

Degradation of Ethylene Diaminetetra Acetic Acid With Ferrous Ions Using Fenton's Reagent in Absence of Light

Ajay Kumar Mishra¹, S Velmurugan², B S Panigrahi³, Biplob Paul¹, S Chitra¹, S K Khandelwal¹

¹Centralized Waste Management Facility, Bhabha Atomic Research Centre Facilities, Kalpakkam, India

²Water Chemistry Division Bhabha Atomic Research Centre Facilities, Kalpakkam, India

³Indira Gandhi Center for Atomic Research, Kalpakkam, India

Correspondence: Ajay Kumar Mishra, Centralized Waste Management Facility, Bhabha Atomic Research Centre Facilities Kalpakkam, India. E-mail: aju612@gmail.com

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Abstract

Accumulation of deposit corrosion products inside secondary side of steam generator can lead to serious issue for pressurized water reactor in operation. One way to avoid accumulation of these deposits is to perform chemical cleaning which removes certain amount of deposits but this kind of operation generates high amount of liquid waste which contains process chemicals and metal ions in complex state. Oxidation of complexes will render radioactive ions in free state enabling us for further treatment to innocuous level and condition. In waste treatment there are various treatment technologies (advance oxidation process, ozone, hydrogen peroxide, electrochemical oxidation, supercritical water oxidation, electro flocculation etc to remove the accumulated deposit.). In decontamination process removal of the deposits was carried out using EDTA. which complexes the metal ions but it generates secondary waste with EDTA. We have made an attempt to degrade ethylene diaminetetra acetic acid (with ferrous ions) using Fenton's reagent in absence of light. This will free the radioactive ion for further treatment. We have studied different volume of hydrogen peroxide (H₂O₂) and different concentration of ethylene diamine tetra acetic acid (EDTA). Study was also done to find the effect of pH and temp on the degradation of EDTA. In the range of concentration of ethylene diamine tetra acetic acid 400ppm to 22500 ppm % degradation was found to change from 57 to 98% in 180 min. The pH was found to change from 4.0 to 8.2. The temperature was found to change from 298K to 328K. The rate constant of the degradation reaction was found to be in the range 10⁻⁴ to 10⁻³ in temperature range 298K to 328K. Activation energy for degradation reaction was found to be 33-88 KJ/mol.

Keywords: Fenton's reagent, degradation, EDTA

1. Introduction

During the operation of Pressurized Water Reactor, corrosion product and impurities are transported into nuclear steam generator by feed water. To mitigate the accumulation of these deposits, chemical cleaning process was carried out. This process uses a mixture of dilute amino carboxylic/carboxylic acids and reducing/oxidizing agents to remove the oxide film and the activity deposited on the out-of-core surfaces of nuclear power reactors. EDTA is normally used as the main chelating agent in the chemical formulation employed [Rufus A L, 2004]. which generates high amount of liquid waste. Depending upon nature of waste to be treated (composition, concentration) specific waste treatment technology has to be selected and optimized. The presence of EDTA used as decontaminating agent in chemical cleaning process waste can cause complexation of cations resulting in interference with their removal during chemical treatment process, (For example chemical precipitation, ion exchange process etc) [Chitra et al, 1991]. Hence the first step involve oxidation of EDTA complexing radioactive ions, for which methods like chemical, photochemical oxidation are opted. Literature indicates uses of complexes like EDTA, NTA PICLONIC ACID for this purpose. In essence, it is imperative to free the radioactive ions from the complexes to enable further treatment (chemical precipitation, ion exchange, membrane process etc.) depending upon activity level and immobilized the radioactive ion containing the materials (sludge etc). in suitable matrix (Cement, bitumen glass etc) to avoid leaching to environment. In this paper we deal with oxidation of EDTA used as complexing agent in view of its versatility, easy availability well known chemistry etc. Also ethylenediamine tetraacetic acid is not easily biodegradable, scarcely degradable by chlorine and hardly retained by activated carbon filters [Hinck ML, 1997; Brauch HJ et al, 1987]. In the present study, degradation of EDTA by using H₂O₂ alone at alkaline pH in absence of light has been reported. After oxidation resulting effluent almost free of activity can be fixed in cement [Rosikoa K et al, 1998].

