STUDY OF C.I. ACID ORANGE 7 REMOVAL IN CONTAMINATED WATER BY PHOTO OXIDATION PROCESSES

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ABSTRACT

C.I. Acid Orange 7 (AO7) commonly used as a textile dye and could be degraded by UV/ZnO, UV/H_2O_2 and UV/H_2O_2/Fe (III) (photofenton) processes. In the photocatalytic degradation of dye by UV/ZnO process, effect of some parameters such as UV irradiation time, presence of ZnO and UV irradiation, pH, concentrations of ZnO, dye, H_2O_2 and ethanol was examined and first order reaction rate constant was calculated equal to 2.39×10^{-2} min^{-1} at experimental condition. The semi-log plot of dye concentration versus time was linear, suggesting first order reaction. Efficiency of photodegradation process in the absence of ZnO photocatalyst and UV light was small. Increasing the UV irradiation time increased AO7 removal. Ethanol had inhibitory effect on this process. Maximum AO7 removal was seen at neutral pH area. In the UV/H_2O_2 process, effect of some parameters such as presence of H_2O_2 and UV irradiation, amount of H_2O_2, effect of pH and addition of bicarbonate on the efficiency of dye removal were examined. Absence of each of UV irradiation or H_2O_2 decreased AO7 removal efficiency near to zero. Increasing H_2O_2 concentration increased dye removal to some extent but at higher H_2O_2 concentrations, dye removal efficiency did not increase. Increasing pH to value about 9 increased the AO7 removal efficiency and increasing bicarbonate anion concentration decreased it. Rate constant of AO7 removal by this process was calculated to be equal to 4.221×10^{-1} min^{-1} at experimental condition. Also, the order of UV/ H_2O_2/Fe (III) > UV/ H_2O_2 > UV/Fe (III) > H_2O_2/Fe (III), was seen for AO7 removal efficiency of these processes. Increasing Fe (III) and oxalate concentration increased dye removal efficiency.

1. INTRODUCTION

Toxic dyes are very important in the viewpoint of environmental protection because they produce toxic aromatic amines and have other harmful environmental effects. They are widely used and have low degradation rate by aerobic treatment processes. Many of dye molecules are resistant to biological degradation (Baouer *et al.*, 2001). Dying industries use approximately 10000 dyes and pigments, which are manufactured 7×10^5 ton per year, 50 % of them are azo dyes (Zhu *et al.*, 2000). Approximately 15 % of synthetic toxic dyes are discharged into the wastewaters.

C.I. Acid Orange 7 (AO7) or Orange II (C.I. 15510) is a mono-azo acidic dye, which is soluble in water and has a tautomeric structure as figure 1. AO7 is widely used in dying, weaving, tanning and paper industries (Mark *et al.*, 1978) and therefore, it has wide environmental effects.
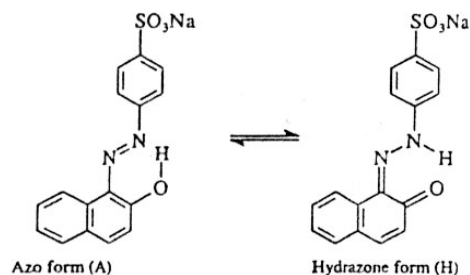
Figure 1. Tautomeric structures of A O7

Advanced oxidation processes (AOPs) are the methods in which OH^o radicals are produced. OH^o is a powerful oxidizing agent and completely degrades the most of organic pollutants. It is possible to use some metallic oxides and sulfides as catalysts for these processes. These photocatalysts have a completed valence band and an empty conduction band. When one electron is excited from valence band to conduction band the photocatalytic property appears. Yeber *et al.* (1999) studied the photocatalytic treatment of paper pulp bleaching wastewater using O_2/ZnO/UV process and the results showed that the biodegradability of the wastewater increases. Lizama *et al.* (2002) studied the photocatalytic degradation of reactive blue 19 on ZnO and TiO_2. They found that after 30 min UV exposure time, the removal is completed. They also found that in the case of RB19, the efficiency of ZnO is much more than TiO_2, which is due to more production of H_2O_2 on the surface of ZnO. Daneshvar *et al.* (2004) studied the photocatalytic removal of acid red 14 on ZnO. They also studied the removal of rhodamin-B using UV/TiO_2 and UV/ZnO processes (Daneshvar *et al.*, 2003; 2004).

