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## KINETIC PARAMETER DETERMINATION FOR MTBE DEGRADATION WITH PERSULFATE AND $\text{Ag}^+$ IONS

### DETERMINACIÓN DE PARÁMETROS CINÉTICOS PARA LA DEGRADACIÓN DE ÉTER METIL TER-BUTÍLICO (EMTB) CON PERSULFATO Y IONES DE $\text{Ag}^+$

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#### Abstract

In this work the kinetics parameters of degradation of MTBE with persulfate catalyzed by  $\text{Ag}^+$  ions in aqueous solution at different temperatures and different concentrations of the oxidizing agent and catalyst, were determined. The experimental results indicate that the reaction is much faster in the presence of  $\text{Ag}^+$  ions. The Arrhenius activation energy for the catalyzed reaction is  $69.89 \times 10^3 \text{ J mol}^{-1}$  (1.14 mol  $\text{m}^{-3}$  MTBE, 25.00 mol  $\text{m}^{-3}$   $\text{Na}_2\text{S}_2\text{O}_8$ , 0.30 mol  $\text{m}^{-3}$   $\text{Ag}^+$ ), whereas in the uncatalyzed reaction is  $105.61 \times 10^3 \text{ J mol}^{-1}$  (1.14 mol  $\text{m}^{-3}$  MTBE, 25.00 mol  $\text{m}^{-3}$   $\text{Na}_2\text{S}_2\text{O}_8$ ) in the temperature range of 20 to 40 °C. The findings in this research stated the fundamentals for a novel wastewater treatment.

**Keywords:**  $\text{Ag}^+$  catalyst; kinetics; methyl *tert*-butyl ether; persulfate; thermodynamics; transition state.

#### Resumen

En este trabajo se estudió y se determinaron parámetros de la cinética de degradación de EMTB con persulfato catalizado por iones de  $\text{Ag}^+$  en soluciones acuosas a diferentes temperaturas y diferentes concentraciones de agente oxidante y catalizador. Los resultados experimentales indican que la reacción es mucho más rápida con la presencia de iones  $\text{Ag}^+$ . La energía de activación de Arrhenius para la reacción catalizada es  $69.89 \times 10^3 \text{ J mol}^{-1}$  (1.14 mol  $\text{m}^{-3}$  EMTB, 25.00 mol  $\text{m}^{-3}$   $\text{Na}_2\text{S}_2\text{O}_8$ , 0.30 mol  $\text{m}^{-3}$   $\text{Ag}^+$ ), mientras que la reacción no catalizada es  $105.61 \times 10^3 \text{ J mol}^{-1}$  (1.14 mol  $\text{m}^{-3}$  MTBE, 25.00 mol  $\text{m}^{-3}$   $\text{Na}_2\text{S}_2\text{O}_8$ ) en el intervalo de temperatura de 20 a 40 °C. Los resultados de esta investigación establecen los fundamentos para un novedoso tratamiento de agua residual.

**Palabras clave:** catalizador  $\text{Ag}^+$ , cinética, éter metil ter-butílico, persulfato, termodinámica, estado de transición.

## 1 Introduction

The presence of trace amounts of MTBE in aquifers that supply drinking water to communities is a serious environmental problem in the world. The contamination of aquifers results from spills of reformulated gasoline known as “oxygenated gasoline” that contains alcohol or ether additives, such as, methyl *t*-butyl ether (MTBE), ethyl *t*-butyl ether (ETBE), *t*-amyl methyl ether (TAME), diisopropyl ether (DIPE) and others (Ahmed 2001). These are known as anti-shock additives and are used to enhance the efficiency of the internal combustion engines and reduce the release of pollutants resulting from

incomplete combustion. MTBE is the most commonly used oxygenate additive. It is miscible with gasoline, has a high octane rating and has a low cost of production and transport (Mitani *et al.* 2002). Only in North America, the production and use of MTBE is high, and is considered the second largest organic contaminant of aquifers (Barreto *et al.* 1995). In 1995, the US production of MTBE was 21 billion kilograms. MTBE is persistent in the environment because it is not biodegradable nor readily adsorbed in soil. It is soluble in water, 43 Kg  $\text{m}^{-3}$ , so it is transported with the water flow. MTBE is a health hazard and a potential carcinogen (Li *et al.* 2008). It is easily detected because it has a low odor threshold,  $2.9 \times 10^{-7}$  Kg  $\text{m}^{-3}$ , and taste, 1.34 Kg  $\text{m}^{-3}$  (Cooper *et al.*