2. Material and Methods

2.1 Chemicals and reagents

EDTA (AR grade), hydrogen peroxide (30% w/v), ammonia (10% w/v), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, MgSO_4 and Eriochrome black-T etc procured from E-Merck were used for the experiments.

pH meter of make Elico was used to study the pH during course of reaction. Standard solution of pH 4.6, 7.2 and 10.5 were used for calibrating the pH meter. Spectrophotometer of make (chemeto-2000) was used for the analysis.

Undegraded ethylenediamine tetra acetic acid was estimated titrimetrically using MgSO_4 with Eriochrome black-T as an indicator. The results of the analysis were cross checked spectrophotometrically with Ferric EDTA Method at λ_{max} 358 to 305nm [Aphaetal pp600].

2.2 Experimental

A stock solution of ethylenediamine tetraacetic acid of strength 24500 ppm was prepared in ammonical medium. Same solution was used for preparing ethylenediamine tetraacetic acid solution of different strengths viz 400 ppm, 1600 ppm, 4000 ppm and 22500ppm. The iron EDTA complex is made by taking 400 ppm to 22,500ppm EDTA with one to two gram of iron in form of FeSO_4 .

Two to nine ml of ammonia (10% w/v), was added for dissolving EDTA. 30 to 45 ml H_2O_2 (30% w/v) was added and made up 1 litre. Undegraded EDTA was estimated at interval of 0 to 24 hour using spectrophotometer.

One litre of 400 ppm was taken in beaker which was wrapped with black paper to avoid intrusion of light. 25 ml of hydrogen peroxide (30% w/v) and 1gm of FeSO_4 were added and mixed thoroughly. Temperature was maintained by thermostating the beaker. pH was monitored as function of time, Sampling (10ml) was done every 30 min and undegraded ethylenediamine tetraacetic acid was carried out. Experiments were repeated without controlling the temperature allowing the temperature to change and pH was monitored at regular interval.

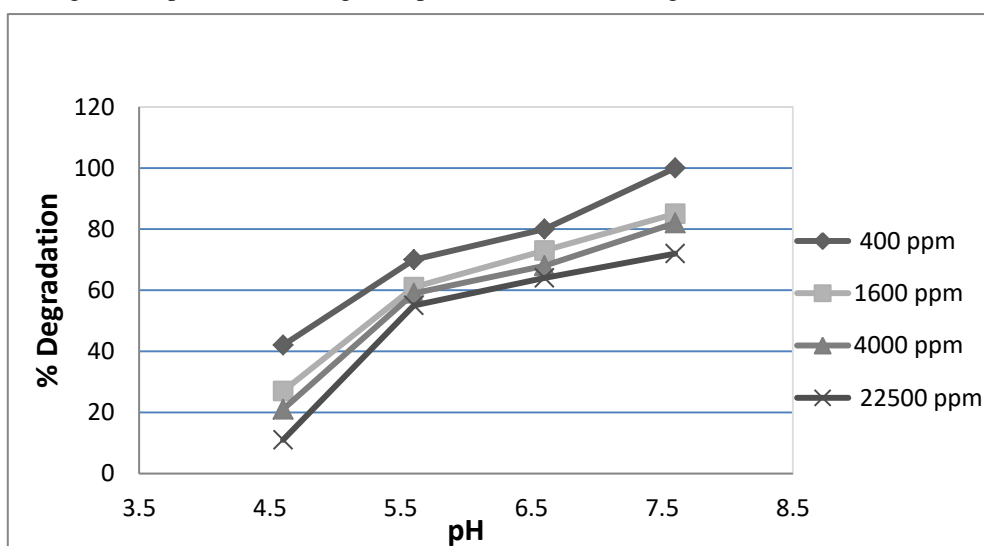


Figure 1. Shows the % degradation of EDTA of different strength as function of pH of the initial solution at 35°C

