Available online at www.elixirpublishers.com (Elixir International Journal)

Chemical Engineering

Elixir Chem. Engg. 53 (2012) 11983-11987

ISSN: 2229-712X

Studies on decolourization and COD reduction of dye effluent using advanced oxidation processes

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ARTICLE INFO

Article history:
Received: 2 October 2012;
Received in revised form:
7 December 2012;
Accepted: 7 December 2012;

Keywords
Decolourization,
Textile effluent,
Methyl orange,
Absorbance,
Photo oxidant.

ABSTRACT

The present paper involves the application of chemical and photochemical homogeneous advanced oxidation processes on the decolourization of textile effluent and Methyl Orange (MO) Dye. The decolourization efficiency of various oxidants such as hydrogen peroxide (H_2O_2), fenton reagent i.e. hydrogen peroxide and hydrated ferrous sulphate (H_2O_2/Fe^{2+}), sodium hypochlorite (NaClO), $UV/H_2O_2/Fe^{2+}$, $Solar/H_2O_2/Fe^{2+}$, UV/NaClO and Solar/NaClO has been investigated. The effect of process parameters viz., oxidant dose, pH, concentration of dye and source of light (UV/Solar) for decolourization and COD reduction of dye effluent and MO has been studied. The decolourization efficiency was estimated from residual concentration spectrophotometrically. The experimental results show that the maximum decolourisation (more than 95 %) and COD reduction (40 %) of effluent occurred using combined Solar/NaClO (20 mg/L) system at pH 6 within 20 minutes. The decolourization efficiency of MO dye with H_2O_2 or UV alone was found to be negligible but more than 95% efficiency could be achieved either with $UV/H_2O_2/Fe^{2+}$ (450 mg/L /150 mg/L) at pH 2 or Solar/NaClO (120 mg/L) at pH 6 within 30 minutes.

Introduction

The textile industries produce dye effluents which are becoming a major source of environmental pollution in India since textile dyes are designated as contaminants in different textile wastewaters and included among the 130 priority contaminants given by US EPA and the European Union due to its toxicity and non-biodegradability [1]. The treatment of spent textile dyeing wastewater by traditional methods (both physical and chemical) has proven to be ineffective for many wastewater treatment facilities [2-5]. However, these techniques are all non-destructive since they transfer non-biodegradable matter into sludge, giving rise to solid waste which further needs treatment [6-8]. The treatment of spent dye effluent is of growing concern for the textile industry because of aesthetic conditions, as well as eco toxicological issues regarding coloured rinsing and process wastewater and the impact of that wastewater on the receiving streams [9]. As regulations become more stringent, the effectiveness and cost of treatment processes becomes more significant.

Recently there has been considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes [10]. AOPs are based on the generation of reactive species such as hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and nonselective [11]. Chemical oxidation technologies, however, seem to have the most potential for future use in the textile wastewater treatment plant [12]. Treatment of spent dye effluent by a process utilizing ultraviolet light (UV) and a strong oxidant is an effective alternative for colour removal. Fenton reagent (H_2O_2+Fe^{2+}) is the most common oxidant used in combination with UV [13-14]. Metcalf E., (2003) [15] stated that an effluent is biodegradable when the relation BOD_5/COD is over 0.4 or BOD_5/TOC over 1.0. Aleboyeh et al., (2003) and Feng et al., (2000) [16-17] studied the decolourization of methyl orange with fenton under both UV and visible light. The literature study revealed that that only scattered work has been reported on the application of homogeneous oxidation processes on real dye effluents. Moreover few references are available on the use of NaClO as an oxidant which has been reported to be released during bleaching either in pulp & paper industry or textile mills along with the industrial effluents [18]. The present paper evaluate the effectiveness of different chemical oxidants for decolourization of dye effluent viz., hydrogen peroxide, fenton reagent, sodium hypochlorite and their combinations of UV/Solar systems ($UV/H_2O_2/Fe^{2+}$, UV/NaClO, $Solar/H_2O_2/Fe^{2+}$, Solar/NaClO). Experiments were also conducted to investigate the effects of various process parameters (oxidant dose, pH, fenton ratio and initial dye concentration) on the decolorization efficiency.