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2009). The remediation of MTBE-contaminated sites is a difficult and expensive process. Remediation is not readily accomplished by conventional methods, either *in situ* methods, such as photooxidation and biodegradation treatments (Deeb *et al.* 2000; Volpe *et al.* 2009; Jo and Yang 2010), or *ex situ* methods, such as, adsorption (Ahunbay *et al.* 2008; Arletti *et al.* 2012; Mirzaei *et al.* 2013), physical removal (Rhim and Kim 2000; Lin *et al.* 2002; Wu *et al.* 2008; Zhou *et al.* 2013), chemical processes (Burbano *et al.* 2005; Burbano *et al.* 2008), electrochemical processes (Wu 2007; Hong *et al.* 2007) and advanced oxidative processes (Acero *et al.* 2001; Mezyk *et al.* 2009; Vaferi *et al.* 2014), where the contaminated water is recycled through a reactor (Cervantes *et al.* 2013), or combinations of these treatments.

A remediation process based on the oxidation of MTBE seems attractive because it is chemically oxidized in aqueous persulfate solutions as is the case for many organic compounds (Kolthoff and Miller 1951; House 1962; Berlin 1986; Liang and Su 2009). Huang *et al.* (2002) reported the oxidation of MTBE in dilute aqueous solutions with persulfate anion,  $S_2O_8^{2-}$ , and the reactions showed pseudo first order kinetic behavior in the presence of a large excess of  $S_2O_8^{2-}$ . The initial concentrations in the solutions were  $31.5 \text{ mol m}^{-3}$  of persulfate and  $0.06 \text{ mol m}^{-3}$  of MTBE and the measured rate constant ( $k$ ) was in the range of  $0.1\text{--}5 \times 10^{-4} \text{ s}^{-1}$  (1-14 hour half-lives) and increased with  $[S_2O_8^{2-}]$  concentration, temperature (in the range 20-50 °C) and the acidity of the solution. The  $k$  values decreased with increasing ionic strength. Acetone, *tert*-butyl formate, *tert*-butyl alcohol and methyl acetate were the initial by-products of reaction and were subsequently oxidized completely after 5 - 10 hours.

Selli *et al.* (2004, 2005) reported the degradation of MTBE in water employing either sonolysis at 20 kHz, or photocatalysis on  $TiO_2$ , or simultaneous sonolysis and photocatalysis (i.e. sono-photocatalysis). In all investigated conditions, MTBE concentration decreased according to a first order rate law; under sonication the degradation rate was stirring-dependent.

Another study conducted by Neppolian *et al.* (2002) reported the sonolytic degradation of MTBE at ultrasonic frequency of 20 kHz. As the concentration of MTBE increased from  $2.84 \times 10^{-2}$  to  $2.84 \times 10^{-1} \text{ mM}$ , the observed pseudo-first-order rate constant decreased from  $1.25 \times 10^{-4}$  to  $5.32 \times 10^{-5} \text{ s}^{-1}$ . The rate of degradation of MTBE increased with the increase of the power density of ultrasonicator. In the presence of  $Na_2S_2O_8$  the sonolytic rate of degradation of MTBE

was accelerated substantially. *tert*-butyl formate (TBF) and acetone were found as the major intermediates of the degradation of MTBE. They reported more than 95% degradation of MTBE ( $2.84 \times 10^{-2} \text{ mM}$ ) along with its intermediate products has been achieved during the coupled ultrasound/ $Fe^{2+}/H_2O_2$  method being a viable method for the degradation MTBE within a short period of time than the ultrasound irradiation process.

Boulamanti and Philippopoulos (2008) evaluated the gas-phase photocatalytic oxidation (PCO) of MTBE over illuminated titanium dioxide. They found that the system was sensitive to the oxygen concentration (up to 15% (v/v)) and moisture (optimum value near 45% relative humidity) for 200 ppm MTBE initial concentration. The PCO oxidation proved to be very effective in the decontamination of MTBE-containing gas streams, obtaining conversions over 99%.