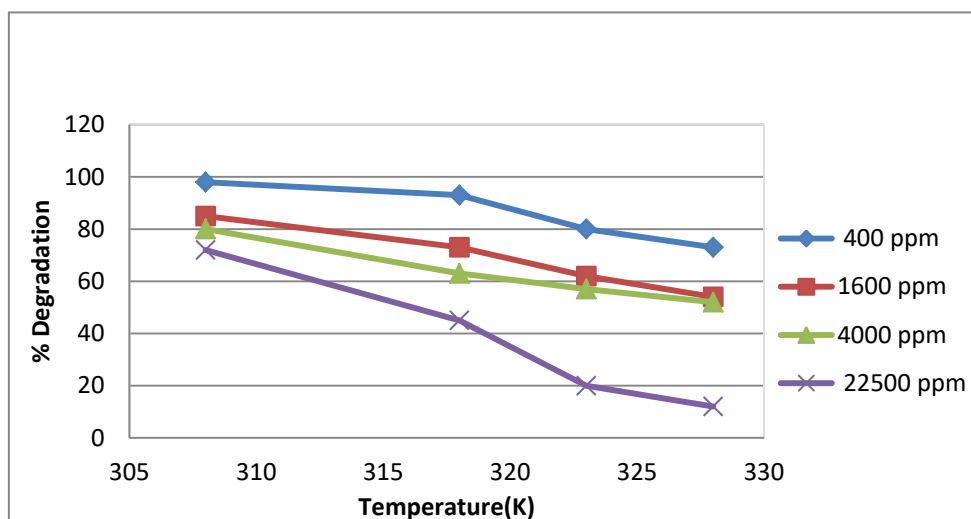


Figure 2. Shows the % degradation of EDTA of different strengths as function of temperature in 180 minutes duration

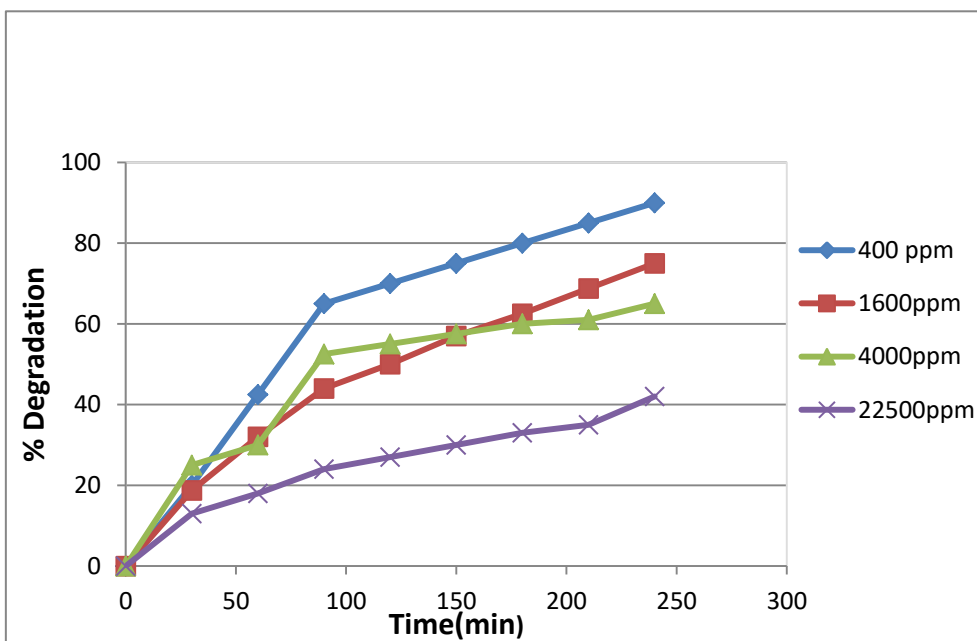


Figure 3. Shows % degradation of EDTA of different strength at function of different time

