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EFFECT OF TEMPERATURE ON FENTON OXIDATION OF YOUNG LANDFILL LEACHATE: KINETIC ASSESSMENT AND SLUDGE PROPERTIES

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ABSTRACT
Treatment of young landfill leachate, collected from municipal solid waste site of city of Konya, was investigated by using the Fenton process. The leachate itself showed the characteristics of pH 7.25, COD 38.2 g L^{-1} and BOD_5 22 g L^{-1}. Ratio of BOD_5 to COD with 0.58 indicates that leachate can be defined young. Fenton oxidation of landfill leachate was expressed in two-stage process, where a fast initial reaction (H_2O_2/Fe^{2+}) was followed by a much slower one (H_2O_2/Fe^{3+}). Overall kinetics can be described by a second-order rate equation followed by zero-order one. The kinetic studies were undertaken at the different temperatures and reaction rates increcesed by increasing temperature. The apparent kinetic constants at 303 K are k = 3.16 x10^{-3} L g^{-1} min^{-1} and k_0 = 0,171 g L^{-1} min^{-1}, respectively. Fenton reagents effectively degraded the leachate organics and most of the degradation was completed within 30 minutes for all temperatures. The performance of Fenton process was not only presented as a COD removal but also expressed as the amount of generated sludge and its properties. Sludge properties were revealed with Capillary Suction Time (CST) and Sludge Volume Index (SVI). The minimum CST value was obtained at the optimum molar ratio of 4.12 mol/mol and increasing temperature resulted in a positive effect on CST values. All SVI values were significantly low which indicates that sludge itself had good settling properties.

KEYWORDS Fenton, kinetic, landfill, leachate, sludge properties.

1. INTRODUCTION

Solid waste landfill is the most common way to eliminate municipal solid waste and still has great importance in waste management all over the world. Leachate is one of the main problems in the landfill sites due to its considerable amounts of organic matter, ammonia and total Kjeldahl nitrogen (TKN), heavy metals, chlorinated organic compounds and inorganic salts. Therefore, Leachate treatment is an important issue that has been undergoing for several years and a universal solution has not been offered yet.

There are several methods that can be used for the treatment of leachate. Aerobic, anaerobic and anoxic processes are some of the biological methods for leachate treatment and usually used together (Agdag and Sponza 2005; Castillo *et al*., 2007; Yilmaz *et al*., 2012). Air stripping and adsorption are major physical methods whereas coagulation, flocculation and chemical oxidation are chemical treatment ones especially effective for COD removal from landfill leachate (Derco *et al*., 2010; Morais and Zamora, 2005; Trebouet *et al*., 2001; Yilmaz *et al*., 2010a; Ilhan *et al*., 2008; Pala and Erden, 2004). Because of high pollutant concentration in leachate, a single method is not sufficient to meet the standards for discharging into the sewer system or the receiving body. The methods often require combined techniques which are designed as modular or multistage units depending on the treatment of pollutants which vary in concentration over the years. The Solid Waste Control Act of Turkey requires that leachates should be collected and treated properly in order to protect the ground and surface waters. Since the characteristics of leachate depend on the nature of the waste on landfill, it is difficult to use a standard treatment method for all landfill leachates. Therefore, leachate characterization has to be identified for the selection of the appropriate treatment method (Durmusoglu and Yilmaz, 2006).

Fenton process is one of the advanced oxidation processes where iron and hydrogen peroxide are major chemicals. Generally, Fenton oxidation process is composed of four steps which are pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. The main factors affecting the efficiency of the Fenton process can be summarized as reaction pH, dosages of Fenton's reagent, addition modes of reagents and temperature (Zhang *et al*., 2005). Fenton process has been extensively studied in recent years and the results indicate this process to be one of the most cost-effective alternatives for leachate treatment (Wu *et al*., 2011).

This process produces ·OH radicals (a strong and nonselective oxidant) from catalytic H_2O_2 decomposition by means of Fe^{2+} at acidic pH. The overall mechanism also involves several secondary reactions. These are regeneration of Fe^{2+} by reaction between Fe^{3+} and H_2O_2 and competitive scavenging reactions involving Fe^{2+}, H_2O_2, and OH (Zazo *et al*., 2011). Fenton reactions are presented by (Eqs. 1–9) in Table 1.