Biological and also, photochemical removal of AO7 on TiO_2 have been previously studied. But, because of wide consumption of AO7 in dying industries and regard to its environmental aspects, it is important to find a more efficient method to treat the wastewaters polluted with AO7. Advanced oxidation processes are good alternatives/complements for conventional methods and it will be beneficial to be studied. In this work we studied the effect of different parameters on AO7 removal by UV/ZnO, UV/H_2O_2, UV/H_2O_2/Fe (III) (photofenton) and UV/H_2O_2/Fe (III)/oxalate processes.

2. EXPERIMENTAL

All experiments in this work were done in a batch photoreactor system consists of a wooden chamber with aluminum foil cover, UV-C lamp (30 W, Philips), magnetic stirrer and a 500 ml beaker as reaction chamber. The system was cooled using air stream.

Proper volumes of AO7 stock solution were mixed with photocatalyst (ZnO) or chemical reagents (H_2O_2, Fe (III), oxalate) and were diluted to 100 ml. These suspensions were agitated in the absence of light for 30 min to reach the equilibrium. Absorbance of this solutions with proper pH (pH meter: Metrohm 744) was determined at λ=485 nm. 50 ml volumes of each of these solutions were transferred into the 500 ml beakers as reactor chambers and were agitated and exposed by UV-C irradiation with the intensity of 0.55 klx[1] (illuminometer: Leybold Heraeus 53050). Then, the absorbance of taken samples was measured spectrophotometrically (spectrophotometer: double beam, Perkin Elmer 550 SE). Dye concentration of the samples was calculated using a calibration plot of absorbance vs. concentration. The conversion fraction of dye was calculated using the equation 1:

$$X = \frac{c_0 - c}{c_0} = 1 - \frac{c}{c_0} \tag{1}$$

in which X was conversion fraction, c was dye concentration (ppm) at time t (min) and c_0 was initial dye concentration (ppm).

The used AO7 had technical grade from Rang-Azar Co., ZnO as photocatalyst and NaOH and H_2SO_4 for pH adjustment were from Merck. Sodium bicarbonate, ethanol, oxalic acid, iron (III) chloride and sodium oxalate as reagents all were from Merck, too. H_2O_2 30 % as oxidizing agent was from Fluka.

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[1] Kilolux: Unit of illuminance

3. RESULTS and DISCUSSION
3.1. UV/ZnO process
3.1.1. Effect of UV irradiation time
Figure 2 shows the effect of UV irradiation time on AO7 removal efficiency for AO7 concentration of 20 ppm and ZnO concentration of 110 ppm. It can be seen that after 150 min irradiation time, conversion fraction of dye reached to 1. This is because of increasing the excited ZnO particles with time and therefore, increasing the number of produced OH^o radicals and positive holes (Daneshvar *et al.*, 2004).

3.1.2. Determination of apparent rate constant of AO7 removal by UV/ZnO process
Using the data, which have been reported in section 3.1.1, it can be seen that plot of Ln c vs. irradiation time (min) was linear and therefore, the reaction belonged to first order rate system (Figure 3) and k value was calculated equal to 2.39×10^{-2} min^{-1}.

3.1.3. Effect of ZnO and UV light
Three solutions of AO7 with the concentration of 20 ppm were prepared. One of them had 160 ppm ZnO and was irradiated with UV light for different times. Another one had 160 ppm ZnO but was not exposed. The other one had not ZnO but exposed to UV light for different times. The results are shown in figure 4 and it can be seen that in the absence of UV light or ZnO, the conversion fraction was near to zero. This shows that both of UV light and ZnO photocatalyst were necessary to efficiently remove the AO7 from solution. In the absence of these two factors, the production of OH^o radicals is negligible which causes low dye removal efficiency.

