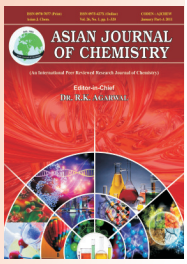

Application of Advanced Oxidations Processes for the Treatments of Textile Effluents

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The effect of various advanced oxidation processes ($FeSO_4/H_2O_2$, $FeSO_4/H_2O_2$/UV, $KMnO_4$, TiO_2/H_2O_2/UV, TiO_2/H_2O_2/dark, H_2O_2 /UV, H_2O_2/dark and sunlight) was compared for the treatment of textile wastewater on the basis of chemical oxygen demand (COD), total organic carbon (TOC), total suspended solids (TSS), dissolved oxygen (DO), phenolics and decolourization. Fenton and photofenton treatment showed highest effect on COD, TOC, TSS and colour reduction, while $KMnO_4$ showed 80-85, 45-50 and 20-30 %, reduction in colour, COD and TOC, respectively. The reduction in COD, TOC and colour using TiO_2/UV was found to be 75-85, 65-70 and 85-95 %, respectively and TiO_2 in dark and sunlight did not showed appreciable effect on water quality parameters *versus* Fenton, $KMnO_4$ and TiO_2/UV. The percentage effect of H_2O_2/UV on colour and COD was 80-85 and 40-45 % and H_2O_2/dark showed 20-25, 10-15 and 45-55 % reduction in COD, TOC and colour, respectively. The mineralization was recorded 95 and 80 % for Fenton and $KMnO_4$ for 6 h of treatment. Results showed that the advanced oxidation processes have promising effect to improve water quality and could be employed for wastewater treatment.

Keywords: Textile wastewater, Oxidants, Decolourization, Advance oxidation process.

INTRODUCTION

Textile industries consume huge amount of water and chemicals for wet processing in desizing, scouring, bleaching, dyeing, printing and finishing. There are more than 8000 chemical products associated with the dyeing process listed in the colour index and over 100000 commercially available dyes exist with 7×10^5 metric tons of production annually. Dyes are extensively used for textile dyeing, printing, colour photography and other industrial applications[1-3]. The textile dyes due to aromaticity and complex structure are difficult to treat biologically. About 15 dyes used for dyeing are lost and mixed with water bodies which are responsible for environmental pollution[4-7]. Effluents of textile industry pollute the environment due to high SS, COD, BOD, colour and other auxiliaries responsible for toxicity and health effects[8-9]. Since most of dyes released in water bodies are resistant to conventional treatment due non-ionizing and toxic nature.

Advanced oxidation processes (AOPs) are alternative methods for decolourization and degradation of recalcitrant wastewater loads that are generated by textile industries. These can quickly and non-selectively oxidize a broad range of organic pollutants[10]. Actually, advanced oxidation processes generate hydroxyl radical ($^{\bullet}OH$) which oxidize the pollutants non selectively[11]. The $^{\bullet}OH$ radical generation can be accelerated by combining some oxidizing agents such as H_2O_2, UV, ferrous and ferric salts (Fe^{2+} and Fe^{3+}) and catalysts such as TiO_2. Among these methods, UV/H_2O_2, Fenton's reagent (H_2O_2/Fe^{2+}), photo-Fenton (UV/H_2O_2/Fe^{2+}), TiO_2-assisted photo-catalysis (UV/TiO_2), UV/H_2O_2/TiO_2 are commonly used. The present study was designed to compare the effect of various advanced oxidation process on COD, TOC, TSS and colour before and after treatment. The effect of different treatment was also evaluated by comparing the mineralization efficiency by each treatment.

EXPERIMENTAL

Wastewater sample collection: Wastewater used in this study was collected from three textile industries from Faisalabad area, Pakistan namely Masood Textile Mill (MTM), Kalash Textile Mill (KTM) and Noor Fatima Textile (NFT). Samples were stored at room temperature within 2 h of collection to prevent any degradation.

The oxidizing agents and other chemical (H_2O_2, ZnO, TiO_2, $FeSO_4$, $KMnO_4$, $K_2Cr_2O_7$, Ag_2SO_4, glucose, potassium ferricyanide, potassium dihydrogen phosphate) were used of analytical grade and purchased for Merck and Fluka.

Advanced oxidation processes (AOPs): The treatments like Fenton, Photo-Fenton, potassium permanganate, H_2O_2/TiO_2/sunlight, H_2O_2/TiO_2/dark, H_2O_2/ZnO/sunlight, H_2O_2/sunlight, H_2O_2/dark and only sunlight were applied as standard methods as precisely described[12,13]. The wastewater collected

form textile industries was diluted and adjusted pH for potassium permanganate treatment < 1.5 and for all other treatment, the pH was maintained between 3-3.5.