Table 1. Inorganic Fenton reactions at pH 3 (Duesterberg and Waite, 2006)

Reaction No	Reactions	Rate constant ($m^{-1}s^{-1}$)
1	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$	41.7
2	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} / O_2^{\bullet-} + H^+$	$2.00x10^{-3}$
3	$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} / O_2^{\bullet-} + H_2O$	$3.30x10^7$
4	$Fe^{3+} + HO_2^{\bullet} / O_2^{\bullet-} \rightarrow Fe^{2+} + O_2 + H^+$	$7.82x10^5$
5	$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$	$3.20x10^8$
6	$Fe^{2+} + HO_2^{\bullet} / O_2^{\bullet-} \rightarrow Fe^{3+} + H_2O_2$	$1.34x10^6$
7	$HO_2^{\bullet} / O_2^{\bullet-} + HO_2^{\bullet} / O_2^{\bullet-} \rightarrow H_2O_2 + O_2$	$2.33x10^6$
8	${}^{\bullet}OH + HO_2^{\bullet} / O_2^{\bullet-} \rightarrow H_2O + O_2$	$7.15x10^9$
9	${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$	$5.20x10^9$

Reaction of Fenton oxidation is rather complex. It is difficult to use conventional kinetic approaches to describe the degradation reaction of landfill leachate by using Fenton process due to landfill leachate contains plenty of soluble orgnic matters and inorganic ions at high concentrations (Lema *et al*., 1988).

Wu *et al*., (2011) explained oxidation reaction kinetics for treatment of landfill leachate in Fenton process. Fenton process reactions can be divided two stages, which a fast stage was followed by a much slower one in Fenton process. In the first reaction stage, almost all of the OH* is generated and most of the Fe^{2+} and H_2O_2 are consumed. The second reaction stage can be considered as a series of Fenton-like reactions. So the use of a two-stage reaction is necessary to get a full picture of the process (Wu *et al*., 2011). An appropriate understanding of Fenton reactions allows the development of kinetic models to optimize the performance and efficiency of Fenton process.

One of the important factors is temperature on reaction ratio in kinetic studies. Operating temperature likely increased the reaction rate between hydrogen peroxide and any form of ferrous/ferric iron, thus increasing the rate of generation of oxidizing species (hydroxyl radicals or highvalence iron species). Simultaneously, on the other hand, temperature also influences the inefficient decomposition of hydrogen peroxide into inactive species (water and oxygen).

Guedes *et al*. (2003) reported that, the reaction rate was smaller at 293 K and the efficiency continued to increase at 303 K. They also reported further increase of operating temperature will result in significant ineffciency of H_2O_2 decomposition. However, Hermosilla *et al*. (2009), claims that there was no significant increase in the COD removal when the temperature was increased from 298 to 318 K and COD removal results were constant at about 64%. Zazo *et al*. (2011) reported that increasing operating temperature had possitive effect on the TOC reduction. They found that TOC reduction of almost 80% was achieved at 363 K. Beyond this temperature no significant improvement was observed, although the rate of the process was considerably enhanced. As a result of all this findings, effect of operating temperature on Fenton process performance due to the idea of thermal decomposition of H_2O_2 into O_2 and H_2O_2 has been so far scarcely investigated.

The reaction parameters affecting the COD and color removals such as the dosages of Fenton reagents, initial pH have been discussed in our previous study (Yilmaz *et al.*, 2010b). The aim of this study was to investigate the effect of temperature and reaction time on the performance of the Fenton process. So far, the effect of temperature on reaction kinetics of leachate treated by Fenton process has been scarcely investigated. The performance of Fenton process was not only presented as a COD removal but also expressed as the amount of generated sludge and its properties. Sludge properties were evaluated with CST and SVI.

2. MATERIALS AND METHODS

2.1. Leachate

Leachate was collected from Municipal landfill site, city of Konya, Turkey. The population of the city is about 1 million. Landfill currently occupies 24 ha area with an average height of 8 m over the total area of 350 ha. The average flow rate of leachate is about 100 m^3 d^{-1}. Samples were collected from the active detention pond filled with leachate that is less than 5 years old. They were placed in plastic containers during transportation to the laboratory and stored at 4 ^{0}C in a refrigerator. The composition of the leachate is presented in Table 2. With 0.58 BOD_5/COD ratio and high contents of COD, BOD_5, and alkalinity, the leachate can be classified as “young” (Deng and Englehardt, 2007).