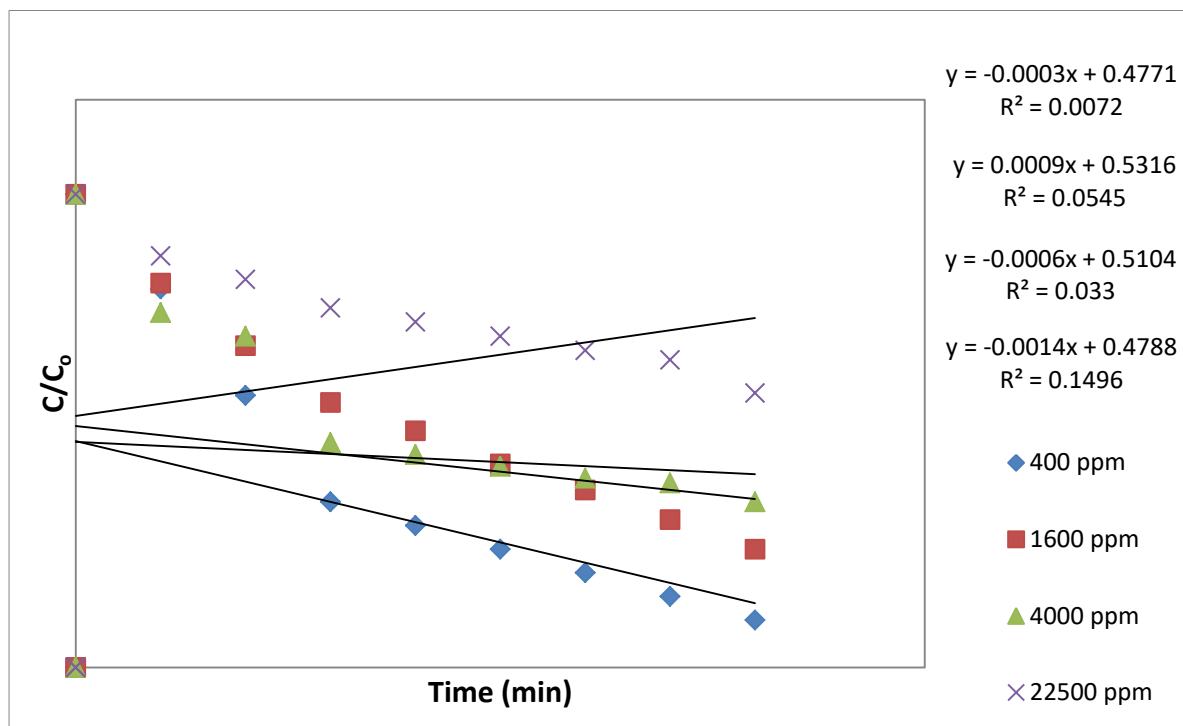


Figure 4. Shows variation of (C/C_0) of EDTA of different strength as function of reaction time. Where C and C_0 are the strength of EDTA at various instants and initial strengths respectively