There are two main approaches for organic compound degradation by photochemical methods: heterogeneous or homogeneous phase. The heterogeneous phase requires a semiconductor irradiated to promotes electrons from valence band ( $e_{vb}^-$ ) to conduction band ( $e_{cb}^-$ ), generating positive holes ( $h^+$ ).  $e_{cb}^-$  promotes reduction reactions, while  $h^+$  are responsible of the oxidation of water molecules generating  $\cdot OH$ . Most of the time is necessary an electron acceptor (eg.,  $O_2$ ,  $O_3$  etc.) in order to avoid recombination process (Moctezuma *et al.* 2016). On the other hand homogeneous phase consists in the irradiation of oxidizing reagent such as  $H_2O_2$ ,  $O_3$ ,  $S_2O_8^{2-}$ , etc. Nevertheless, the main disadvantages of heterogeneous phase photocatalysis are related to the removal of the nano particulated catalyst after the treatment, as well as the expenses for the acquisition of the irradiation sources with adequate power in both approaches.

Photocatalytic degradation of MTBE has been also reported (Seddigi *et al.* 2014; Seddigi *et al.* 2015; Safari *et al.* 2013; Safari *et al.* 2014) by using different catalyst such as  $Pd/ZnO$ ,  $Fe_3O_4/ZnO$ ,  $TiO_2$ , and doped  $TiO_2$ .

There is reported a glow discharge plasma method for the degradation of MTBE aqueous solutions, is noteworthy to point out that two disadvantages of this technology is the generated plasma zone, which depends on electrode size (higher electrode size a higher plasma zone) and the use of Pt as electrode material. These two features could difficult to scale up this process (Tong *et al.*, 2011).

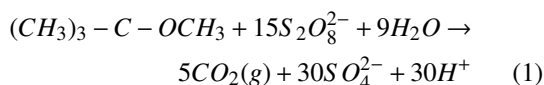
Kim *et al.* (2012) showed that the MTBE

degradation was observed in presence and absence of oxygen by sonolysis, however there are significant differences in the intermediates formed depending upon the media.

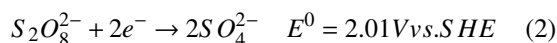
Xu *et al.* (2004) reported the degradation of MTBE by 99% within 2 h at the best experimental conditions,  $[\text{Fe}^{2+}] = 2 \text{ mM}$ ,  $[\text{MTBE}] = 1 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 15 \text{ mM}$ ,  $\text{pH} = 2.8$  and room temperature. The main disadvantage of this approach is the extremely acid media required for Fenton reaction. Authors showed that MTBE degradation is a two-stage process, attributed to a fast degradation by  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  (with a large amount of  $\cdot\text{OH}$  produced) and  $\text{Fe}_3^+/\text{H}_2\text{O}_2$ , those reaction rate constant are 53 and  $0.02 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

The reactions of persulfate (also known as peroxydisulfate and peroxodisulfate) ions with various organic and inorganic compounds have been extensively studied (Kolthoff and Miller 1951; House 1962). Persulfate oxidation is generally conducted under heat (Huang *et al.* 2002; Liang and Su 2009), photo (Hori *et al.* 2005), microwave assisted (Shiying *et al.* 2009) or metal-catalyzed (Liang *et al.* 2004) conditions, because the oxidation rates can be greatly accelerated. High reactive species such as sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) and hydroxyl radicals ( $\cdot\text{OH}$ ) are generated as a result of photolysis or heat decomposition of persulfate ions in aqueous phases (Berlin 1986; Liang and Su 2009). Ultraviolet (UV) light, heat or some metal catalysts are able to oxidize many organic substances into carbon dioxide.

