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Original Article

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Abstract

Treatment of textile wastewater is challenging because the water contains toxic compounds that have low biodegradability.This study discusses the textile dying effluent treatment by chemical oxidation technique which is experimentally optimizedfor treatment of industrial effluents.The disappearance of Basic yellow 28 from the effluent has been performed using Fenton's reagent (Fe^{2+} and H_2O_2). The effects of different reaction parameters such as initial pH, the initial hydrogen peroxide concentration ($[H_2O_2]_0$), the initial ferrous concentration ($[Fe^{2+}]_0$), the initial Basic yellow 28 concentration ($[dye]_0$) and the temperature on the disappearance of Basic yellow 28 have been assessed. The optimal reaction conditions were found to be; initial pH = 3.00, $[H_2O_2]_0$ = 0.20 mM, $[Fe^{2+}]_0$ = 0.14 mM for $[dye]_0$ = 0.04 mM at 25 °C. Under optimal conditions, 94 % disappearance efficiency of dye from aqueous solution was achieved after 120 min of reaction. The changes and percentage of color, chemical oxygen demand (COD), biological oxygen demand (BOD) were determined. The results showed that color was removed effectively in the aqueous solution. Under these conditions the percentage of color and COD removal efficiencies were reached 91, while for BOD removals the percentage reached 94.

1. Introduction

Textile industry causes considerable higher impacts to water pollution by discharging their effluents into various receiving bodies includes ponds, rivers and other public sewer. Major pollutants load from the textile industries are from the several of their wet processing operations like scouring, bleaching, mercerizing and dyeing. Among these various processes, dyeing process normally uses large amount of water for dyeing, fixing and washing processes **(Latha*et al.*,2017).**

Chemical oxidation is reported to be very effective but the efficiency strongly depends on the type of oxidant and the nature of dye. The disappearance of Basic yellow 28 from aqueous solution had been investigated using Fenton's reagent Advanced Oxidation Process using Fenton's reagent have common principles in terms of the participation of hydroxyl radicals that are assumed to be operative during the reaction. Due to the instability of hydroxyl radical, it must be generated continuously in situ through chemical or photochemical reactions (**Yoon *et al.*, 2001**).

2. Materials and Methods

2.1. Sample Collection and Analysis

The industrial effluent and the dye (basic yellow 28) under investigation were obtained from EL-MansoraTex factory for textile industry (Gamasa industrial area-Daqahlya, Egypt). The dye was used without further purification.

Stock solution (1×10^{-2} M) was prepared in methanol and stored in a refrigerator at 4 °C. Standard solutions were prepared daily by diluting of the stock solution with a selected supporting electrolyte.

2.2. Physicochemical Analysis of textile wastewater

The average of three pH values of the sample were measured directly using pH meter, 3305, Jenway, UK according to Standard Methods (1992). Total dissolved solids (TDS) were measured according to APHA (1992).Total hardness (TS) was determined according to EDTA titrimetric method (Adams, 1990). Calcium hardness was determined according to EDTA titrimetric method (EPA, 1983).Sulphate (SO_4^{-2}) ion was measured by turbidimetric method and absorbance was determined spectrophotometrically at λ = 420 nm. Nitrate (NO_3^-) was determined according to EPA (1983). Nitrite (NO_2^-) was determined according to diazotization method (Parsons *et al.*, 1984). Ammonia (NH_4^+) was determined by low-level indo phenol method (Adams, 1990).CL- was determined by Argentometric titration (Mohr method).

2.3. Organic Constituents and COD/BOD Ratio

Biological oxygen demand (BOD) was determined according to Adams (1990). Chemical oxygen demand (COD) was measured by manual method using dichromate Reflux according to Adams (1990). COD/BOD ratio was estimated to measure the biodegradability of the organic constituents. In general, the COD/ BOD ratio of textile industry effluent ranges from 3 to 4 meaning that the effluent is moderately biodegradable but dyes which have low biodegradability; the COD/ BOD ratio will be > 4 (Marmagne and Coste, 1996).

2.4. Color Determination of textile wastewater

The UV-vis spectra of dye were recorded over the wavelength range from 200 to 800 nm using a UV-vis spectrophotometer. A quartz cell with a 1.0 cm path length was used. The maximum absorbance wavelength (λmax) of Basic yellow 28 was found at 438 nm. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by the addition of ferrous ion solution.