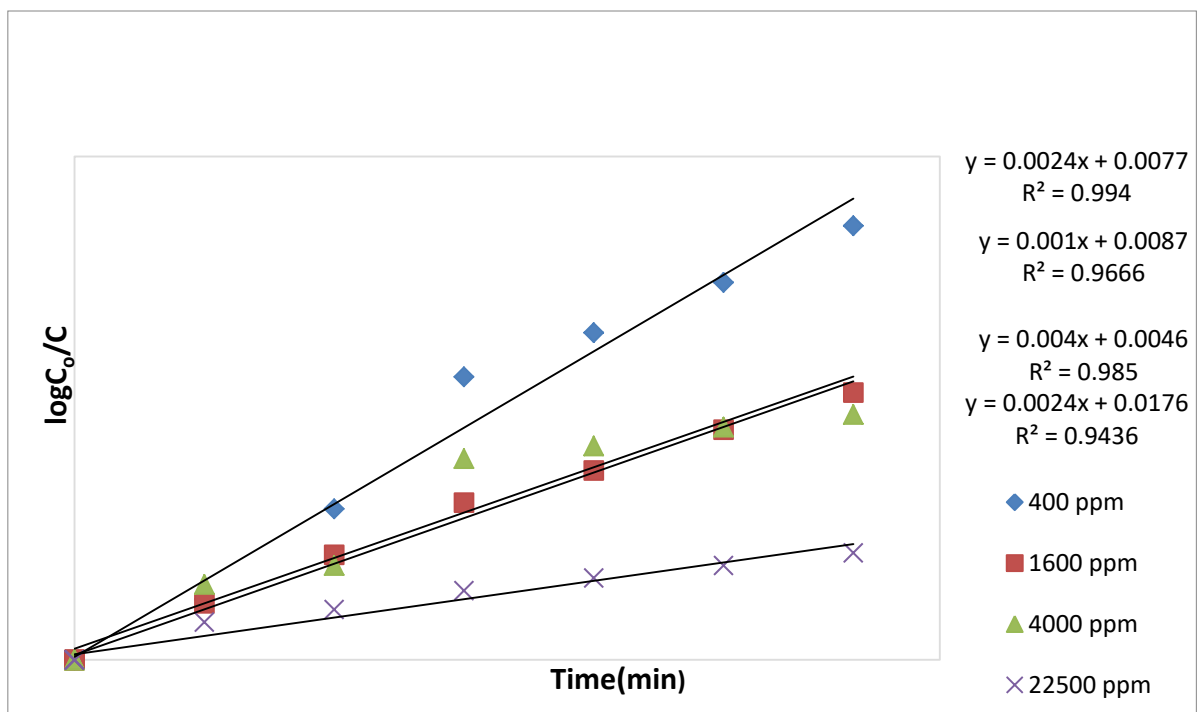
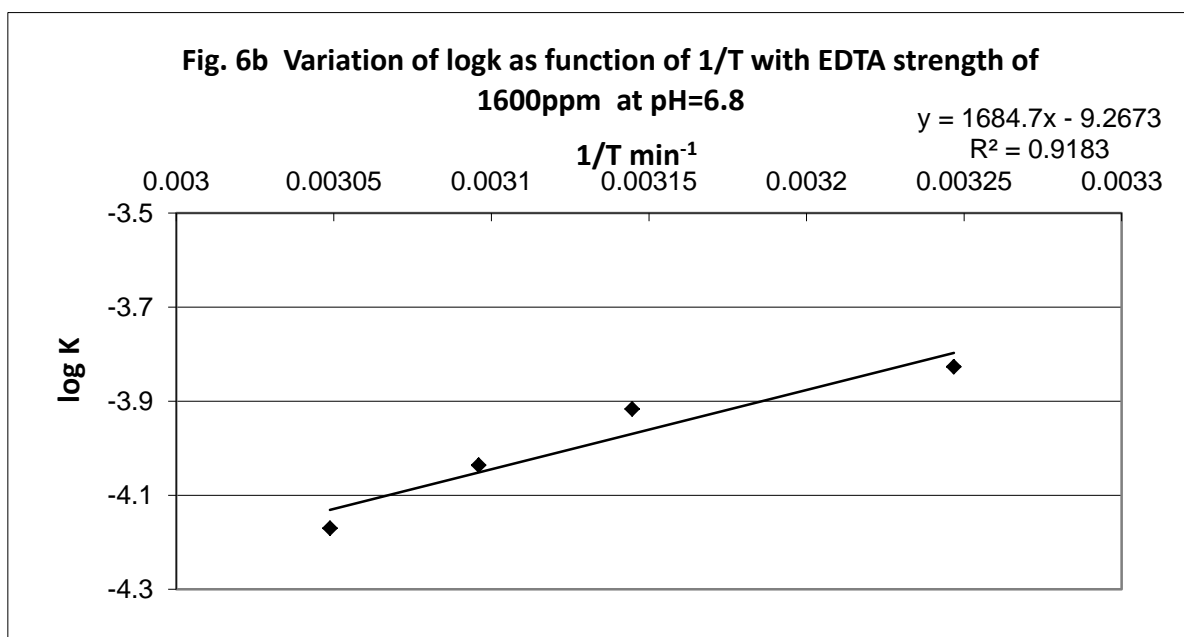
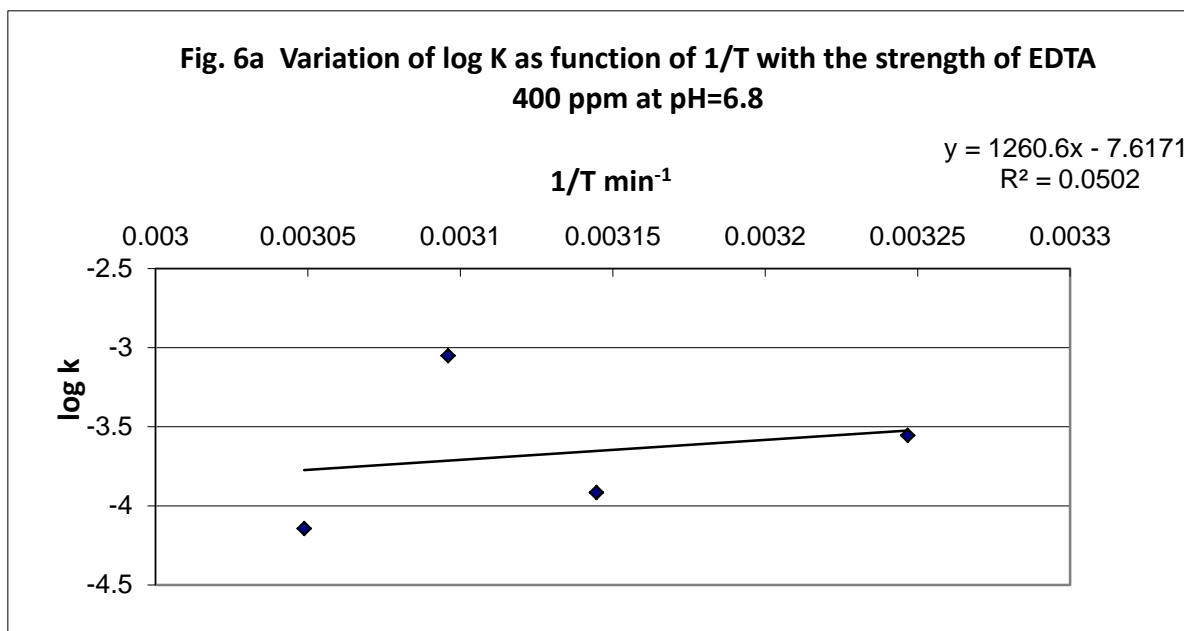


