

# Color and COD removal from waste water containing acrylic water base color using Fenton's oxidation process

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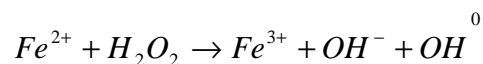
## Abstract

Degradation of acrylic water base color from synthetic wastewater by the Fenton process was performed. Experiments were conducted on the sample containing 100 and 400 mg/l of Acrylic water base color. The study was performed for searching optimum values of FeSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> concentration, pH and temperature. The H<sub>2</sub>O<sub>2</sub> requirement seems to be related to initial COD of the sample. FeSO<sub>4</sub>/ H<sub>2</sub>O<sub>2</sub> ratios found were not changed for the temperature affected the COD removal significantly at high degrees.

**Key words:** Color and COD removal, acrylic water base color, Fenton's oxidation process

## Introduction

Water base color was the earliest type of paint and go the down of history water born coating have been around in one form or another for decades but have demonstrated greatly improved performance characteristics in recent years. Acrylic media made by suspending pigment in synthetic polymer emulsified by water. The release of colored wastewater in the environment is considerable source of non aesthetic pollution and eutrophication and can originate dangerous by products through oxidation, hydrolysis or other chemical reaction taking place in the wastewater phase. Decolonization of dye effluents has therefore received increasing attention. Many chemical treatment processes have been used extensively to treat wastewaters including color. Most of the studies, such as biological methods (Porter, 1979; forster & gallely, 1979), chemical precipitation (Georgiou, 2003), adsorption by activated carbon (Aysegul pala A, 2002) and some natural absorbents (paul, 1996), photo catalytic oxidation (Franciscoa P. and Konstantinou ioannis, 2004) and Fenton's oxidation (Kang shyh-fang, 2000; Swaninatan, 2003; sheng, 2003; Sureyya meric, 2004) focused on color removal. Advanced oxidation processes (AOPs) processes are defined as the processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize majority of the complex chemical present in the effluent water. These processes include (O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV and Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>). Fenton oxidation (FO) process which is one of the oldest advanced oxidation processes that discovered about 100 years ago but its application toxic organics was not applied until the late 1960 s (Huang *et al*, 2005). Fenton's reagent is a mixture of H<sub>2</sub>O<sub>2</sub> and ferrous iron which generates hydrates hydroxyl radicals according to the reaction (Sureyya *et al*, 2004).



The ferrous iron ( $Fe^{2+}$ ) initiates and catalyses the decomposition of  $H_2O_2$ . Resulting in the generation of hydroxyl radicals that attack and destroy the organic pollutants (Kardag *et al.*, 1998). Fenton's process performed in four stages, which are pH adjustment to low acidic values, oxidation reaction neutralization and coagulation at pH lower than 3.  $H_2O_2$  and ferrous ions are more stable resulting in a better redox system and decolorizing better. However, at pH values higher than four, ferrous ions easily form ferric ions which have a tendency to produce ferric hydroxide complexes  $H_2O_2$  is unstable and easily decompose itself in the basic (pH>10) solutions (Sostar *et al.*, 2004; Süreyya, 2003). The global effects produced in the wastewater are organic pollutant destruction, toxicity reduction. Biodegradability improvement BOD, COD, odor and color removed (Sostar *et al.*, 2004). However, application of FO process is rare in practice. Although organic content of wastewater is oxidized to the end products by the FO process, the sludge produced contains high amount of Fe (III) which needs to be managed by a safe disposal method.