Materials and Methods

Chemicals

Methyl Orange (MO) and Hydrogen peroxide (30% w/v) was procured from Ranbaxy Chemicals Ltd., India and used as such without purification. Ferrous sulphate hydrated ($FeSO_4.7H_2O$) was obtained from Ranbaxy Chemicals Ltd., India and prepared as a 0.1 M solution in 1 M H_2SO_4 solution. Sodium Hypochlorite (4 % w/v) was procured from Merck and used as such without further purification. Double distilled MilliQ water (Millipore Distillation unit) is used for preparation

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of various solutions. pH of the solutions was adjusted with 1M HCl or 1M NaOH.

Textile effluent characteristics

The wastewater samples used in this study were effluents from the wastewater treatment plant (WWTP) of textile dye mill near Ludhiana (India). The plant treats approximately 4 million gallons per day and discharges into the local River. During this work, colour levels in samples of the WWTP final clarifier effluent were consistently greater than the permissible colour levels. Analytical data describing the daily clarifier-effluent quality was not available, but the following are representative values based on analysis at the laboratory: pH = 6.55, Abs = 0.989 units, conductivity = 12.5 μS and COD = 517 mg/L The effluent was a murky, orange/maroon color and relatively frees of particulate matter.

Instruments

The photochemical decolourization experiments were carried out in specially designed double walled reaction vessels (500 ml) in the UV reactor equipped with 5 UV tubes each of 30W (Philips) having wavelength of 365 nm. Constant stirring of solution was insured by using magnetic stirrers and aeration was done with the help of aquarium aerators. The temperature was maintained constant throughout the reaction time by circulating the water in the jacketed wall reactor. For solar experiments, the borosilicate glass reactors of diameter 0.17m and 800ml capacity were made with ports at the top for sampling, gas purge and gas outlet. The solar experiments were performed in day time between 10AM to 4PM in the month of April-May when the intensity of sun is at its maximum. The rate of decolourization of dyes were estimated by measuring absorbance in HACH DR 4000U UV/VIS spectrophotometer, USA having a wavelength range from 190-1100nm using a 1 cm quartz cell. COD was determined with the help of Thermo Orion COD-125 meter of Thermo Electron Corporation (USA) using standard methods [35]. pH was adjusted using Thermo Orion 920A digital pH meter.

Experimental

The effectiveness of the various oxidative treatments for reducing colour in dye solutions and textile effluent was evaluated in batch reactors at 298 K. To 100 ml of dye solution or effluent, photo oxidant was added and subjected to irradiation under UV and solar light. Experiments were also conducted with oxidant alone. A matrix of experimental variables was developed in which the UV exposure time, pH, oxidant concentration, & fenton ratio (H_2O_2/Fe^{2+}) were varied and applied to each dye solution. The aqueous mixture was magnetically stirred throughout the experiment. At different time intervals, a sample was taken out with the help of a syringe and their absorption spectrum was recorded. The rate of decolourization was observed in terms of change in intensity at the wavelength where characteristic peak occurred. The decolorization efficiency was calculated as:

Decolourization Efficiency (%) = $[(C_0 - C)*100/ C_0]$

Where C_o is the initial concentration of specimen (MO or dye effluent) and C is the concentration of specimen after photo irradiation.

Results and discussion

The present paper investigated the use of different oxidants viz., H_2O_2, H_2O_2/Fe^{2+} and NaClO for their decolourization efficiency (%) of MO and dye effluent. The efficiency of the oxidative treatments was dependent on the initial colour intensity of the test solutions. The treatments involving NaClO relied on the NaClO demand required by the test solutions, which was also a response to the initial colour intensity.