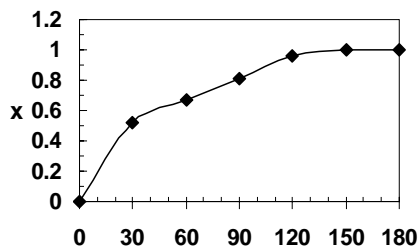Figure 2. conversion Fraction vs. irradiation time in UV/ZnO process, [AO7]=20 ppm, [ZnO]=110 ppm
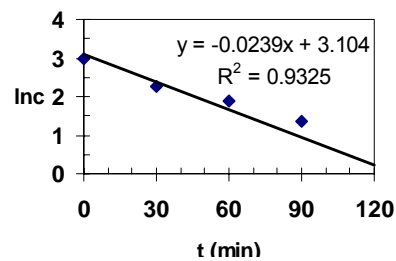

Figure 3. Ln [AO7] vs. irradiation time (min) plot to find first order rate constant of UV/ZnO process, using the data of section 3.1.1

3.1.4. Effect of pH
Figure 5 shows the effect of different pH values on AO7 removal at 60 min irradiation time and AO7 concentration of 20 ppm and ZnO concentration of 160 ppm. It can be seen that removal efficiency was maximum at neutral pH area. At acidic pH values ZnO is dissolved as Zn^{2+} and has not any photocatalytic properties, and at basic pH values, ZnO particles have negative surface charge and repulse dye anion-molecules (Daneshvar *et al.*, 2004). Negative charge on dye molecule originates from SO_3^- group substituted on aromatic ring.
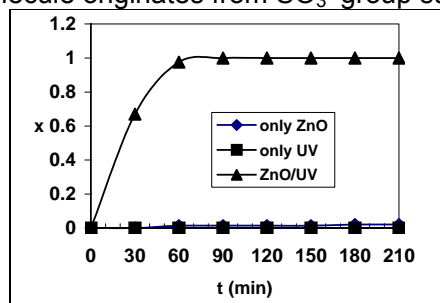

Figure 4. Effect of ZnO and UV irradiation in UV/ZnO process, [AO7]=20PPM,[ZnO]=0 or 160 ppm
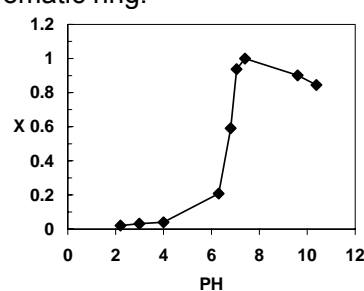

Figure 5. Effect of pH on AO7 removal in UV/ZnO process, [AO7]=20 ppm, [ZnO]=160 ppm, t = 60 min

3.1.5. Effect of ethanol concentration on AO7 removal

Figure 6 shows inhibitory effect of ethanol on AO7 removal after 60 min UV irradiation time at AO7 concentration of 20 ppm and ZnO concentration of 160 ppm. It can be seen that increasing ethanol concentration, decreased the efficiency of AO7 removal because ethanol quenches OH^o radicals.

3.1.6. Effect of ZnO concentration on AO7 removal

Figure 7 shows the effect of ZnO concentration on AO7 removal during 180 min UV irradiation time at AO7 concentration of 20 ppm and ZnO concentration ranging from 100 ppm to 200 ppm. It can be seen that 160 ppm concentration of ZnO had the maximum dye removal efficiency about 100% after 90 min irradiation time. This result could be explained by increasing photocatalitically active sites of ZnO with increasing its concentration up to 160 ppm. Further increasing ZnO concentration increases solution turbidity and decreases UV light penetration into the solution and therefore, the removal efficiency decreases (Kartal *et al.*, 2001).
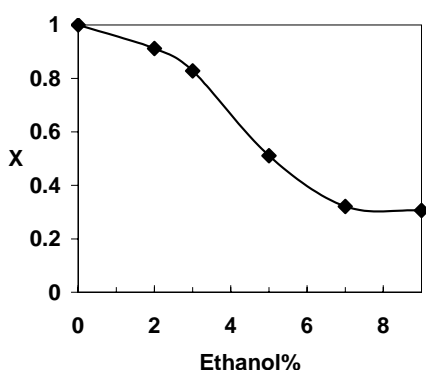