## Material and Method

Experimental study was designed to obtain maximum COD and color removal at optimum pH, temperature and  $FeSO_4$  and  $H_2O_2$  doses. FO process was performed considering Kvo s (1992) method with a modification of 2 min rapid mixing at 100 rpm and the 20 min slow mixing at 30 rpm and subsequently settling for 30 min. First, the pH of sample was lowered up to desired pH value using 1 N  $FeSO_4$ . Later,  $FeSO_4$  and  $H_2O_2$  were added to the 500 ml beakers containing 100 and 400 mg/l AWB solutions. After rapid and slow mixing and settling period, pH of the supernatant was readjusted using 1 N NaOH up to 7.5 and supernatant was left to settle for 2 hr. purring mixing, reactors were kept at constant temperature. Experiments were conducted on the AWB solutions at 10, 20, 25,30,40,50 and 60 C temperature ranges. Experimental study was designed in four stages. In first stage  $H_2O_2$ , temperature, pH was kept constant to determine  $FeSO_4$  concentration for maximum color and COD removal. For that  $FeSO_4$  concentration and the same oxidation condition, optimum  $H_2O_2$  concentration was investigated in the second stage. By considering the optimum doses of first and second stages, optimum pH and temperature were investigated in the third, fourth stages, respectively (Porter, 1979).

## Analytical methods

COD was measured according to standard methods (1998). Absorbance measurements were made using PU870 series UV/VIS spectrometer for color removal. The supernatant in each beaker were filtered by 0.45  $\mu$ m Millipore membrane filter before measuring COD and absorbance. Dye solution was determined. The color removal was based on the change of the maximum absorbance.

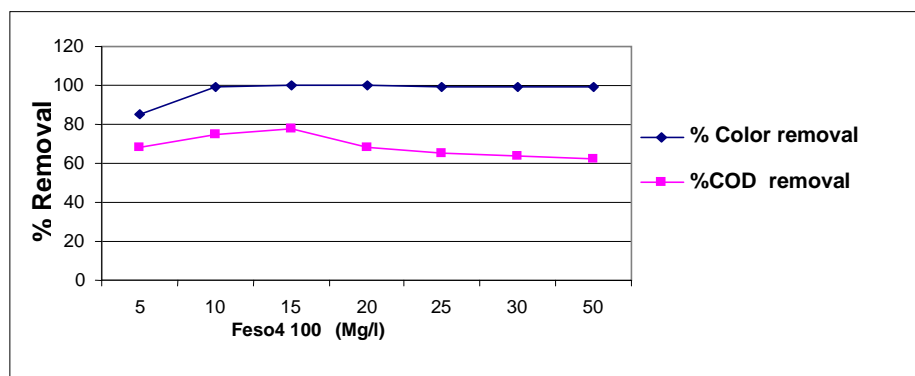
$$\text{Removal (\%)} = (C/C_0)/C_0$$

Where  $C_0$  and  $C$  are the initial and final absorbance or COD values of simulated wastewater, respectively (Süreyya, 2004).

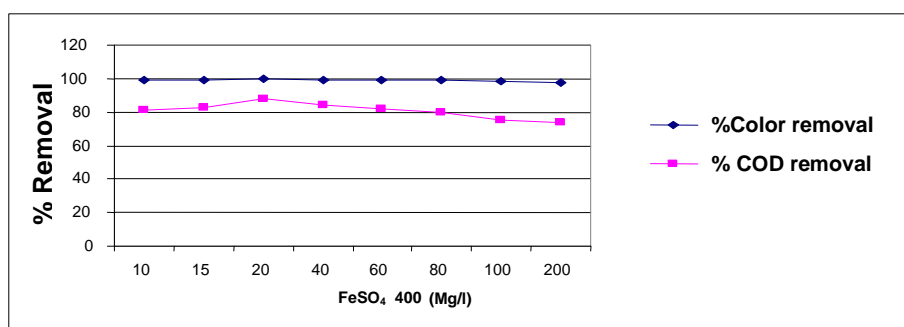
## Results and Discussion

### Effect of $FeSO_4$ concentration

The effect of  $FeSO_4$  concentration on COD removal efficiency for 100 and 400 mg/l of WBA is given in figure 1 and 2.