Dye and effluent characteristics

Methyl orange (MO) is an azo dye having sulphonate (SO_3^-) and azo groups (Fig.1). In MO, the azo (-N=N-) group is most active site for oxidative attack in visible region [19]. Methyl orange shows characteristic absorption at 450 nm & 197 nm and dye effluent shows characteristic absorption at 506 nm & 200 nm. The decolourization experiments were carried out with oxidants alone as well as oxidant with either UV or solar light. The decolourization efficiency was recorded with respect to change in intensity of absorption peaks at 450 nm for MO & 506 nm for effluent.

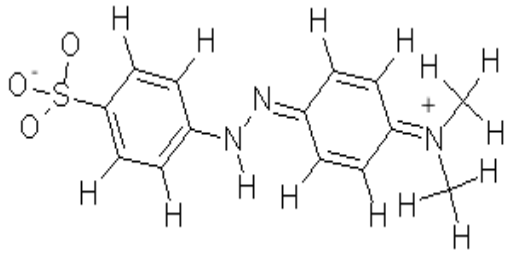

Fig.1 Structure of Methyl Orange

Decolourization of MO dye using different oxidants

Decolourization efficiency of MO dye has been studied using different oxidants viz., hydrogen peroxide, fenton and sodium hypochlorite. Since decolourization with H_2O_2 alone was less than 5% for MO dye even up to 6 hrs of exposure as shown in Table 1. These results are in confirmation with earlier findings [20-22], thus H_2O_2 alone is not a viable oxidative agent. Then experiments were conducted using fenton and hypo as oxidants which showed significant decolourization efficiency. The effect of variables including pH, oxidant dose, fenton ratio, dye concentration and UV/Solar effect on decolourization of MO dye were investigated.

Table 1. Decolourization efficiency (%) of MO dye (50 ppm) and dye effluent with 300 mg/L of H_2O_2

Time (Hrs)	Decolourization efficiency (%) using H_2O_2 alone	
	MO	Effluent
1	0.55	2.42
2	2.43	4.52
3	3.57	6.25
6	4.54	6.89

Effect of pH

Waste water containing dyes is discharged at different pH, therefore it is important to study the role of pH on decolouration of dye. Experiments were carried out at pH, ranging from 2-10, for constant dye concentration (50 ppm MO) and oxidant dose of 450 mg/L H_2O_2 & 150 mg/L $FeSO_4$. For NaClO, 120 mg/L of the oxidant was used for decolourization of MO dye (50 ppm). Fig. 2 shows the decolourization efficiency of MO with fenton and hypo as a function of pH. It has been observed that in case of treatment of dye with fenton, the decolourization efficiency increase with the decrease in pH exhibiting maximum rate at pH 2. Similar behavior has also been reported for the decolourization efficiency of fenton on azo dyes [23]. The process is more efficient in acidic medium (pH 2–3). Increase of pH from 2 to 10 decreases the decolourization from 99.4 to 26.1%. The lowering of decolourization efficiency in this pH range is due to reduction of hydroxyl radical concentration. Under this condition H_2O_2 undergoes photodecomposition to water and oxygen rather than hydroxyl radical. In case of hypo

treatment, the process is more efficient at pH 6. Increase of pH from 6 to 8 decreases the decolourization from 98.1 to 73.5%.