Table 2. Composition of the landfill leachate

Parameter	Value
pH	7.25
Color (Pt-Co)	3510 ± 82
Chemical oxygen demand (COD) (g L^{-1})	38.2 ± 0.34
Biochemical oxygen demand (BOD_5) (g L^{-1})	22 ± 0.19
BOD_5 /COD	0.58
Alkalinity (g L^{-1} $CaCO_3$)	10.25 ± 0.15
Cl (mg L^{-1})	3240
Fe (mg L^{-1})	7.27
Pb (mg L^{-1})	0.204
Cd (mg L^{-1})	0.118
Cr (mg L^{-1})	0.661
Cu (mg L^{-1})	< 0.01
Ni (mg L^{-1})	0.385
Zn (mg L^{-1})	0.177
Mg (mg L^{-1})	698
Ca (mg L^{-1})	139.5

2.2. Analytical Methods

pH, COD, BOD_5, color, chlorine and alkalinity were analyzed in the laboratory using Standard Methods (APHA, AWWA, WEF, 2005). pH measurements were performed by using the WTW Multiparameter 340i. Closed reflux titrimetric method (Method 5220.C) was used for COD analysis. BOD_5, color, and alkalinity were analyzed by 5-day BOD test (Method 5210), spectrophotometer method (Method 2120.C) and titration method (Method 2320 B), respectively. COD, BOD_5, color and alkalinity measurements were performed as three replicates. Heavy metals (Fe, Pb, Cd, Cr, Cu, Ni, Zn) and Ca-Mg measurements were performed by using the Perkinelmer Optima 2200 DV ICP-OES.

The CST test determines the rate of water release from sludge. It provides a quantity in seconds and assesses how quickly the sludge releases its water. To avoid any possible errors CST measurement has been carried out five times per sample and the average of the results was reported. SVI is volume in milliliters occupied by 1 g of a suspension after 30 min settling which is used to monitor settling characteristics of sludge. CST measurements (Method 2710.G) and SVI analyses (Method

2710.D) were performed according to the methods suggested by Standard Methods (APHA, AWWA, WEF, 2005).

2.3. Experimental Procedure

Batch experiments, in which jar test equipment was used for mixing and operated at 120 rpm, were set up in 500 ml beakers. At predetermined time intervals, 5 ml of homogenized sample was taken from the beakers. Sufficient amount of MnO_2 was added (Guclu *et al*., 2011) into these samples and H_2O_2 residual was checked by using Test Strips (Merck Merckoquant Peroxide Test) (Ustun *et al*., 2007). pH was kept between 7.5 and 8.0 to prevent H_2O_2 interference on COD analysis. The solutions were filtrated with 0.45 µm glass fiber filter and analyzed COD. Acidic and alkaline conditions were provided using 3 M sulfuric acid and 10 M sodium hydroxide and checked with a pH-meter. Granular ferrous sulfate ($FeSO_4.7H_2O$), H_2O_2 (35% w/w), manganese (IV) oxide, NaOH, and H_2SO_4 98% of AR were supplied by Merck.

Optimum pH was 3 and Fenton reagents were determined as 2 g L^{-1} Fe^{2+} and 5 g L^{-1} H_2O_2 in our previous experiment (Yilmaz *et al*., 2010b). In order to the effect of operating temperatures (288, 293, 298 and 303 K) and reaction times (up to 120 min) on process performance a number of experiments were conducted. All experimental runs were performed at atmospheric preasure. Properties of the Fenton sludge were revealed with different H_2O_2/Fe^{2+} molar ratios and different temperature applications.

3. RESULTS AND DISCUSSION

3.1. Effect of Reaction time

The effects of different reaction times and temperatures on Fenton process is illustrated in Figure 1. Optimum COD removal (55.7%) was obtained at 30 min reaction time while the effluent COD decreased to 16.94 g L^{-1}, when the temperature was 298 K. After 30 min, the increase in the COD removal efficiency became insignificant and only around 1% increase was observed. Zhang *et al*. (2005) observed similar results and COD removal efficiency in their study was significant for the first 20 min. Therefore, the optimum reaction time was set up as 30 min.