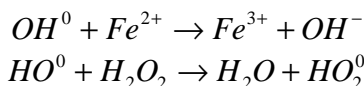


**Figure 1 :** Effect of FeSO<sub>4</sub> concentration on COD and color removal (Color=100 mg/l , pH=3 , H<sub>2</sub>O<sub>2</sub> = 80 mg/l , FeSO<sub>4</sub>= 5-50 mg/l)



**Figure 2 :** Effect of FeSO<sub>4</sub> concentration on COD and color removal (Color=400 mg/l , pH=3 , H<sub>2</sub>O<sub>2</sub> = 100 mg/l , FeSO<sub>4</sub>= 10-200 mg/l)

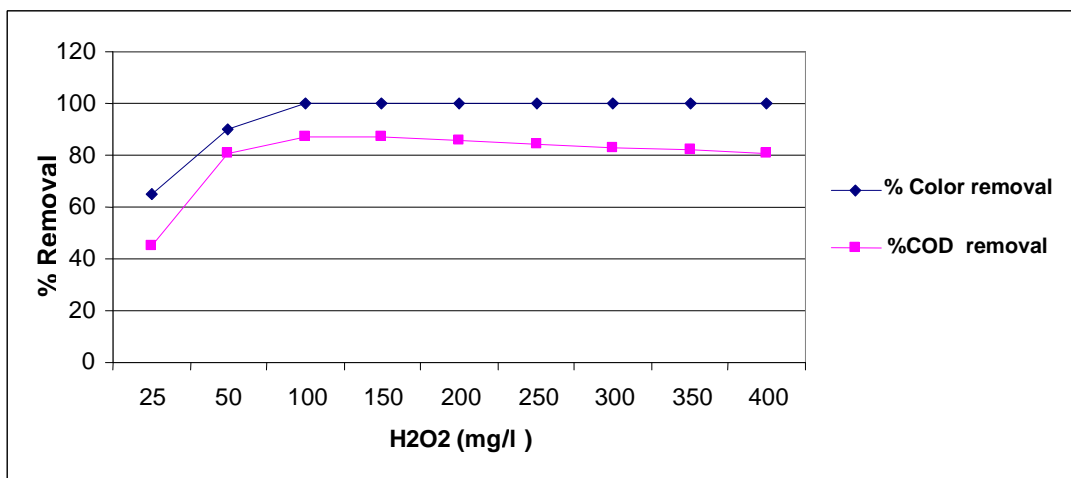
According to figure 1 and 2, maximum COD removal (78%) for 100 mg/l of WBA was obtained in the case of using 15 mg/l FeSO<sub>4</sub> and 80 mg/l of H<sub>2</sub>O<sub>2</sub>. pH and temperature were kept at 3 and 25 C ,respectively . at the same time more than 99% color removal was obtained at all FeSO<sub>4</sub> concentration (10-50 mg/l). Although for 10 mg/l concentration of FeSO<sub>4</sub> color removal was also high as well as using 15 mg/l of FeSO<sub>4</sub> higher hydroxyl radicals produced during FO process resulting in higher COD removal forced us to choose 15 mg/l of FeSO<sub>4</sub> as optimum concentration at which 78% COD removal was obtained. However as seen figure 1 and 2 the COD removal efficiency started to decrease for 20 mg/l dose of FeSO<sub>4</sub>. it may be explained by redox reactions since OH radicals may be scavenged by the reaction with the hydrogen peroxide present or with another Fe<sup>2+</sup> molecule as below .(Benitez.*et al*,2001).