Therefore, the concentration of the dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at λmax= 438 nm and from a calibration curve. The color removal percent of Basic yellow 28 was calculated as follows:

Color removal percent (%) = $C_0 - C_t / C_0$ X 100

Where C_0 is the initial concentration of Basic yellow 28, and C_t is the concentration of Basic yellow 28 at reaction time t (min).

3. Results and Discussion

3.1. Physicochemical Parameters

Table (1) summarizes the physicochemical analysis of textile effluent sample; the mean value of pH was nearly alkaline (9.3) which was in similar with that found by **Husain and Hussain (2012)**, however **Benaïssa (2005)** found the pH values were nearly acidic (6.03, 5.09, 5.40 and 5.28) for different dyes.

The values of TDS, TS concentrations were found to be 2690 and 2950 mg/l, respectively. The results showed that the hardness and Ca ion concentrations were 312.3 and 55.4 mg/l, respectively, and chloride and sulfate exhibited higher mean values of 196.2 and 301 mg/l, respectively. Whereas, Nitrate recorded high value compared with standard values of environmental law 4 / 94. The mean values of TN and TP were 340 and 230mg/l, respectively.

Table 1: Physicochemical Parameters of the Industrial Effluent Sampleat **pH= 9.3.**

Examined Parameters	Values(mg/l)	Standard Limitsaccording to environmental law 4/1994
Ammonia	24.5	**100**
Nitrate	92.2	**30**
Hardness	312.3	-
Nitrite	65.4	-
TN	340	-
TP	230	-
TS	2950	**800**
TDS	2690	-
Calcium	55.4	-
Chloride	196.2	-
Sulfate	301	-

3.2.1. Organic Constituents

The organic constituents which gave high values so COD and BOD values were 2470 and 950 mg/l which were very high comparable with standard values (1100 and 600 mg/l), respectively, as shown in Table (2). However, BOD value was 460 mg/l determined by **Husain and Hussai (2012**).

Whereas COD value was nearly similar to the value recorded by **Husain and Hussain (2012**) was 2700 mg/l. and COD / BOD ratio was 2.6. However, the results recorded by **Marmagne and Coste(1996)** ranged from (3-4%).

Table 2: Organic Constituent Values of the Industrial Effluent Sample.

Parameters (mg/l)	Values(mg/l)	tandard Limits (environmental law 4/1994)	COD/BOD ratio
COD	2470	1100	**2.6**
BOD	950	600	

3.2. Decolorization and Degradation of dye by Fenton's Reaction

Effect of initial pH

pH of the solution is an important parameter for Fenton oxidation process, which controls the production rate of hydroxyl radical. In order to find the optimal pH of reaction mixture for the disappearance of Basic yellow 28 in Fenton oxidation, a series of tests were conducted at different pH valuesof 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6 and 6.5 and realized its effect on the color removal percent after 20, 40, 60, 80, 100, 120 min. As seen at Table (3), the color removal percent increased during acidic medium and the maximum removal occurred at PH 3 after 120 min and then the percent decreased at the alkaline medium (Fig. 7). These results were in agreement with **Jaafar and Boussaoud (2014**) that the maximum color removal percent occurred at PH from 3-3.5. **Wu *et al.* (2003)** also found the maximum color removal percent occurred at PH from 3-3.5 and the color removal percent decreased at higher PH values.

Table 3: Effect of PH on the Color Removal (%)

pH	Color Removal Percent (%)After(min)					
	20	**40**	**60**	**80**	**100**	**120**
2	54	56	60	62	65	67
2.5	55	58	64	66	68	70
3	75	77	85	87	90	92
3.5	82	84	90	91	93	95
4	70	72	74	75	76	80
4.5	50	56	62	64	66	68
5	40	44	72	75	77	80
5.5	36	38	43	45	47	52
6	25	33	40	41	43	45
6.5	15	22	24	30	31	34

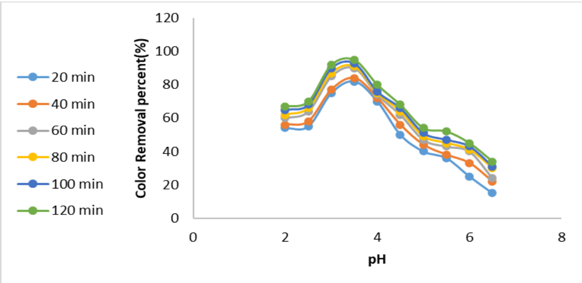

Fig. 1: Effect of PH on the Color Removal (%).