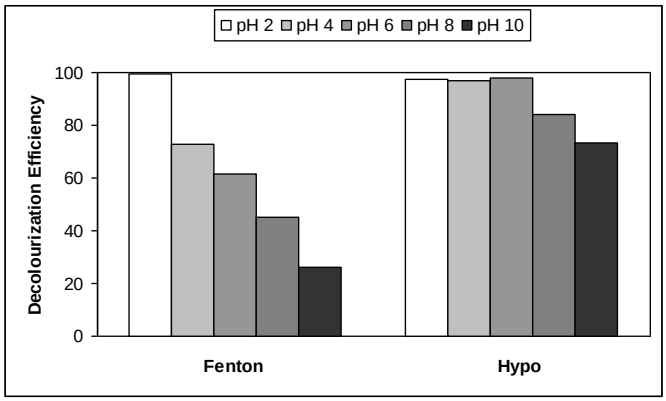

Fig. 2 Effect of variation of pH on the decolourization efficiency (%) of MO dye (50 ppm) by fenton reagent at 3:1 ratio (450mg/L of H_2O_2 & 150mg/L of $FeSO_4$) and 120 mg/L NaClO

Effect of fenton ratio

In order to study the effect of variation in fenton ratio i.e. ratio of hydrogen peroxide to hydrated ferrous sulphate, the experiments were conducted at 1:1, 2:1, 3:1 ratios of H_2O_2/Fe^{2+} for decolourization of MO dye (50 ppm) under optimized pH 2 as depicted in Fig. 3. The maximum decolourization efficiency was obtained with 3:1 ratio at which 99.4% decolourization was achieved in 30 minutes as compared to 89.3% in 60 minutes with 1:1 fenton ratio.

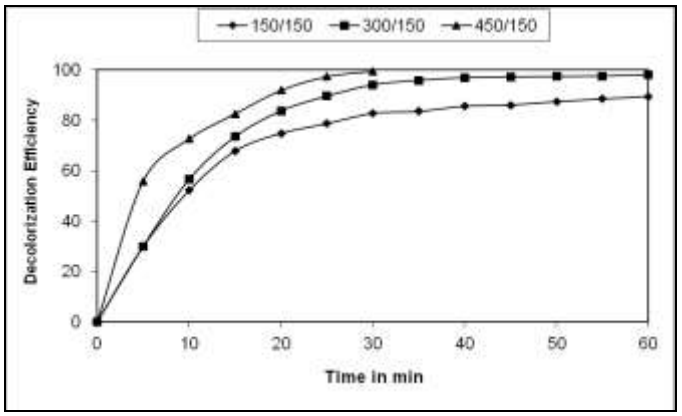

Fig. 3 Effect of variation in ratio of fenton reagent on the decolourization efficiency (%) of MO dye (50 ppm) at pH 2

Effect of oxidant dose

In order to determine the optimum dose of oxidant, the experiments were performed by varying concentration of H_2O_2/Fe^{2+} from 300/100 mg/L to 1500/500 mg/L at pH 2 as well as NaClO from 40 to 200 mg/L at pH 6 for MO dye solutions (50 ppm) as shown in Fig. 4. The increase in fenton dose from 300/100 mg/L to 450/150 mg/L increases the decolourization efficiency from 60 to 84 % in 15 min. Further increase in the dose of fenton reduces the time required to attain the decolourization of 99 % but with higher recurring costs. Hence 450/150 mg/L of H_2O_2/Fe^{2+} concentration is the optimal dose for the oxidation of dye solutions. The increase in decolourization efficiency with higher dose of H_2O_2 (300–1500 mg/L) is due to increase in the hydroxyl radical concentration. Others researchers also documented that decolourization of textile dye by fenton/UV increases as dose of effective hydrogen peroxide is increased [24-25]. In case of NaClO, the decolourization efficiency (94%) was observed after 15 minutes with 120 mg/L of NaClO dosage.