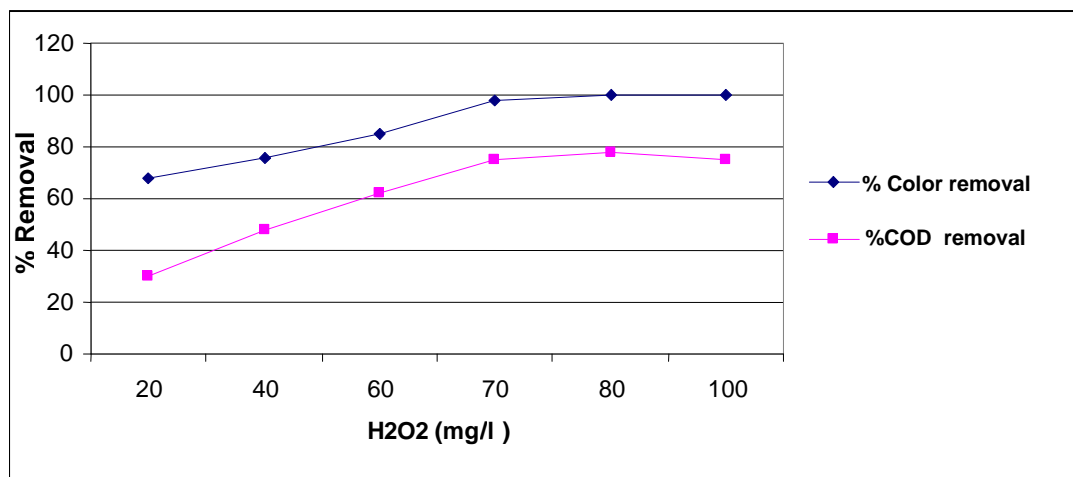
The Fe<sup>2+</sup> formed can react with H<sub>2</sub>O<sub>2</sub> as well as with hydroperoxy radicals with regeneration of Fe<sup>2+</sup> in the solution resulting in decrease in COD removal. For 400 mg/l WBA, the concentration of FeSO<sub>4</sub> was changed between 10 mg/l and 200 mg/l by keeping H<sub>2</sub>O<sub>2</sub> concentration constant as 110 mg/l at ph 3 and at 25 C. Maximum COD removal 87/5% was obtained at 20 mg/l of FeSO<sub>4</sub> concentration. Color removal was more than 99 % at all FeSO<sub>4</sub> concentrations. The same decrease in COD removal after 20 mg/l of FeSO<sub>4</sub> can be explained due to the scavenging effect of over doses of FeSO<sub>4</sub> or H<sub>2</sub>O<sub>2</sub> on OH radicals.

### Effect of h2o2 concentration

The effect of H<sub>2</sub>O<sub>2</sub> concentration on COD removal efficiency for 100 and 400 mg/l of WBA is given in figure 3 and 4.



**Figure 3 : Effect of H<sub>2</sub>O<sub>2</sub> concentration on COD and color removal**  
(Color=400 mg/l , pH=3 , H<sub>2</sub>O<sub>2</sub> = 25-400 mg/l , FeSO<sub>4</sub>= 20 mg/l)