Mineralization: In order to evaluate mineralization efficiency of various AOPs, the wastewater samples were treated with different AOPs for 6 h. After every 2 h, sample was withdrawn from reaction mixture and tested for mineralization[10].

Water quality parameter measurement: The COD, TOC and colour were measured as per the standard methods[14], while DO was determined using DO meter (Lavibond, SensoDirect 150). Briefly, 1.5 mL digestion solution and 3.5 mL catalytic solution along with 2.5 mL sample were poured in COD vials and kept at 150 °C for 2 h. After heating COD vials were cooled and absorbance was measured at 600 nm (Cecil 7200) using potassium dihydrogen phosphate as a standard and COD was calculated using formula (Eqn. 1). For TOC, 1.6 mL of H_2SO_4 and 1 mL of 2N $K_2Cr_2O_7$ along with 4 mL sample were mixed in vials and kept at 110 °C for 1.5 h. After incubation absorbance were recorded at 590 nm using glucose as standard and TOC was calculated using formula (Eqn. 2). For TSS measurement, the known amount of sample was passed through pre weighed filter paper, oven dried and weighed again and TSS was determined using formula shown in eqn. 3. For phenolic contents measurement, the wastewaters diluted 10 times, mixed with 2.5 mL of 0.5 N NH_4OH solution along with standards and immediately adjust the pH 7.9 ± 0.1 with phosphate buffer. Then 1 mL of 4-aminoantipyrine solution and 1 mL of potassium ferricyanide was also added. After 15 min the absorbance was measured at 500 nm and phenolic contents were estimated (Eqn. 4). Decolourization was checked by measuring the absorbance of treated and untreated sample at the maximum wavelength and %age degradation was calculated by using formula (eqn. 5).

SF = Standard COD/OD

$$COD\ (mg/L) = SF \times OD\ (sample) \quad (1)$$

SF = Glucose conc (mg/L)/OD

$$TOC\ (mg/L) = SF \times OD\ (sample) \quad (2)$$

$$TSS\ (mgL^{-1}) = (final\text{-}initial\ wt.)\ (Amount\ of\ sample\ taken)^{-1} \times 1000 \quad (3)$$

$$Phenols\ (mg/L) = (C \times ODc \times 1000)/(ODc \times B) \quad (4)$$

C = Standard solution, ODc = Absorbance (standard)

E = Absorbance (sample), B = Volume

$$Decolourization\ (\%) = A_i\text{-}A_f/A_i \times 100 \quad (5)$$

where, A_i was the initial absorbance and At was the absorbance at incubation time t.

Statistical analysis: All experiment seeded in triplicate and data thus obtained was averaged.

RESULTS AND DISCUSSION

The textile wastewater samples were analyzed for COD, TOC, TSS, DO, pH, phenolic before and after treatment along percentage removal of dye contents as a result of different treatments. The water quality characteristics before and after treatment are given 1-3 of Noor Fatima, Masood textile mill and Kalash textile mills wastewater effluent (Tables 1-3).

TABLE-1
WATER QUALITY PARAMETER VALUE OF NOOR FATIMA TEXTILE MILL SUBJECTED TO VARIOUS ADVANCED OXIDATION PROCESSES TREATMENT

	COD (mg/L)	TOC (mg/L)	TSS (mg/L)	DO (mg/L)	Ph (mg/L)	D (%)
Before treatment	1006.96	730.92	1205	5.31	-	-
After treatment	-	-	-	-	-	-
Fenton	201.46	116.95	157	9.78	144.32	93.6
Photo-Fenton	161.64	101.72	111	10.45	31.54	89.5
$KMnO_4$	546.09	578.12	689	6.34	756.03	81
H_2O_2/UV	588.67	545.34	865	7.03	-	79.6
H_2O_2/dark	702.65	563.02	984	7.02	-	53
TiO_2/H_2O_2/UV	202.54	321.39	-	8.45	61.53	92
TiO_2/H_2O_2/dark	745.56	523.49	-	6.16	35.54	29
ZnO/H_2O_2/UV	602.04	373.67	-	7.31	143.04	94
UV/O_2	906.26	669.73	1074	5.59	-	43

COD-Chemical oxygen demand, TOC-Total organic carbon, TSS- Total suspended solids, DO-Dissolved oxygen, Ph-Phenol and D-Decolorization