Figure 6. Effect of ethanol concentration on conversion fraction of AO7 in UV/ZnO process, [AO7]=20 ppm, [ZnO]=160 ppm, t=60 min
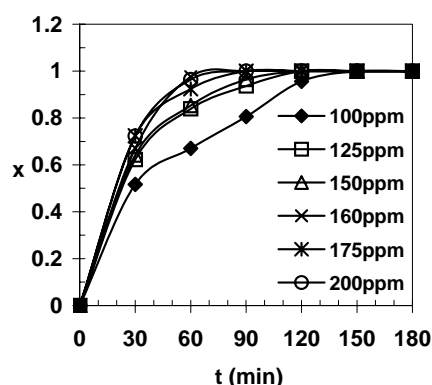
Figure 7. Effect of ZnO concentration on AO7 removal in UV/ZnO process, [AO7]=20 ppm

3.1.7. Effect of AO7 concentration on its removal

Figure 8 shows the effect of AO7 concentration on its removal during 150 min UV irradiation time at AO7 concentration ranging from 20 ppm to 60 ppm and ZnO concentration of 160 ppm. It can be seen that increasing dye concentration from 20 ppm to 60 ppm decreased removal efficiency of dye in the solution. The AO7 solution with a high initial concentration substantially absorbs more UV light than that with a low initial concentration, as a result, the number of photons becomes less due to the decrease intensity of UV light, leading a decrease in the formation of hydroxyl radicals and this, decreases AO7 removal efficiency (Daneshvar *et al.*, 2004).

3.1.8. Effect of H_2O_2 concentration on AO7 removal

Figure 9 shows effect of H_2O_2 concentration on AO7 removal during 20 min UV irradiation time at AO7 concentration of 20 ppm and ZnO concentration of 160 ppm. It can be seen that increasing H_2O_2 concentration up to 10 mmol l^{-1}, increased AO7 removal efficiency to more than 90%, which is due to capture of photochemically released electrons on the photocatalyst surface. This increases OH^o concentration and so, AO7 removal efficiency increases (Daneshvar *et al.*, 2004).

$$H_2O_2 + ZnO(\bar{e}) \rightarrow 2OH^O + ZnO \tag{2}$$

At higher concentrations, H_2O_2 quenches OH^o radicals and so, dye removal efficiency decreases (Daneshvar *et al.*, 2004).
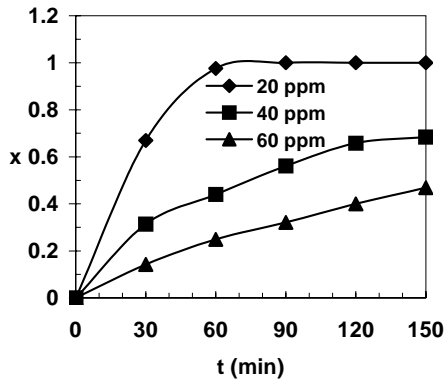
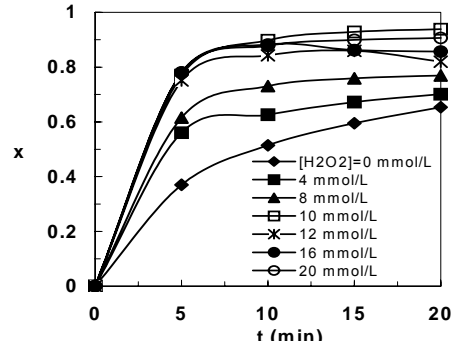Figure 8. Effect of AO7 concentration on its removal in UV/ZnO process, [ZnO]=160 ppm