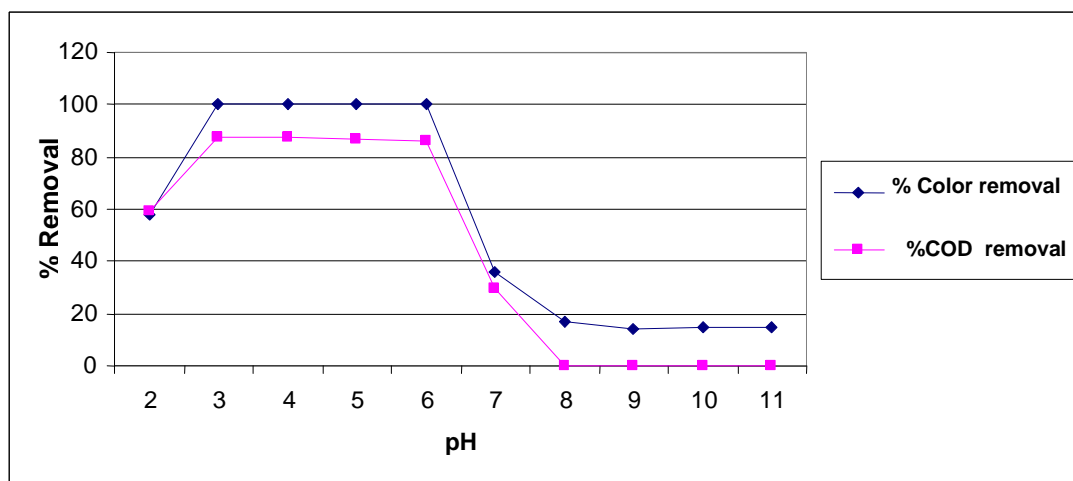


**Figure 4 : Effect of H<sub>2</sub>O<sub>2</sub> concentration on COD and color removal**  
(Color=100 mg/l , pH=3 , H<sub>2</sub>O<sub>2</sub> = 20-100 mg/l , FeSO<sub>4</sub>= 15 mg/l)

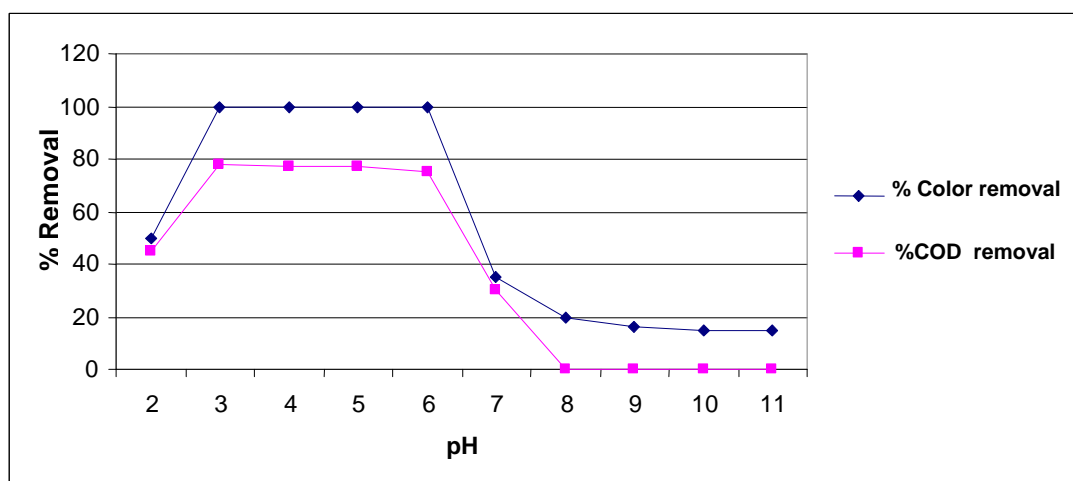
For 100 mg/l WBA color removal efficiency increased by increasing H<sub>2</sub>O<sub>2</sub> concentration from 20 mg/l (68%) to 100 mg/l (99.99%). 80 mg/l of H<sub>2</sub>O<sub>2</sub> was defined as optimum concentration providing 99 % color and 78% COD removals. The results of H<sub>2</sub>O<sub>2</sub> optimization for 400 mg/l of WBA indicated the optimum conditions (H<sub>2</sub>O<sub>2</sub>=110 mg/l , FeSO<sub>4</sub>=20 mg/l ) yielding 87.5% COD removal. Increasing the concentration of H<sub>2</sub>O<sub>2</sub> up to 400 mg/l did not improve cod removal more in turn it decreased to 81% , because of scavenging effect of H<sub>2</sub>O<sub>2</sub> on oh radicals as explained above . (Benitez.*et al*,2001). Color removal efficiency increased by increasing H<sub>2</sub>O<sub>2</sub> concentration from 25 mg/l (65%) to 400 mg/l (99.99%).

### Effect of pH

To determine the optimum pH, pH was changed between 2 -11 as illustrated in figure 6. 78% cod removal was obtained at 3.0 pH for 100 mg/l wba , and the maximum cod removal (87.5 %) was proved at 3.0 pH for 400 mg/l of wba . color removal was more than 99 % between pH 3 and 6.