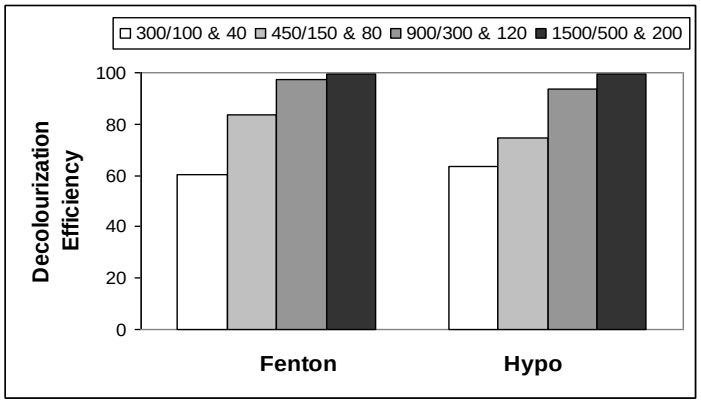

Fig. 4 Effect of variation in fenton dose at pH 2 & hypo dose at pH 6 on the decolourization efficiency (%) of MO (50 ppm) after 15 minutes of exposure

Effect of concentration of dye

After optimizing the ph and oxidant dose i.e., 450/150 mg/l of fenton at ph 2 and 120 mg/l of naclo at pH 6, the decolourization of dye with both oxidants were carried out by varying the initial concentrations of the dye from 5-100 ppm in order to assess the efficiency of the oxidants. As the concentration of the dye is increased, the decolourization efficiency decreases indicating either to increase the oxidant dose or time span has to be increased for the complete decolourization. Fig.5 depicts the effect of variation in dye concentrations (MO) on the decolourization efficiency with fenton and hypo. Previous research documented the similar inverse relationship between the initial dye concentration and the decolorization efficiency [26].

Effect of UV light/solar light

The effect of UV-light/Solar light on the decolourization of MO by fenton (Fig. 6) and hypo (Fig. 7) has been studied. The results clearly show that the decolourization efficiency steadily increased by increasing UV light with a linear relationship in confirmation with earlier findings [27]. The enhancement in decolourization efficiency is due to increase in hydroxyl radical concentration.

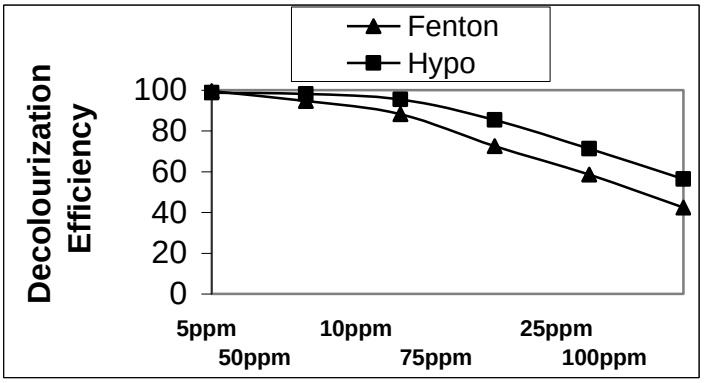

Fig. 5 Effect of initial dye concentration on decolourization efficiency (%) at 3:1 ratio of fenton reagent at pH 2 and 120 mg/L of hypo at pH 6

The rate of photolysis of H_2O_2 depends directly on the incident power. At low UV power the photolysis of H_2O_2 is limited. The similar relationship between UV light intensity and dye decomposition in UV/H_2O_2 process has been investigated [28]. The dye solutions was decolourized by the combination of UV and NaClO in a fashion similar to that seen by UV/H_2O_2/Fe^{2+}. In hypo treatment UV acts as additional source for decolourisation of dye.

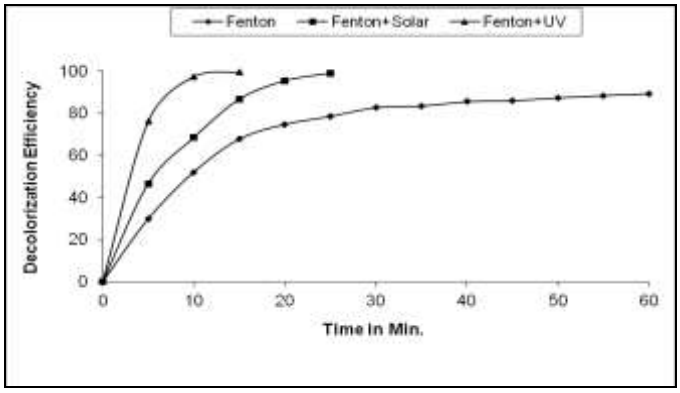

Fig. 6 Effect of UV and solar irradiations on the decolourization efficiency (%) of MO Dye (50 ppm) using fenton reagent (450/150 mg/L) at pH 2.