Figure 9. Effect of H_2O_2 concentration on AO7 removal in UV/ZnO process, [AO7]=20 ppm,[ZnO]=160 ppm

3.2. UV/H_2O_2 process

3.2.1. Effect of UV light and H_2O_2 on AO7 removal

Figure10 compares the AO7 removal efficiency between three solutions with 20 ppm AO7, one in presence of UV light and H_2O_2 (0.5 mmol l^{-1}), another one in absence of H_2O_2 and the other one in the absence of UV irradiation. It is obvious that absence of each of UV irradiation or H_2O_2, decreased production of OH^o radicals and therefore AO7 removal efficiency was near to zero.

3.2.2. Effect of different concentrations of H_2O_2 on AO7 removal

Figure 11 shows the effect of different concentrations of H_2O_2 on AO7 removal after 12.5 min UV irradiation time at AO7 concentration of 20 ppm. It can be seen that increasing H_2O_2 concentration, increased AO7 removal efficiency but at high H_2O_2 concentrations, the produced OH^o radicals react with each other and therefore, AO7 removal efficiency did not more increase.
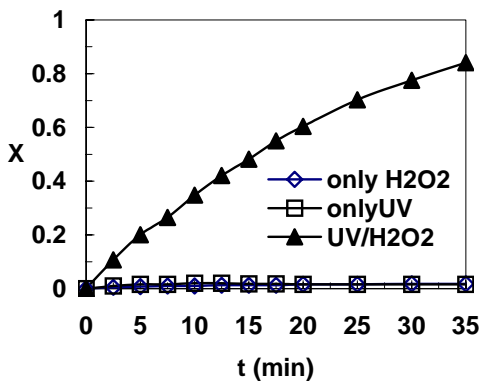

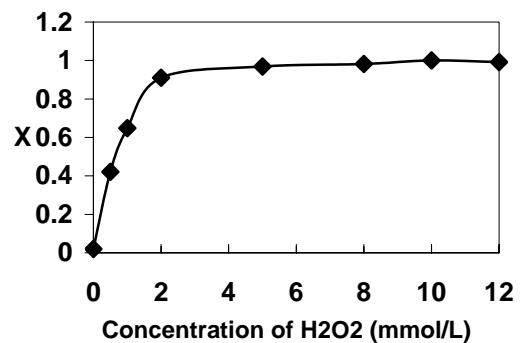Figure 10. Effect of presence of H_2O_2 and UV irradiation on AO7 removal in UV/H_2O_2 process, [AO7]=20 ppm

Figure 11. Effect of concentration of H_2O_2 on AO7 removal in UV/H_2O_2 process, [AO7]=20 ppm, t=12.5 min

3.2.3. Effect of bicarbonate anion on AO7 removal efficiency

As it is shown in figure 12, increasing bicarbonate concentration up to 2 mmol l^{-1} in a solution with AO7 concentration of 20 ppm and 10 mmol l^{-1} of H_2O_2, decreased AO7 removal efficiency because bicarbonate reacts with OH^o as follow (Pirkanniemi and Sillanpaa, 2002):

$$OH^o + HCO_3^- \rightarrow H_2O + CO_3^{o-} \tag{3}$$

$$OH^o + CO_3^{2-} \rightarrow OH^- + CO_3^{o-} \tag{4}$$

3.2.4. Effect of pH on AO7 removal

Figure 13 shows the conversion fraction of AO7 in a solution with its initial concentration of 20 ppm and concentration of H_2O_2 equal to 10 mmol l^{-1}, at basic pH values was more than acidic solutions. Since, at higher pH values according to equations 5 and 6, some excess OH^o radicals are produced as followings:

$$H_2O_2 \leftrightarrow H^+ + HO_2^- \qquad K_a = 2.7 \times 10^{-12} \qquad (5)$$