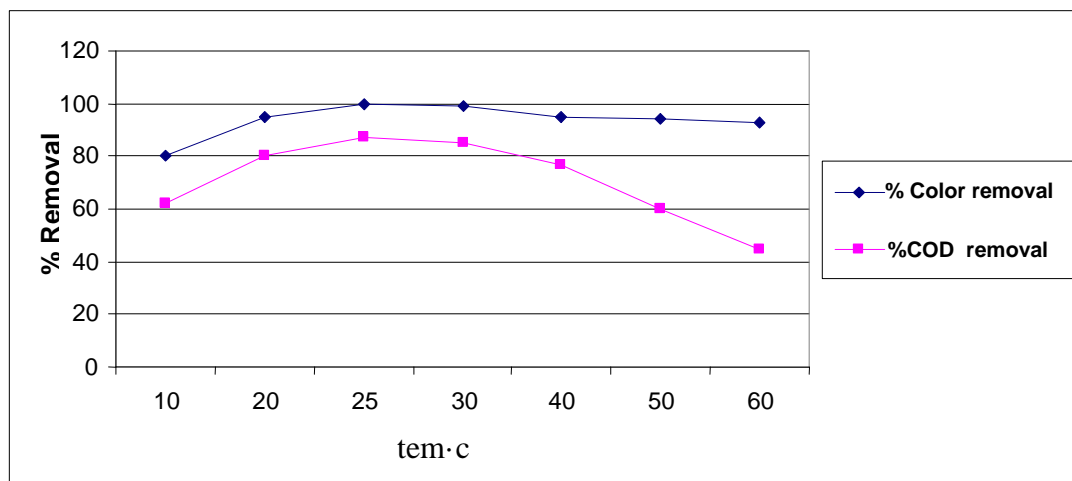
**Figure 6:** Effect of pH on COD and color removal  
(Color=400 mg/l · H<sub>2</sub>O<sub>2</sub> = 100 mg/l · FeSO<sub>4</sub>= 20 mg/l, Time=15 min)



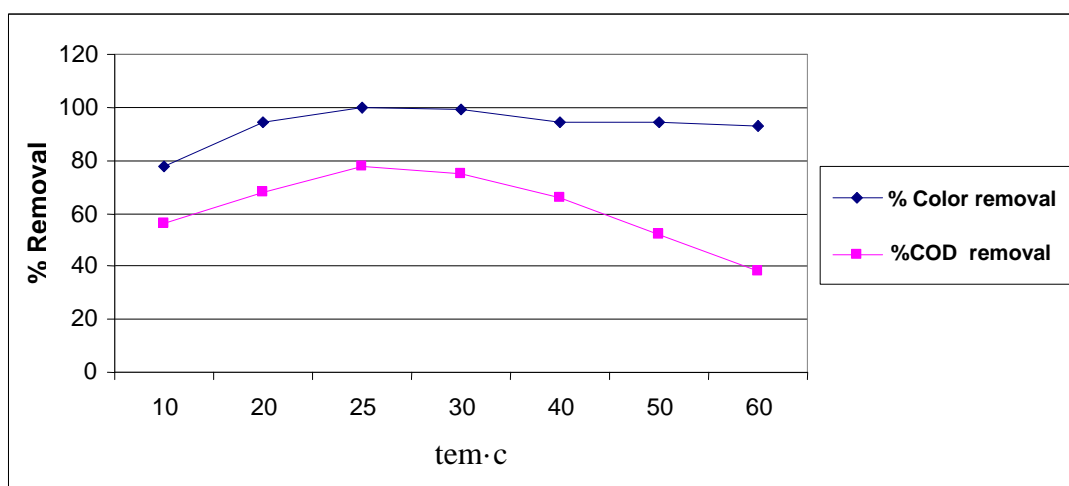
**Figure 7:** Effect of pH on COD and color removal  
(Color=100 mg/l · H<sub>2</sub>O<sub>2</sub> = 80 mg/l · FeSO<sub>4</sub>= 15 mg/l, Time=15 min)

### Effect of temperature

As seen from figure 7, optimum temperature is 25.c at which 78% cod and 99% color removal were obtained for 100 mg/l of wba concentration. The maximum cod removal (87%) for 400 mg/l of WBA was also obtained at 25 c.