Figure 5. Study of kinetics of degradation of EDTA at various strength

Rate constants of the degradation reactions were computed and $\log K$ was plotted against $1/T$. Fig 6a to 6d shows variation of $\log K$ (rate constant) as function of $1/T$ for EDTA solution of different strength.

6a-6d shows the rate constants for all the concentrations of EDTA at 298 K and $\text{pH}=6.8$.



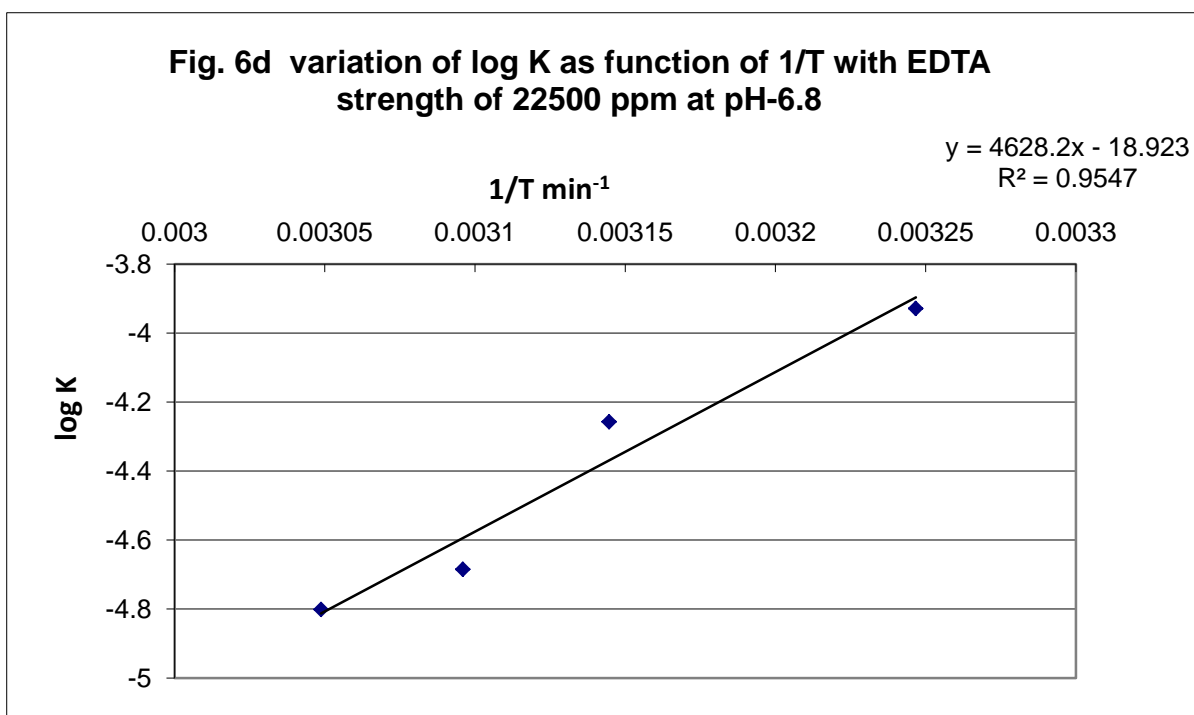
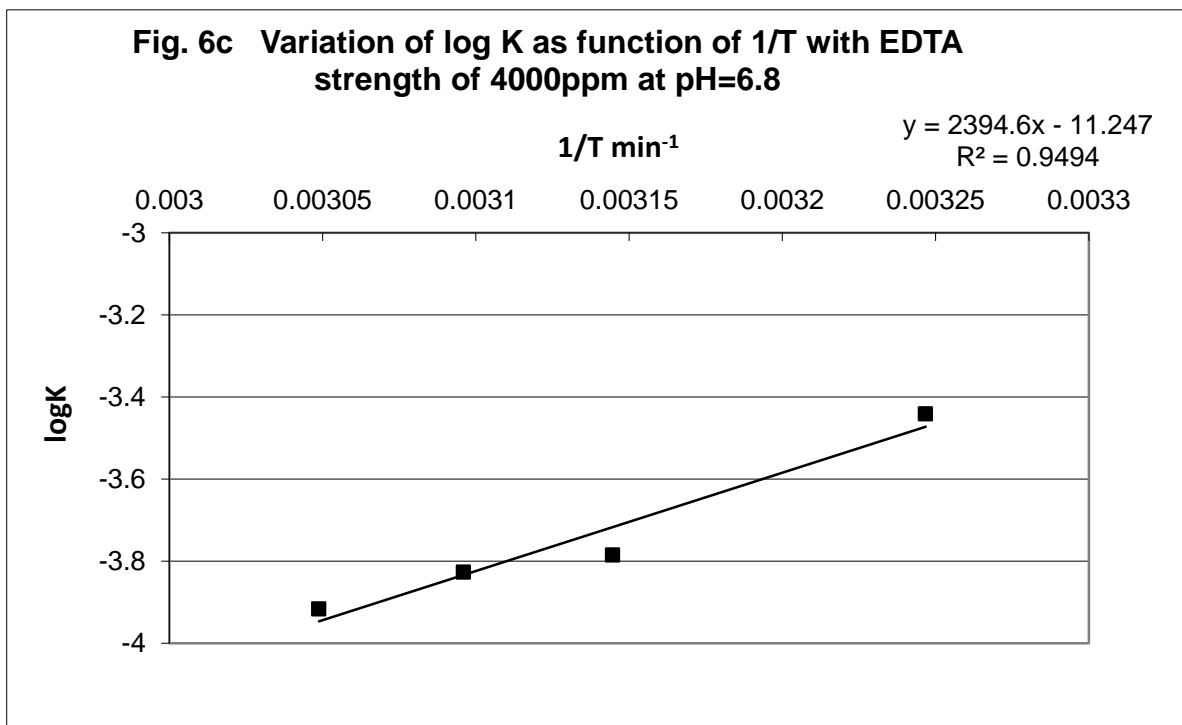