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2^- + \dot{O}H \qquad (6)$$

3.2.5. Further studies

Study of other parameters such as UV irradiation time and initial dye concentration, found that there were trends similar to ones about UV/ZnO process. Also, determination of apparent rate constant of AO7 removal by UV/H_2O_2 process in an experiment with AO7 concentration of 20 ppm and H_2O_2 concentration of 10 mmol l^{-1} with a method similar to one about UV/ZnO process, gave K=4.221×10^{-1} min^{-1}.
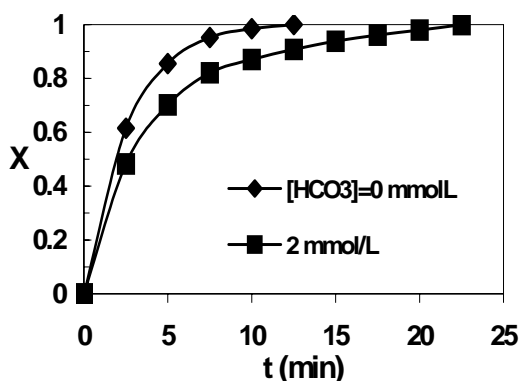

Figure 12. Effect of bicarbonate on AO7 removal in UV/ H_2O_2 process, [AO7]=20 ppm, [H_2O_2]=10 mmol l^{-1}
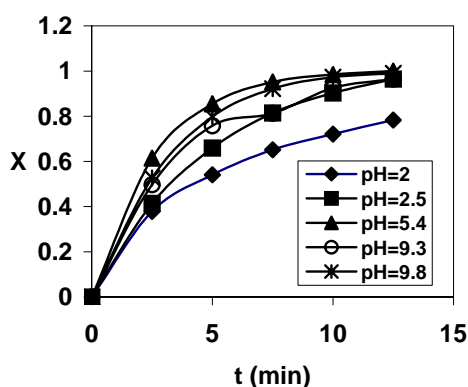
Figure 13. Effect of pH on AO7 removal in UV/H_2O_2 process, [AO7]=20 ppm, [H_2O_2]=10 mmol l^{-1}

3.3. UV/H_2O_2/Fe (III) and UV/ H_2O_2/Fe (III)/ oxalate processes

3.3.1. Effect of UV irradiation, Fe (III) and H_2O_2 on AO7 removal

Figure 14 shows the effect of UV irradiation, Fe (III) and H_2O_2 on conversion fraction of AO7 in a 20-ppm dye solution. The concentrations of H_2O_2 and Fe (III) were 5 and 0.1 mmol l^{-1}, respectively when they were present in the solution. It is obvious that the photofenton (UV/ H_2O_2/Fe (III)) process had the highest AO7 removal efficiency, and UV/ H_2O_2, UV/Fe (III) and H_2O_2/Fe (III) processes had lower efficiencies, respectively. This order can be related to the amount of OH^o radicals produced in each process.

3.3.2. Effect of amount of Fe (III) on AO7 removal

Figure 15 shows the effect of Fe (III) on AO7 removal in a solution with dye concentration of 20 ppm and H_2O_2 concentration of 5 mmol l^{-1} and UV irradiation time of 10 min. It shows that increasing the concentration of Fe (III), increased AO7 removal efficiency, up to 100 % at Fe (III) concentration of 0.08 mmol l^{-1}. This is because of increasing OH^o radicals in the presence of Fe (III) but at high Fe (III) concentrations, the increase of a brown turbidity in the solution during the photooxidation process, which hinders the absorption of the UV light required for the process, and consumption of OH^o by high amounts of Fe (II) produced, decreases the concentration of OH^o radicals which decreases dye removal efficiency (Daneshvar *et al.*, 2006).