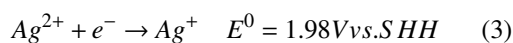
The reaction that takes place in the MTBE degradation process by persulfate is accordingly to Eq. (1):



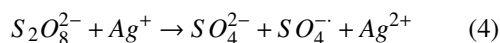
The theoretical scheme for oxidation process by using silver ion and persulfate as oxidant couple can be expressed accordingly to Eq. (2)-Eq. (7):



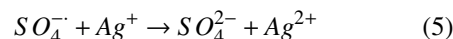
Persulfate can oxidize  $\text{Ag}^+$  to  $\text{Ag}^{2+}$ :



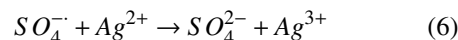
Furthermore,  $\text{Ag}^+$  ions are capable of catalyzing the formation of sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) from persulfate (Bacon, Grime and Munro 1954):



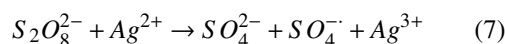
Once sulfate radicals are formed, next reaction can take place:



Additionally,  $\text{Ag}^{2+}$  ions emerging from Eq. (4),  $\text{Ag}^{2+}$  can react with sulfate radicals following the reaction:



Also, persulfate can react with  $\text{Ag}^{2+}$  to generate  $\text{Ag}^{3+}$ :



Bi or trivalent silver ions can degrade organic compound as MTBE. On other hand, the main advantage of metal-catalyzed persulfate oxidation is that metal ions are not consumed, therefore, the ions seems to be a renewable source capable to oxidize organic pollutants. On the other hand, a synergistic effect can be observed, since persulfate,  $\text{Ag}^{2+/3+}$  ions, persulfate and  $\text{SO}_4^{\cdot-}$ , can degrade organic compounds like MTBE.

Since transient species generated by  $\text{S}_2\text{O}_8^{2-}$  catalyzed by  $\text{Ag}^+$  ions are strongly oxidizing agents that can be used to oxidize either organic or inorganic compounds. Xu *et al.* (2008) reported the oxidative absorption of mercury by  $\text{S}_2\text{O}_8^{2-}$  catalyzed by  $\text{Ag}^+$  ions. Regarding organic compounds, Sun *et al.* (2013) reported the degradation of phenol in aqueous solution with  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Ag}^+$  ions activated under UV light. However no thermodynamic or kinetic parameters of the system were studied and only 23% of the phenol was degraded within 3 h.

For the first time, an extensive study of the kinetic and thermodynamics of MTBE degradation is reported by sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) catalyzed by  $\text{Ag}^+$  ions, this approach is used as a potential alternative oxidant for the remediation of groundwater contaminated. The different factors such as rate constant, activation energy ( $E_a$ ) and parameters of transition state ( $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$  and  $\Delta S^\ddagger$ ) were calculated in order to compare this AOP with other works reported.

## 2 Materials and methods

### 2.1 Materials

ACS-grade sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ , 99.9%), silver nitrate ( $\text{AgNO}_3$ ,  $\geq 99.0\%$ ) and methyl *tert*-butyl ether (MTBE, 99.9%) were supplied by Sigma-Aldrich. All solutions were prepared with deionized

(DI) water from SYBRON/Barnstead purification system model 02610.

### 2.1.1 Experiments

The experiments were carried out in a jacketed reaction beaker (500 mL) for temperature controlled reaction, equipped with a stop-cork through which a thermometer is placed. The stirring and the temperature of the reacting solution were kept constant throughout the experiment. Temperature was controlled with VWR heated/refrigerated circulator model 1166. Sample solutions withdrawn from the reactor at reaction times of 0, 30, 60, 120, 180, 240, 300 and 360 minutes, were immediately analyzed for MTBE concentration.

## 2.2 MTBE determination

Analysis of MTBE was conducted using an HP 5890 II chromatograph (Santa Clara CA) equipped with and electron capture detector and an HP-5 column (cross-linked 5% PH ME Silicone). The column was 30 m long and 0.33 mm diameter and had a 0.25  $\mu\text{m}$  film coating. For these analyses, the temperature was set initially at 40  $^{\circ}\text{C}$  for one minute, than ramped at 20  $^{\circ}\text{C}/\text{minute}$  to 120  $^{\circ}\text{C}$  and held for one minute. The head pressure was 15 psig, oven temperature was 40  $^{\circ}\text{C}$  and the flow rate was 27.3  $\text{cm}^3 \text{min}^{-1}$ . One milliliter aliquots from the reaction solution were diluted with 4 mL of deionized water, hermetically sealed, equilibrated to  $60 \pm 0.5$   $^{\circ}\text{C}$  in a water bath for 30 minutes then 5 mL of vapor sample was taken by head space technique and was transferred to autosampler vials (15 mL) equipped with rubber stoppers and aluminum crimp seals.