TABLE-2
WATER QUALITY PARAMETER VALUE OF MASOOD TEXTILE MILL SUBJECTED TO VARIOUS ADVANCED OXIDATION PROCESSES TREATMENT

	COD (mg/L)	TOC (mg/L)	TSS (mg/L)	DO (mg/L)	Ph (mg/L)	D (%)
Before treatment	1611	1374.63	3870	2.3	-	-
After treatment	-	-	-	-	-	-
Fenton	310.07	210.3	485	4.78	450.75	92
Photo-Fenton	92.7	160.94	302	6.78	124.8	94.6
$KMnO_4$	895.076	1119.31	1181	3.06	1284.25	83
H_2O_2/UV	965.4	1038.17	1315	3.15	-	80.8
H_2O_2/dark	1238.92	1135.18	1645	3.87	-	46
TiO_2/H_2O_2/UV	321.76	477.24	-	6.45	92.03	26
TiO_2/H_2O_2/dark	1341.76	992.03	-	3.11	-	26
ZnO/H_2O_2/UV	1214.74	938.25	-	4.61	513.15	93.2
UV/O_2	1449.9	1245.17	3596	2.63	-	40

TABLE-3
WATER QUALITY PARAMETER VALUE OF KALASH TEXTILE MILL SUBJECTED TO VARIOUS ADVANCED OXIDATION PROCESSES TREATMENT

	COD (mg/L)	TOC (mg/L)	TSS (mg/L)	DO (mg/L)	Ph (mg/L)	D (%)
Before treatment	1438.51	995.7	2560	3.98	-	-
After treatment	-	-	-	-	-	-
Fenton	361.22	310.75	337	6.63	227.34	89
Photo-Fenton	86.37	119.49	196	7.56	63.23	90
$KMnO_4$	699.23	676.15	821	5.12	821.67	87.8
H_2O_2/UV	699.16	763.01	1155	5.54	98.13	83
H_2O_2/dark	1070.16	799.19	1393	4.76	-	37
TiO_2/H_2O_2/UV	256.78	312.78	-	7.06	52.35	93
TiO_2/H_2O_2/dark	1141.52	713.41	-	4.77	20.01	33
ZnO/H_2O_2/UV	978.92	603.2	-	4.89	321.76	89.9
UV/O_2	1294.65	897.03	2256	4.09	-	32

Decolourization effect of advanced oxidation processes: The effect of different oxidizing treatment for the decolourization of textile was found very promising. The ZnO/H_2O_2/UV showed the highest decolourization of wastewater followed by Fenton, TiO_2/H_2O_2/UV and photo fenton treatment. Overall, the decolourization order was found as; ZnO/H_2O_2/UV > Fenton > TiO_2/H_2O_2/UV > Photo Fenton > $KMnO_4$ > H_2O_2/UV > H_2O_2/dark > UV/O_2 > TiO_2/H_2O_2/dark. The decolourization trends was found similar for three type of samples collected form different textile mills.

Effect on total organic carbon: The effect of advanced oxidation processes on COD variation was also found significant for textile wastewater. The treatment effect regarding COD variation was found in following order; Photo Fenton > Fenton > TiO_2/H_2O_2/UV > ZnO/H_2O_2/UV > TiO_2/H_2O_2/dark > H_2O_2/UV > H_2O_2/dark > $KMnO_4$ > UV/O_2. The decolourization trends was found similar for three types of samples collected form different textile mills.

Effect on chemical oxygen demand: The effect of AOPs on COD variation was also found accelerating for textile wastewater, but overall, the effect was not so much prominent as compared to TOC, TSS, DO, degradation and mineralization. The treatment effect on COD reduction was found in following order; Photo Fenton > Fenton > TiO_2/H_2O_2/UV > $KMnO_4$ > H_2O_2/UV > ZnO/H_2O_2/UV > H_2O_2/dark > TiO_2/H_2O_2/dark > UV/O_2. The reduction in COD trends was found similar for three types of samples collected form different textile mills.

Effect on total suspended solid, dissolved oxygen and phenolic: The effect of advanced oxidation processes on TSS, phenolic contents and DO was also found to be promising like COD and TOC. The difference between treated and untreated was significant at 95 % confidence interval of mean. The lowest value of TSS and phenolic and highest value of DO was found for photo fenton treatment, while UV/O_2 was found less efficient among all treatments.