3.3.3. Effect of oxalate anion on AO7 removal

Figure 16 shows the effect of different oxalate concentrations on AO7 removal in solutions with dye concentration of 20 ppm, H_2O_2 concentration of 5 mmol l^{-1} and Fe (III) concentration of 0.08 mmol l^{-1}. It can be seen that increasing the oxalate concentration, increased AO7 removal efficiency, which is due to increasing the OH^o concentration (Safarzadeh *et al.*, 1997).
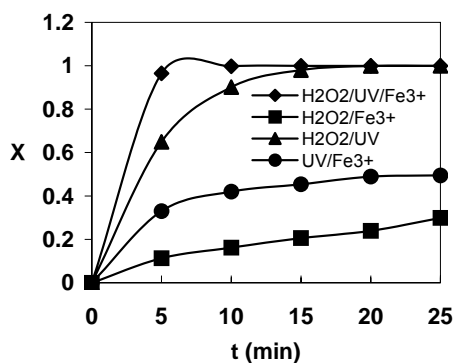

Figure 14. Effect of H_2O_2, Fe (III) and UV irradiation on AO7 removal, [AO7]=20 ppm

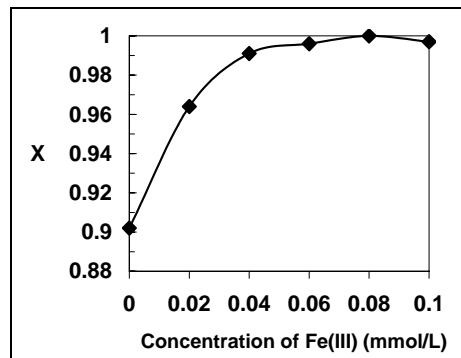*Figure 15.* Effect of Fe (III) on AO7 removal in UV/H_2O_2/Fe (III) process, [AO7]=20 ppm, [H_2O_2]= 5 mmol l^{-1}, t =10 min
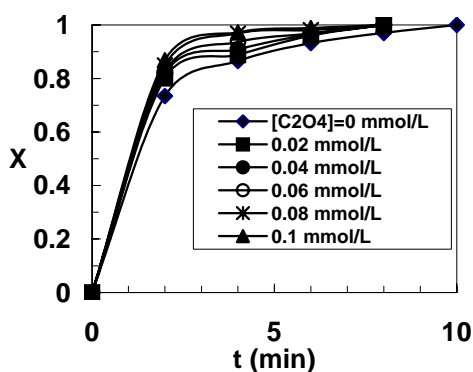
Figure 16. Effect of oxalate on AO7 removal in UV/H_2O_2/Fe (III) process, [AO7]=20 ppm, [H_2O_2]=5 mmol l^{-1}, [Fe (III)]=0.08 mmol l^{-1}

4. CONCLUSIONS

Advanced oxidation processes of UV/ZnO, UV/H_2O_2, UV/H_2O_2/Fe (III) and UV/H_2O_2/Fe (III)/oxalate systems were efficient methods to remove AO7 from aqueous solutions. From the data which were obtained in the experimental conditions it is obvious that:

- In UV/ZnO process, increasing the UV irradiation time increased the AO7 removal. This process belonged to first order rate system. In this system, absence of each of ZnO or UV irradiation decreased AO7 removal efficiency near to zero. Increasing ZnO concentration first increased dye removal efficiency but after some extent, removal efficiency decreased. Also H_2O_2 had similar effect to ZnO but with different mechanism. Maximum AO7 removal efficiency was seen in neutral pH area, and increasing ethanol concentration decreased removal of dye.
- In UV/H_2O_2 process the absence of each of UV irradiation or H_2O_2 decreased AO7 removal efficiency near to zero. Increasing H_2O_2 concentration increased dye removal to some extent but at higher H_2O_2 concentrations dye removal efficiency did not more increase. Increasing pH to values about 9, increased AO7 removal efficiency. This process belonged to first order rate system, too. Increasing bicarbonate anion concentration decreased AO7 removal efficiency.
- This order: UV/ H_2O_2/Fe (III) > UV/ H_2O_2 > UV/Fe (III) > H_2O_2/Fe (III), was seen for AO7 removal efficiency and increasing Fe (III) and oxalate concentration increased dye removal efficiency.

ACKNOWLEDGEMENT

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