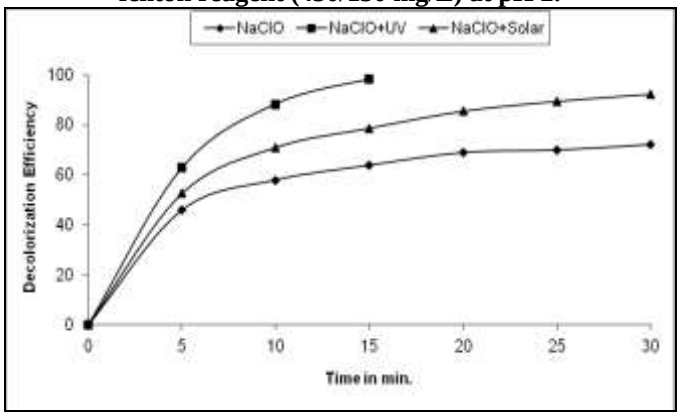

Fig. 7 Effect of UV and solar irradiations on the decolourization efficiency (%) of MO dye (50 ppm) using hypo (120 mg/L) at pH 6

UV source has some limitations; it is not only hazardous but also expensive because of large input of electric power to generate UV irradiation. In tropical countries intense sunlight is available throughout the year. Although sunlight has only 5% of optimum energy for photo excitation and ultimately for decolourization of pollutants, but it could be safe and cost effective source for degradation of pollutants in wastewater. Moreover there is no material deterioration in case that sunlight is used as a radiation source [29]. The photo assisted decolourisation of MO was also carried out using fenton and hypo at the same conditions and solar irradiation as light source. In case of fenton, the decolourization efficiency of more than 95% was observed in 25 minutes of solar irradiation time, whereas in the presence of UV irradiation 98.1% decolourisation efficiency was recorded in the duration of 15 minutes. In case of hypo, the decolourization efficiency of about 84% was observed with solar light in 30 minutes and more than 95% with UV in 15 minutes of exposure.

Decolourization of dye effluent using different oxidants

Decolourization of dye effluent with H_2O_2 alone was less than 7% even up to 6 hrs of exposure as shown in Table 1.The variation in decolourisation efficiency of effluent with NaClO at different time exposures has been shown in Fig. 8 and with fenton in Fig. 9. When treatment with 20 mg/L NaClO was followed by UV irradiation, decolourisation of the dye effluent was significant in short time span of 10 minutes. Figures show that about 88% of decolourisation can be achieved using solar-fenton process in 30 minutes as compared to 97% with Solar/NaClO in 20 minutes. The UV exposure time required to reach more than 95% of decolourization for the effluent was slightly shorter for UV/NaClO (20 mg/L) than for UV/H_2O_2/Fe^{2+} (150/50 mg/L). If more than 95% decolourization was required, the Solar/NaClO appeared to be the optimal treatment. These findings imply that NaClO oxidized the dyes better than H_2O_2/Fe^{2+}.