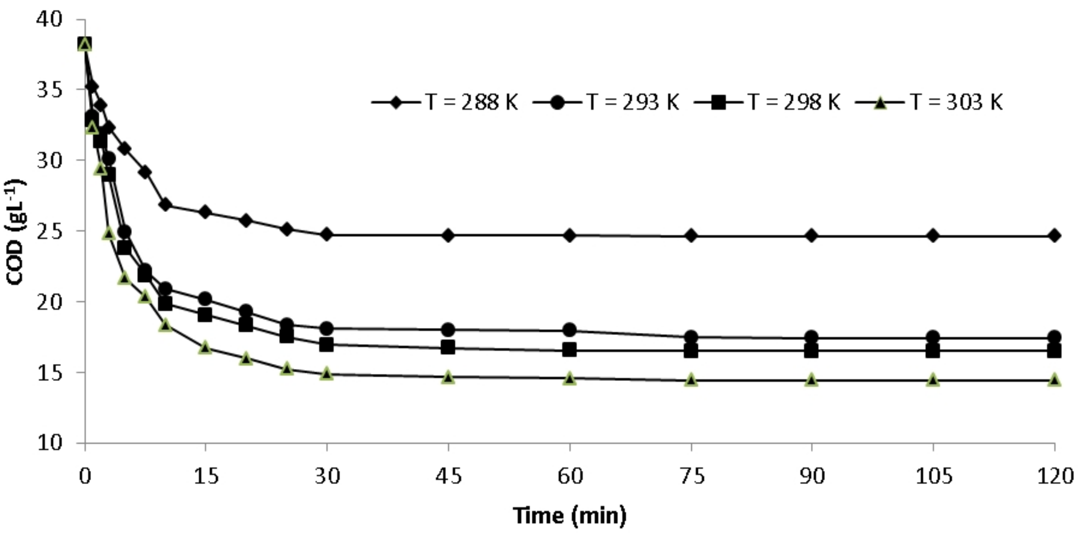

Figure 1. Evolution of the COD concentration for different reaction temperature

3.2. Effect of operating temperature on COD removal

Temperature is one of the important factor influencing catalytic oxidation reaction rates in Fenton. Results show that COD removal efficiency, affected by temperature and increases by increasing temperature. With an initial COD of 38.2 g L^{-1}, COD removal efficiency rise from 35.3% to 61.1% by increasing the temperature from 288 K to 303 K in the first 30 min. When the temperature increased from 288 to 293 K, the COD removal efficiency was increased further 17.3% and increase of temperature from 293 to 303 K the COD removal efficiency was increased only 8.5%. Increasing operating temperature had a favorable effect on the COD removal. Similar to our results, Zhang *et al.* (2005), claims that COD removal efficiency in landfill leachate treatment increased from 31.6% to 44.8% as temperature increased from 288 to 308 K.

3.3. Effect of operating temperature on reaction kinetic

Many studies can be found in the literature related with the Fenton's process kinetics. Due to the Fenton reaction complexity rate constants vary from studies to studies (Ramirez *et al*., 2009). In spite of the oxidation kinetics complexity, it is often assumed that, under certain conditions, the process mechanism can be significantly simplified (Sun *et al*., 2007).

The decay of the landfill leachate was observed rapidly in the first 10 min for all reaction temperatures. This is followed by a much more slow retardation stage, which was likely due to the depletion of oxidants in the solution (see Figure 1). A number of researchers suggested that the Fenton process should be a simple first-order reaction, while others believe that it could be a second-order reaction. Degradation of organic matter in leachate Fenton's process can be considered in two-stage reactions. These stages are illustrated in Figure 2A and 2B.

First stage (Fe^{2+}/H_2O_2), which is faster than second one (Fe^{3+}/H_2O_2) since ferrous ions react with hydrogen peroxide. This is a well-known behavior; ferrous ions react very quickly with hydrogen peroxide to produce large amounts of hydroxyl radicals (Malik and Saha, 2003). The rate of oxidation, during the second stage, is slower than the one during first stage due to the slow production of Fe^{2+} from Fe^{3+} (Ramirez *et al*., 2005).