Mineralization efficiency of various advanced oxidation processes: The mineralization efficiency observed for various advanced oxidation processes is shown in Fig. 1. the Fenton, photo-Fenton, $KMnO_4$, H_2O_2/UV, TiO_2/H_2O_2/UV and ZnO/H_2O_2/UV showed mineralization above then 40 %, while H_2O_2/dark and UV/O_2 was found less efficient for mineralization of textile wastewater. The mineralization observed for H_2O_2/dark and UV/O_2 was 18.5 and 16 %, respectively. The

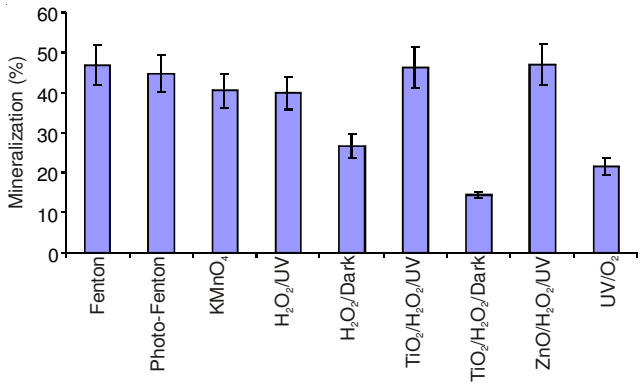

Fig. 1. Effect of various treatments on mineralization (%) of textile effluents (n = 3)

lower value of mineralization indicates the complex nature of textile wastewater.

Effect of advanced oxidation processes on wastewater quality parameter with respect to time: The effect of on three textile effluents with respect to time is shown in Fig. 2. The effect of Fenton, photo-Fenton and potassium permanganate was very fast in starting, reduces the phenolic, TSS, TOC and COD sharply until ½ h, then there was slow reduction until 6 h. Among treatments, the photo-Fenton was most efficient followed by Fenton and potassium permanganate.

Mechanism of action of different advanced oxidation processes: The oxidation mechanism in the Fenton process involves the reactive hydroxyl radical generated under acidic conditions by the catalytic decomposition of hydrogen peroxide, which reacts unselectively with organic compound (RH), which are based on carbon chains or rings and also contain hydrogen, oxygen, nitrogen, or other elements[15,16]. The reaction mechanism of various advanced oxidation processes are shown in eqn. 6-19.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (6)$$

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \ (2) \quad (7)$$

$$R^{\bullet} + Fe^{3+} \rightarrow \text{product} + Fe^{2+} \quad (8)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (9)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad (10)$$

The probable reason for the decrease in reaction rate is that in the first stage Fe^{2+} reacts with hydrogen peroxide to produce a large amount of hydroxyl radical as compared to ZnO/H_2O_2/UV as:

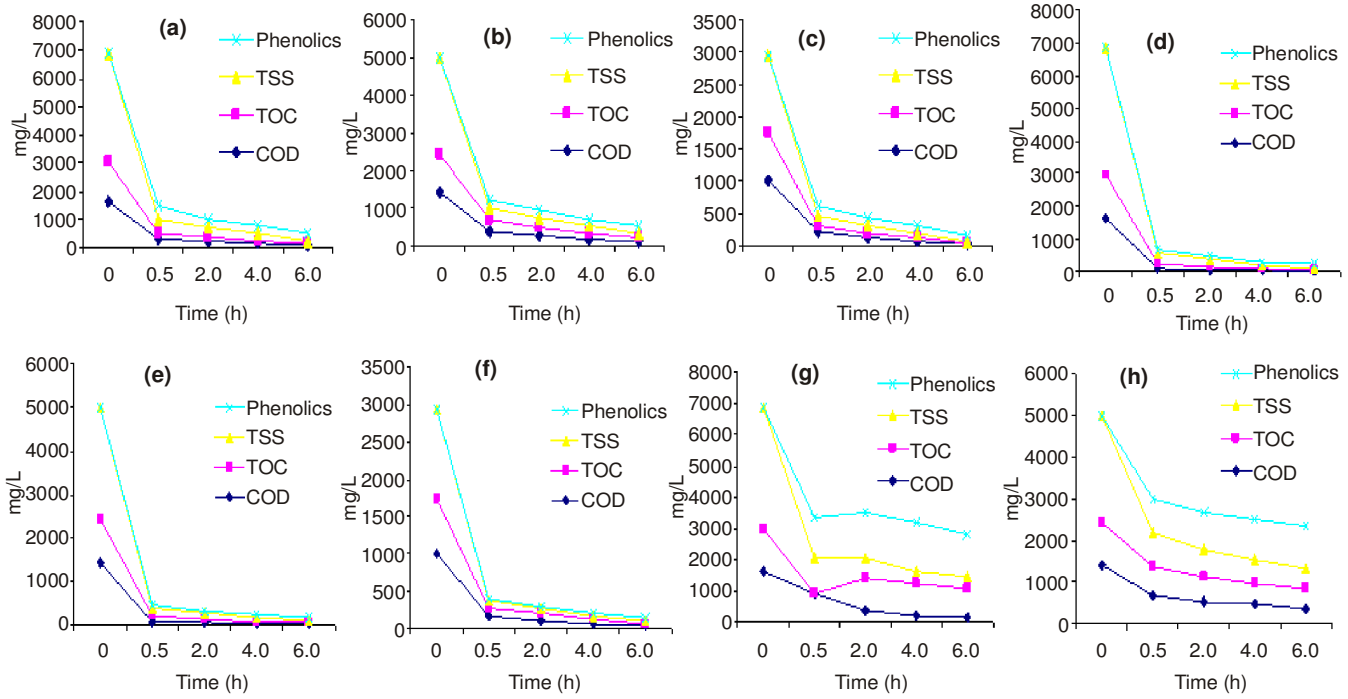

Fig 2. Time dependent effect of various advanced oxidation processes on phenolic, TSS, TSS, COD: (a), (b) and (c) Fenton treatment of Kalash Textile Mill (MTM), Kalash and Noor Fatima effluents, (d), (e) and (f) Photo fenton treatment of MTM, Kalash and Noor Fatima effluents, (g) and (h) Potassium permanganate treatment of MTM and Kalash effluent

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \quad (11)$$

Furthermore, Fe^{3+} produced in the first stage react with hydrogen peroxide to produce hydroperoxyl radicals ($HO_2^{\bullet}$) and Fe^{2+} as:

$$H_2O_2 + Fe^{3+} \rightarrow H^+ + FeOOH^{2+} \quad (12)$$

$$FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (13)$$

Oxidation capability of hydroxyl radical is much more than the hydroperoxyl radicals and as result of this rate of chemical reaction becomes slow[17].

The lower decolourization of dye wastewater by photo-Fenton treatment is due to the reason of Fe^{2+} to Fe^{3+} conversion (Eqn. 14), as the reduction of Fe^{3+} to Fe^{2+} by hydrogen peroxide (Eqn. 15) is much slower than reaction (14)[18-23].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (14)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)_2 + H^+ \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (15)$$

Potassium permanganate form MnO_2 (Eqn. 5), while TiO_2, H_2O_2 and ZnO form hydroxyl radical (Eqn. 16-18). The MnO_2 exhibited promising adsorptive activity which is responsible maximum degradation[24], while the hydroxyl radicals are strong oxidizing agents and can oxidize the organic compounds[25].

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2(s) + 2H_2O + 1.70\ V \quad (16)$$

$$TiO_2 + hv \rightarrow e_{CB\_} + h_{VB+\bullet}$$

$$h_{VB}^+ + OH^- \rightarrow {}^{\bullet}OH \quad (17)$$

$$H_2O_2 + UV \rightarrow 2OH^{\bullet} \quad (18)$$

$$ZnO + hv \rightarrow (energy\ \_\ 3.2\ ev)\ e^- + h^+$$

$$e^- + O_2\ (ads) \rightarrow {}^{\bullet}O_2$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad (19)$$

Generally, the effect of various advanced oxidation processes on different operational parameters of wastewater was found promising. Result showed that Fenton, Photo-Fenton and titanium dioxide, in the presence of UV, efficiently decrease pollution load of waste water. Fenton method results in 80-95 % degradation of dyes. The efficiency of AOPs is attributed to the formation of hydroxyl radical[26]. Photo-Fenton was found more efficient in decreasing pollution load of waste water as compared to other because in the presence of light the generation of hydroxyl become fast which is responsible for enhanced degradation and improvement of water quality parameter. Secondly, in photo fenton process, the involvement of Fe^{3+} catalyzed reactions in the light-enhanced degradation process because Fe^{3+} ions produced form complexes with both water and organic compounds. These complexes absorb visible light and electron transfer processes may regenerate Fe and resultantly increases the production rate of hydroxyl radicals[27,28].

Result showed that Fenton, photo-Fenton and titanium dioxide in the presence of UV efficiently decrease pollution load of waste water. As a result of photo-Fenton treatment, > 95 % degradation of dyes wastewater was achieved. The maximum mineralization was achieved by using Fenton, photo-Fenton and $KMnO_4$ for 6 h, however, for first ½ h the process was very fast which mineralized the compound present in wastewater > 90 %. The advanced oxidation processes under study can be used practically for textile wastewater treatment due to their efficiency for the reduction of TOC, COD, TSS, colour and phenolics.

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