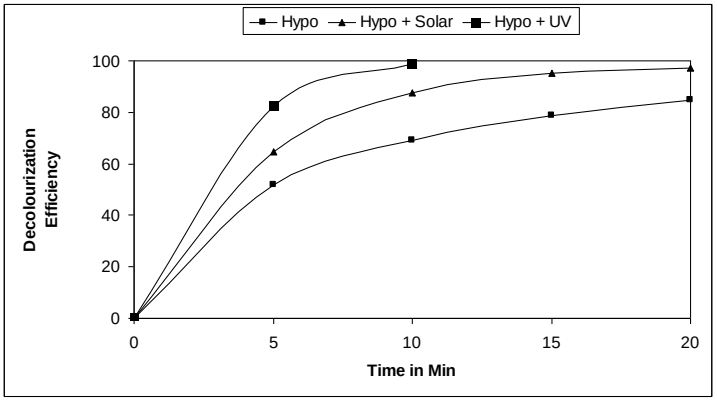

Fig. 8 Effect of UV and Solar light on the decolourization efficiency (%) of effluent with 20 mg/L of hypo at pH 6.

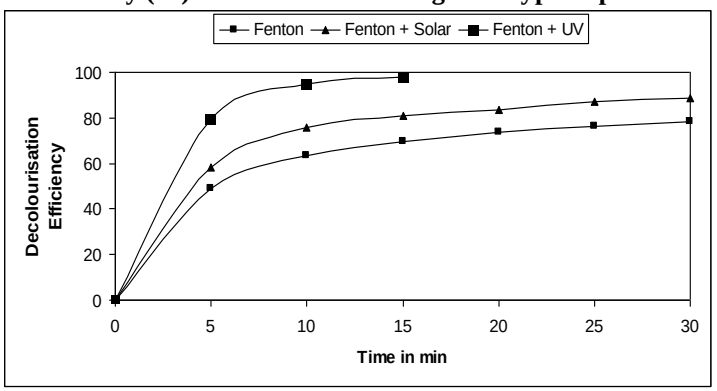

Fig. 9 Effect of UV and Solar light on the decolourization efficiency (%) of effluent with 150/50 mg/L of fenton reagent at pH 2.

Mineralization studies of MO and effluent

Treatments of MO and dye effluent with various oxidants result in change of their physical and chemical characteristics. The change has been measured in terms of chemical oxygen demand. As the reduction of COD reflects the extent of degradation or mineralization of an organic species, the percentage change in COD of methyl orange dye (50 ppm) and effluent has been studied under optimized conditions. Table 2 gives the reduction in COD of MO dye and effluent with Hypo and Fenton respectively at various time exposures. The reduction in COD of methyl orange dye and effluent was observed to be more with fenton (83.8% & 47.4%) as compared to hypo (53.7% & 40.4%) respectively after one hour of exposure.

Conclusion

The effectiveness of various treatments was found to vary with the oxidant systems used. The relative decolourization order established for MO dye was: H_2O_2 < H_2O_2/Fe^{2+} < NaClO < H_2O_2/Fe^{2+}/Solar < NaClO/Solar < H_2O_2/Fe^{2+}/UV < NaClO/UV. Experimental results indicated that decolorization efficiency of dye effluents is facilitated in the presence of H_2O_2/Fe^{2+} & hypo alone.

As the initial concentration of dye was increased, the decolourization efficiency decreased. NaClO/Solar may be considered as the best treatment process in terms of commercial applications particularly for industries where NaClO is employed as raw material. Thus it can be concluded that photo oxidation system employing NaClO and solar light has potential

to decolorize the textile dyes and is recommended as a pretreatment step before conventional biological treatments for consideration at the effluent treatment plant.

Table 2. Reduction in COD (%) of MO dye (50 ppm) and effluent varying time

S. No.	Time (min.)	Methyl Orange Dye		Effluent	
		Fenton	Hypo	Fenton	Hypo
1.	0	0.0	0.0	0	0.0
2.	5	16.3	18.8	10.6	14.9
3.	10	37.5	25.0	13.9	21.5
4.	15	51.3	28.7	18.8	26.1
5.	20	66.3	35.0	28.2	29.1
6.	25	70.0	42.5	32.7	33.9
7.	30	78.8	46.3	38.3	36.7
8.	60	83.8	53.7	47.4	40.4

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