Effect of Temperature

Temperature is critical to the reaction rate, the product yield and distribution. The generation rate of OH promoted by the high temperature will accelerate the heterogeneous Fenton-like oxidation reaction and can therefore enhance the dye decolorization (**sun *et al.*,2009**). In addition, it is possible that higher temperatures may enhance the adsorption rate of dye and H_2O_2 through improving their diffusion rate at the solid/water interface.

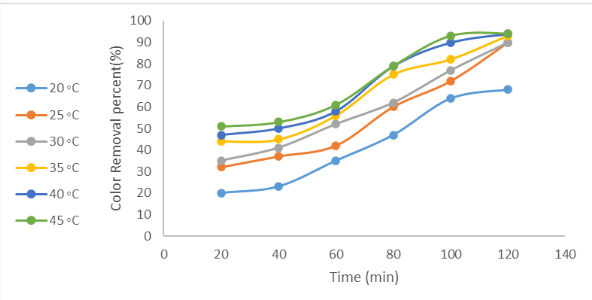

Fig. 2: Effect of Temperature (^{0}C) on the Color Removal (%)

The influence of temperature at decolorization percent was also investigated in this study (Table 6). In order to determine the effect of reaction temperatures; 20, 25, 30, 35, 40 and 45◦C on the disappearance of Basic yellow 28 a series of experiments were conducted by varying temperature from 15 °C to 45 °C. The results are illustrated in Fig. (2). were in agreement with **Jaafar and Boussaoud (2014)** found that with the raising temperature, the color removal percent increased during time increased.

Table 3: Effect of Temperature (^{0}C) on Color Removal (%)

Temperature (^{0}C)	Color Removal Percent (%) After (min)					
	20	**40**	**60**	**80**	**100**	**120**
20	18	25	32	38	41	45
25	22	36	40	47	52	55
30	30	44	54	60	66	70
35	44	60	62	75	79	79
40	52	72	77	82	90	93
45	67	90	90	93	94	94

3.3. Effect of Fenton's reagent doses on Color Removal (%) of Basic Yellow Dye

To elucidate the role of Fenton's reagent concentrations on the degradation of Basic yellow 28 by Fenton oxidation, a series of experiments were conducted with different doses from 0.05 mM to 0.4 mM (Table 7). Fig. 3 shows the effect of Fenton's doses on the disappearance of Basic yellow 28 by Fenton's oxidation. These results were in agreement with **Jaafar and Boussaoud (2014)** and**Florenza*et al.*** **(2014),** which demonstrated that by increasing the doses of Fenton's, the color removal percent increased.On the other hand, **Pachhade*et al.* (2009)** who achieved 97% decolorization in 30 minutes by the ozonation of Procion Red MX-5B.**Fu *et al.* (2009)** also reported that 96.8% decolorization accomplished by the Fenton oxidation of C.I. Acid Red 73 in 30 minutes using of zero valent iron catalyst.

Table 4: Doses of Fenton's Reagent (mM) and its Effect on Color Removal (%)

Doses of Fenton's(mM)	Color Removal Percent (%) after					
	20	**40**	**60**	**80**	**100**	**120**
0.05	28	33	40	43	49	51
0.1	32	35	45	47	52	56
0.15	38	42	48	50	55	58
0.2	44	53	55	58	62	65
0.25	48	58	60	62	65	67
0.3	56	61	63	68	70	74
0.35	65	70	72	75	77	80
0.4	82	84	87	92	93	94

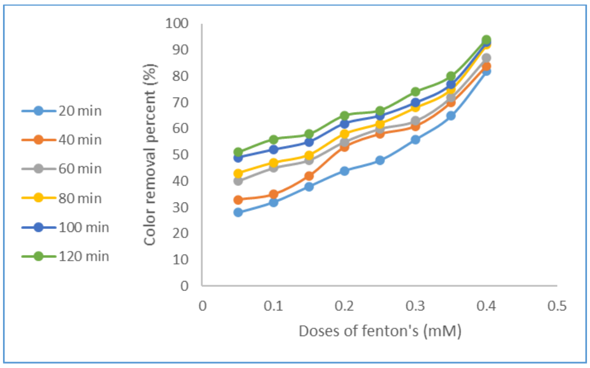

Fig. 3: Doses of Fenton's Reagent (mM) and its Effect on the Color Removal (%)