Figure 6. Shows the plot of logK as function of 1/T

Table 1. Activation energy of the degradation reaction was carried out at various strengths of EDTA using Arrhenius equation and table shows the variation of activation energy as function of strength of EDTA (Activation Energy for Degradation of different strength of EDTA in ppm)

Table 1. Activation Energy for Degradation of different strength of EDTA in ppm

SN	Strength (ppm)	Activation energy (KJ/mol)
1	400	32.25
2	1600	40.21
3	4000	45.85
4	22500	88.616

Table 2. which is the variation of pH with % degradation of EDTA pH values of EDTA becomes alkaline with more degradation because of the production of ammonia as the degradation process progresses

Table 2. Effect of pH at 35°C time 180 min

pH	% degradation of 400 ppm	% degradation of 1600 ppm	% degradation of 4000 ppm	% degradation of 22500 ppm
4.6	42	27	21	11
5.6	70	61	59	55
6.6	80	73	68	64
7.6	100	85	82	72

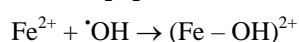
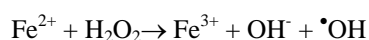
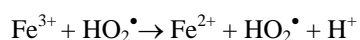
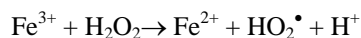
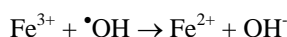
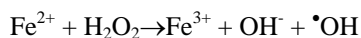
Table 3. shows that the temp rise with time during degradation process under uncontrolled condition. Moreover the increase in temperature is more during degradation EDTA of lower concentration.

Table 3. Effect of uncontrolled Temperature 180 min

Time min	Temperature of EDTA sol of Different Concentration			
	% degradation of 400 ppm	% degradation of 1600 ppm	% degradation of 4000 ppm	% degradation of 22500 ppm
00	28	28	28	28
30	39	36	35	30
60	42	40	38	39
90	44	42	40	40
120	46	44	42	41
150	48	46	44	42
180	50	48	46	44

3. Result and Discussion

The oxidation of EDTA was carried out by the hydroxyl radicals generated from H₂O₂ [Gilbert E et al, 1990; Soresen M, 1995; Tucker MD, 1999; Krapfenbauer K, 1999; Su Y, 1998]. The generation of hydroxyl radical depends upon pH value. Formation of Hydroxyl radical by Using Fenton process occurs according to the following equation.