**Figure 8:** Effect of temperature on COD and color removal  
(Color=400 mg/l · H<sub>2</sub>O<sub>2</sub> = 100 mg/l · FeSO<sub>4</sub>= 20 mg/l · Time=15 min · pH=3)



**Figure 9:** Effect of temperature on COD and color removal  
(Color=100 mg/l · H<sub>2</sub>O<sub>2</sub> = 80 mg/l · FeSO<sub>4</sub>= 15 mg/l · Time=15 min · pH=3)

As seen from figure 8 optimum temperatures is 25 c at which 78% COD and 99% color removal were obtained for 100 mg/l wba concentration. The maximum cod removal (87%) for 400 mg/l of wba was also obtained at 25c. Highest temperature up to 40 c affected cod removal negatively due to the destabilization of flocks resulting in increased ferrous ions which scavenged oh radicals during fentons reactions (Benitez.et al, 2001).

### Effect of slow mixing time

Maximum COD removal for both dye concentrations (78 and 87.5 %, respectively) were obtained at 20<sup>th</sup> min when mixing time increased up to 30 min COD removal decreased to 65% for 100mg/l of wba due to floc destabilization. Color was removed higher than 99% for all mixing times. Optimum condition determined for each concentration of wba is summarized in table 1 . as shown in table 1 molar ratio between FeSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> was constant.

**Table 1: Optimum condition**

WBA Color (mg/ l)	100 (mg/l )	400 (mg/l )
pH	3	3
H <sub>2</sub> O <sub>2</sub>	80	100
FeSO <sub>4</sub>	15	20
Fe <sup>2+</sup> / H <sub>2</sub> O <sub>2</sub> (molar ratio )	0.023	0.025
H <sub>2</sub> O <sub>2</sub> / color	0.25	0.8
Color Removal %		>99/99 %

Color removal was obtained (higher than 99%) at almost all conditions, absorbance measurements were more indicating for defining the optimum process conditions. Results of this study indicated that the H<sub>2</sub>O<sub>2</sub> requirement seems to be related to initial COD of the sample. The optimum pH determined (3) corresponds the range of 2-11 given for FO process in the previous studies (Smeric, 2004; Xiang –Rong xu, 2004). The temperature affected the COD removal negatively at high degrees. With this in mind it can be dedicated that applying FO process directly to the spent baths having high temperature needs to be evaluated in detail. The method of FO process application in this study with 2 min rapid mixing before slow mixing served as accelerator for formation and the consuming up the radicals in the oxidation reactions resulting in the shortened total reaction time and yielding higher color and COD removal.

### Conclusion

In this study the removal of color and COD of wba water base acrylic was studied using FO process. A systematic approach was followed for the determination of FeSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> concentrations. Effective pH, temperature values which are the important parameters for FO process. The following results can be summarized of this study. Optimum pH, temperature were observed as 3, 25 c for 100 mg/l of wba using 15 mg/l FeSO<sub>4</sub> and 80 mg/l of H<sub>2</sub>O<sub>2</sub>. The pH and temperature values did not change for decolorizing 400 mg/l of wba using 20 mg/l FeSO<sub>4</sub> and 110 mg/l of H<sub>2</sub>O<sub>2</sub>. Thus, increasing the concentration of wba from 100 to 400 mg/l did not change the optimum conditions drastically, especially on the basis of the molar ratio between FeSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>. COD removal efficiency was not affected significantly when concentration of FeSO<sub>4</sub> was increased whereas the change of pH and temperature affected system performance more. TOC measurement is strongly recommended for avoiding the possible interference of H<sub>2</sub>O<sub>2</sub> on COD via scavenging effects on OH radicals produced during FO oxidation which is one of advanced oxidation processes producing hydroxyl radicals.

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