3.4. Effect of Fenton's reagent doses on COD Removal Percent of Basic Yellow Dye

It could be concluded that the most important parameter for the reduction of COD is Fenton's concentration and this concentration affected positively, the removal increased when concentration increased while, after 0.35 m M the COD removal percent decreased.

These results were in agreement with **Chen *et al.* (2013**) found COD removal percent increased during the increase of Fenton's concentration and then decreased.

Table 5: Doses of Fenton's Reagent (mM) and its Effect on the COD Removal (%)

Doses of Fenton's (mM)	COD Removal (%) After (min)					
	20	40	60	80	100	120
0.05	16	19	22	25	25	29
0.1	23	25	33	35	37	42
0.15	31	45	46	60	63	68
0.2	55	58	62	65	72	77
0.25	78	81	83	85	88	88
0.3	83	85	87	90	91	91
0.35	63	66	68	68	72	78
0.4	44	47	50	53	55	64

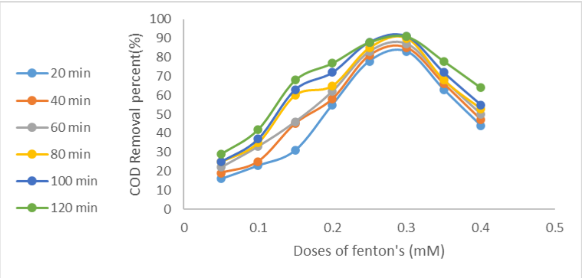

Fig. 4: Doses of Fenton's Reagent (mM) and its Effect on the COD Removal (%).

Effect of Fenton's reagent doses on the BOD Removal Percent of the Basic Yellow Dye

BOD is an important parameter for study the effect of Fenton's on the removal of BOD. By increasing the Fenton's concentration, the BOD removal increased, while after 0.25 mM the BOD removal percent decreased (Table 9 and Fig. 5).

Table 9: Doses of Fenton's Reagent (mM) and its Effect on the BOD Removal (%).

Doses of Fenton's (mM)	BOD Removal (%) After (min)					
	20	40	60	80	100	120
0.05	23	36	44	56	68	77
0.1	33	45	59	62	74	82
0.15	50	63	68	78	82	82
0.2	62	74	77	88	92	94
0.25	60	65	70	80	81	83
0.3	54	60	64	71	75	75

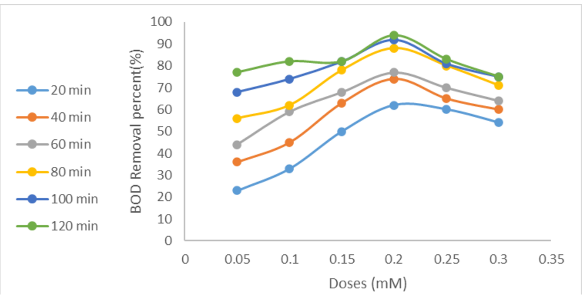

Fig. 5: Doses of Fenton's Reagent (mM) and its Effect on BOD Removal (%).

CONCLUSIONS

Treatment of textile wastewater is challenging because the water contains toxic compounds that have low biodegradability. Therefore, treatment of textile wastewater containing Basic yellow 28 dye using Fenton oxidation process had been taken into consideration in the present study. The results show that pH, initial H_2O_2 concentration, the initial Fe^{2+} concentration, initial dye concentration and the temperature were the main factors that had strong influences on the disappearance of Basic yellow 28 by Fenton oxidation process. The optimal operation parameters for the Fenton oxidation of Basic yellow 28 were 0.20 mM $[H_2O_2]0$, 0.14 mM $[Fe_2+]0$ for 0.05 mM [dye]0 at an initial pH of 3.00 with 25 °C temperature. Under these conditions, 94 % disappearance efficiency of dye in aqueous solution was achieved after 120 min of reaction with dose 0.4 mM of Fenton's reagent.

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