Since hydroxyl radical react with H_2O_2 the later contribute to hydroxyl scavengers [Ghalyetal, 2001]. There was pH changing to alkaline condition in which case formation of acidic intermediate is possible. This is in agreement with the result obtain by other investigator regarding the mechanism of chemical degradation of EDTA [VirtapohjaJ,1998].Effectively EDTA gets degraded into CO_2 and NH_3 by the Hydroxyl radical generated as in the above equation.

First our Fe^{+2}/H_2O_2 produces hydroxyl radical and recycling the ferrous catalyst increases Fe(II) ions by reduction of Fe(III) to Fe(II). As a result, concentration Fe^{+2} increases and therefore gross reaction is accelerated and hence increase in rate of degradation to 80%.The oxidizing power of hydroxyl radical is more than hydro peroxide radical.

From Figure 1 we find that in the pH value change 4.6 to 7.6 the % degradation was found to increase at all initial strength of EDTA (400 ppm to 22500 ppm) indicating that the alkaline conditions favour the oxidation reactions.

From Figure 2 (which shows the % degradation of EDTA as function of temperature) under controlled temperature condition in period of 180 min time shows that degradation is more at lower temperatures indicating exothermicity of the reaction.

From Table 1 we find that Activation energy in KJ/mol ranges between 32.25 to 88.62 in the concentration range of 400 to 22500 ppm .

From table 2 we find that % degradation decreases with conc with pH ranging 4.6 to 7.6 at 35°C in 180 min duration.

From Table 3 which indicates the increase in temperature as the degradation progresses shows that the temperature increases with more oxidation giving credence to the exothermic nature of the reaction.

Also the Degradation was found to be more with lesser initial concentration of EDTA. The availability of more hydroxyl radicals with lesser initial strength of EDTA aids in the more degradability of EDTA of lower strength.

Figure 4 Which indicates variation of C/C_0 (C strength at various instance and C_0 initial conc.) shows that with more initial conc. degradation is less.

From figure 5 we observe that the plot of $\log(C/C_0)$ as a function of time are straight lines passing through origin indicating first order kinetics of the reaction.

Rate constant at various temperature is carried out using first order rate expression

$$k = \frac{2.303}{t} \log \left(\frac{C_0}{C} \right)$$

Where C_0 - Initial concentration of ethylenediamine tetraacetic acid

C-remaining concentration of ethylenediamine tetraacetic acid

k - Rate constant for different concentration at various temperature.

Rate constant was found to change from 0.0003622 sec^{-1} to .00001212 sec^{-1} in time interval 0 sec to 10800 sec and temperature change was 35°C to 55°C for 400 ppm concentration.

Rate constant was found to change from 0.0001756 sec^{-1} to .0000729 sec^{-1} in time interval 0 sec to 10800 sec and temperature change was 35°C to 55°C for 1600 ppm concentration.

Rate constant was found to change from 0.000149 sec^{-1} to .0000675 sec^{-1} in time intervals 0 sec to 10800 sec and temperature change was 35°C to 55°C for 4000 ppm concentration.

Rate constant was found to change from 0.0001178 sec^{-1} to .0001183 sec^{-1} in time intervals 0 sec to 10800 sec and temperature change was 35°C to 55°C for 22500 ppm concentration.

Rate constant was found to decrease with increase in the temperature confirming further the exothermicity of reaction.

Activation energy was calculated by plotting $\log K$ Vs $1/T$ using equation

$$K = Ae^{-\frac{Ea}{RT}}$$

where R – Gas constantS

Ea – Activation energy

A – Arrhenius constant

The activation energy for the % degradation reaction was carried out by plot $\log K$ vs $1/T$. From the negative(-ve) slope of line the activation energy was calculated, which was found to be 24.18KJ/mole to 88KJ/mole in the concentration

range of 400-22500 ppm of EDTA which is in conformity with result of Ramunas J etal who have reported the activation energy 119.66 KJ/mole for the EDTA oxidation reactions[Ramunas J etal, 2011].

4. Conclusion

Degradation of EDTA using Fenton reagent in absent of light is successfully completed. Under optimized condition, the maximum degradation was accomplished leading to 57% to 98% degradation in concentration range of EDTA 22500ppm to 400 ppm. Also the reaction was found to be exothermic with activation energy of 32.25 KJ/mole to 88 KJ/mol. in the concentration range of 400 to 22500 ppm.

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