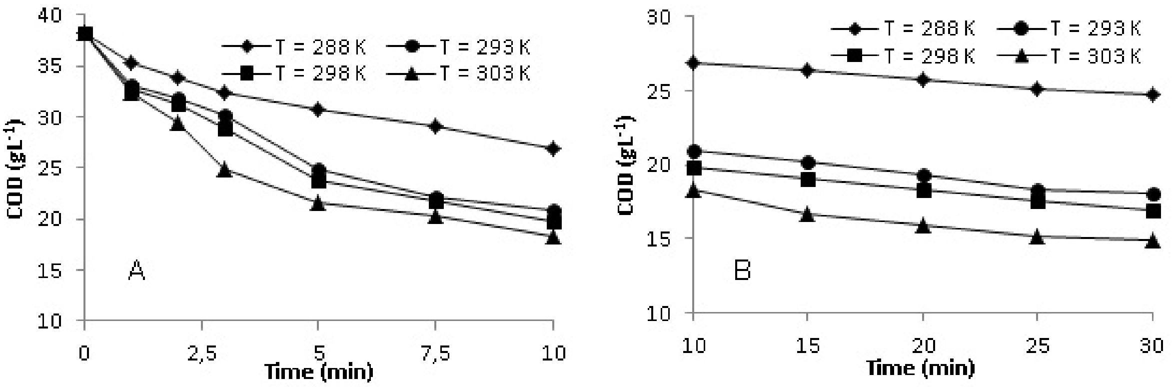

Figure 2. A) Evolution of the COD concentration in first stage B) Evolution of the COD concentration in second stage

In order to determine the oxidation kinetics of landfill leachate by Fenton Process, the kinetic parameters were studied for different reaction times from 1 to 10 min for the first stage reactions and for the second stage reaction times ranging from 10 to 30 min.

Statistically the regression of the data, was conducted for zero order kinetic (Eq. 7), for the first order kinetic (Eq. 8) (Gulkaya *et al*., 2006) and for second order kinetic (Eq. 9) (Argun *et al*., 2010) at two reaction steps.

$$C_t = C_o - k_0 t \quad (7)$$

$$\ln C_t = \ln C_o - k_1 t \quad (8)$$

$$\frac{1}{C_t} = \frac{1}{C_0} - k_2 t \quad (9)$$

where; C_o is the initial COD concentration of landfill leachate (g L^{-1}), C_t is the effluent COD concentration of landfill leachate at time *t*. k_0 (g L^{-1} min^{-1}) k_1 (min^{-1}) and k_2 (L g^{-1} min^{-1}) are the rate constants of zero-order, first-order and second-order kinetic equations, respectively.

Second order kinetic models provided better R^2 values than zero and first-order kinetic for first stage of Fenton process while zero-order kinetic models possessed better results in second stage of Fenton process. R^2 values for different temperature at both Fenton process stages are given in Table 3. Kinetic plots for both stages for different temperature are illustrated in Figure 3 and Figure 4.

Table 3. R^2 values at different temperature for both Fenton process stages

Temperature / Type of Kinetic	288 K		293 K		298 K		303 K	
	1. Stage	2. Stage	1. Stage	2. Stage	1. Stage	2. Stage	1. Stage	2. Stage
Zero Order	0.85	0.99	0.84	0.98	0.82	0.99	0.67	0.93
First Order	0.91	0.98	0.92	0.96	0.91	0.97	0.81	0.92
Second Order	0.95	0.94	0.97	0.96	0.97	0.95	0.92	0.88

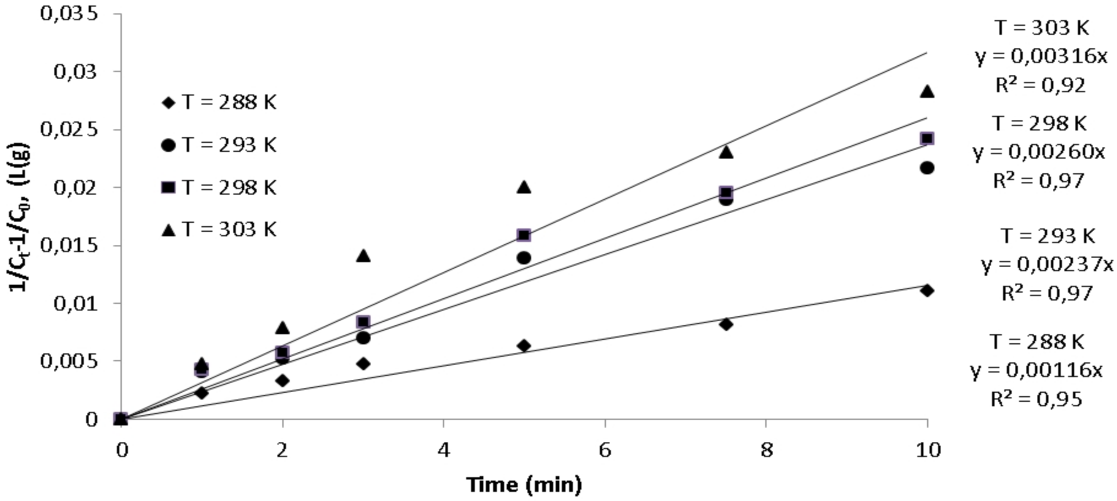

Figure 3. Second order kinetic plots for different temperature in first stage

During the first stage the apparent kinetic constant obtained by linear regression analysis are 1.16×10^{-3} L g^{-1} min^{-1}, 2.37×10^{-3} L g^{-1}.min^{-1}, 2.60×10^{-3} L g^{-1} min^{-1}, 3.16×10^{-3} L g^{-1} min^{-1} for the temperature of 288 K, 293 K, 298 K and 303 K, respectively. Kinetic constants increased approximately three times as the temperature increased from 288 K to 303 K.

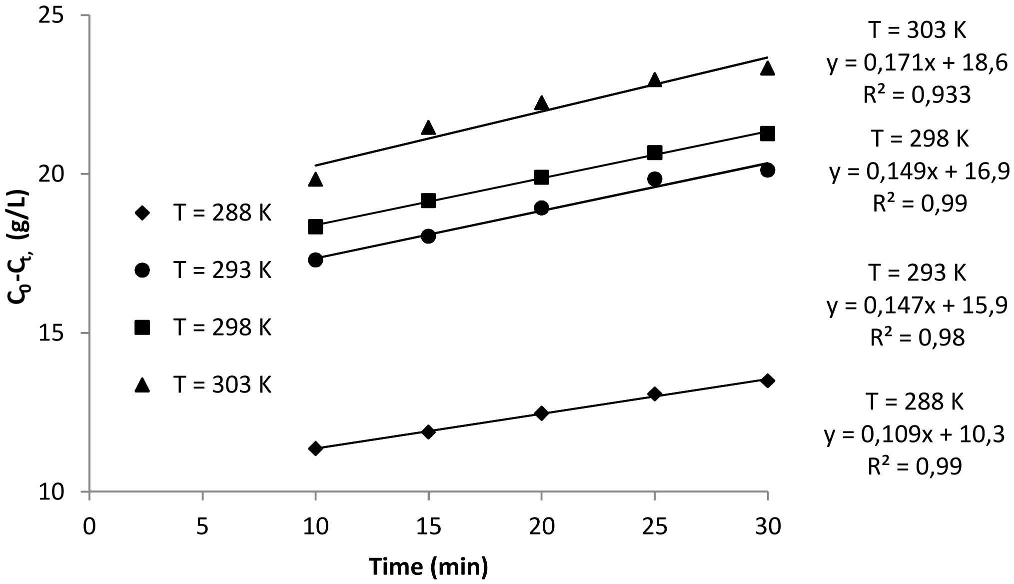

Figure 4. Zero order kinetic plots for different temperature in second stage

Similarly, during the second stage the apparent kinetic constant obtained by linear regression analysis, are 0.109 g L^{-1} min^{-1}, 0.147 g L^{-1} min^{-1}, 0.149 g L^{-1} min^{-1}, 0.171 g L^{-1} min^{-1} for the temperature of 288 K, 293 K, 298 K and 303 K, respectively. By increasing temperature, kinetic constants again increased.

Different reaction temperatures were chosen in order to investigate its effects on the overall kinetics and to allow the determination of the Arrhenius-type dependence of the kinetic constant k on the temperature: The temperature dependence of the kinetic parameters of Fenton treatment was calculated by (Sun *et al*., 2009).

$$\ln k = \ln A - \left(\frac{E_a}{RT} \right) \tag{10}$$

where: k is the rate constant which controls process, A is the Arrhenius constant, T is the solution temperature in K, E_a is the activation energy (kJ mol^{-1}) and R is the ideal gas constant (0.0083 kJ mol^{-1} K^{-1}).

From the corresponding Arrhenius-type plot (Figure 5a) values of A and E_a can be calculated as 2.15 x 10^5 L g^{-1} min^{-1}, 45.14 kJ mol^{-1}, respectively. Temperature and kinetic constant are higly correlated (R^2=0.85). At the second stage of Fenton process, similarly from Arrhenius-type plot (Figure 5b) values of A and E_a can be calculated as 465 g L^{-1} min^{-1}, 19.83 kJ mol^{-1}, respectively. Again temperature and kinetic constant are highly correlated (R^2=0.87).

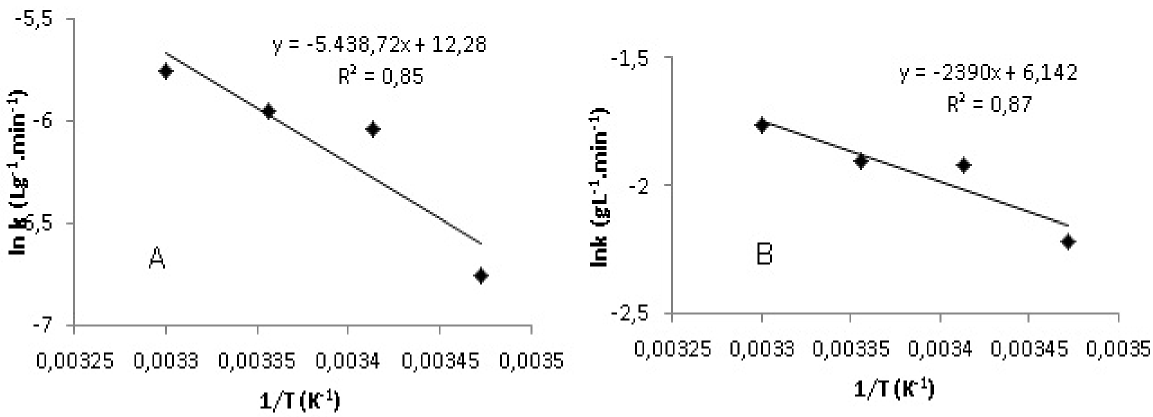

Figure 5. a) Arrhenius-type plot of the apparent second-order kinetic constants (fist stage)
b) Arrhenius-type plot of the apparent zero-order kinetic constants (second stage)

3.4. Sludge Properties

The effect of different Fe^{2+}/H_2O_2 molar ratios on sludge properties SVI and CST, are summarized in Table 4. The SVI parameter indicates sludge settling properties. The CST test provides information regarding how easy it is to separate the water portion from the sludge mixture. This test is very effectively used to determine the optimum conditions for dewatering.

The optimum molar ratio for this study was determined 4.12 mol/mol Fe^{2+}/H_2O_2 where CST reached its minimum value of 21.5s. For all molar ratios, SVI values were significantly low that they could be related to the quality of Fenton's sludge and the settling property. Mahiroglu *et al.* (2009), reported similar SVI values for treatment of copper mine wastewater by Fenton process.

Table 4. Effect of different molar ratios on sludge properties

H_2O_2/Fe^{2+} (mol mol^{-1})	SVI (mL g^{-1})	CST (s)
8.24	12.71	23.6
4.12	15.05	21.5
2.75	20.28	23.1
2.06	18.95	26.6
1.65	26.54	33.6
1.37	28.12	30.7

To study the effect of temperature on sludge properties, Fenton oxidation experiments were conducted at pH 3 for 30 min with 5 g L^{-1} H_2O_2 and 2 g L^{-1} Fe^{2+} concentrations. Dewaterability of sludge improved by increasing the temperature and reached its minimum value at the highest temperature. CST was 26.8 s at 288 K whereas it was 20.4 s at 303 K. Furthermore, temperature had positive effects on SVI values. The SVI value of sludge decreased from 16.63 ml g^{-1} to 13.69 ml g^{-1} by increasing the temperature.

4. CONCLUSION

All the findings obtained from this investigation are summarized as below;

- Organic matter was rapidly degraded by Fenton process. This degradation was generally completed within 30 min with a COD removal of 55.7% at room temperature (298 K).
- Temperature increase had positive effects on both COD removal and the dewaterability of sludge. The kinetic study carried out at temperatures ranging from 288 to 303 K.
- Overall kinetics could be described by a second-order rate equation followed by zero-order one and at the apparent kinetic constants at 303 K are k = 3.16 $x10^{-3}$ L g^{-1} min^{-1} and k_0 = 0.171 g L^{-1} min^{-1}, respectively.
- Corresponding Arrhenius-type plots, activation energy could be calculated for second order reaction (45.14 kJ mol^{-1}) and zero order reaction (19.83 kJ mol^{-1}).
- When the temperature was increased, CST values decreased. Decrease in CST values indicates that the sludge had the ability to be dewatered easily.
- Regardless of the temperature and molar ratios, the SVI values were low. Thus, it can be easily concluded that the sludge had good quality together with good settling properties in landfill leachate treatment through Fenton process.

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