## 3 Results and discussion

The rate law for the degradation of MTBE by persulfate is expressed accordingly Eq. (8):

$$-\frac{d[\text{MTBE}]}{dt} = k[\text{MTBE}] \quad (8)$$

where  $k = f(T, [\text{Na}_2\text{S}_2\text{O}_8] \text{ and } [\text{Ag}^+])$  is the pseudo-first-order rate constant that represent a combined rate of MTBE degradation by all oxidizing agents produced.

The results of a series of kinetics experiments under various conditions (i.e., different  $\text{Na}_2\text{S}_2\text{O}_8$  concentration,  $\text{Ag}^+$  concentration and temperature) are presented in Table 1 and Fig. 1-6. Fig. 7 and Fig. 8 show results of kinetics experiments of MTBE degradation by persulfate without  $\text{Ag}^+$  ions like those reported by Huang *et al.* (2002). All experiments were performed by triplicated and the standard deviations of the measurements were lower than 3%. Following we make a detail discussion of the results.

### 3.1 Degradation kinetics of MTBE by persulfate catalyzed with $\text{Ag}^+$ ion

#### 3.1.1 Effect of $\text{Na}_2\text{S}_2\text{O}_8$ concentration

The reaction rates of degradation of MTBE versus time, at various initial concentrations of oxidizing agent  $\text{Na}_2\text{S}_2\text{O}_8$  at constant  $\text{Ag}^+$  catalyst concentration, are presented in Fig. 1. This figure shows that MTBE was rapidly degraded as concentration of sodium persulfate was increased from 0 to 25  $\text{mol m}^{-3}$   $\text{Na}_2\text{S}_2\text{O}_8$ , however further increase of  $\text{Na}_2\text{S}_2\text{O}_8$  concentration, did not increased the pseudo constant rate of reaction. Table 1 shows the pseudo rate constant values that increased from  $0.15 \times 10^{-4}$  to  $0.95 \times 10^{-4} \text{ s}^{-1}$  as the  $\text{Na}_2\text{S}_2\text{O}_8$  concentration increased from 5 to 25  $\text{mol m}^{-3}$ .

Additionally in Fig. 2, the pseudo rate constant  $k$  is plotted against initial concentration of  $\text{Na}_2\text{S}_2\text{O}_8$  and shows a slope of  $4 \times 10^{-6} \text{ m}^{-3} \text{mol}^{-1} \text{ s}^{-1}$  for degradation of MTBE, indicating that degradation rate was directly proportional to initial concentration of  $\text{Na}_2\text{S}_2\text{O}_8$ , from 5  $\text{mol m}^{-3}$  to 25  $\text{mol m}^{-3}$ .

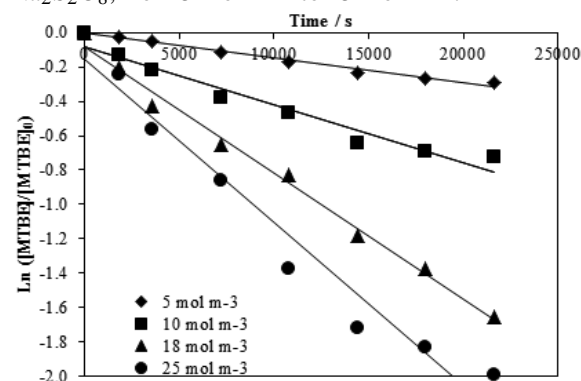
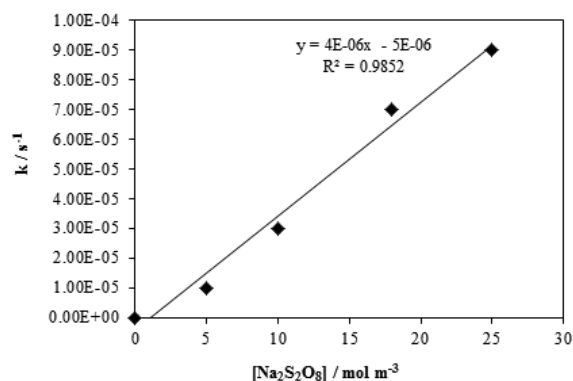
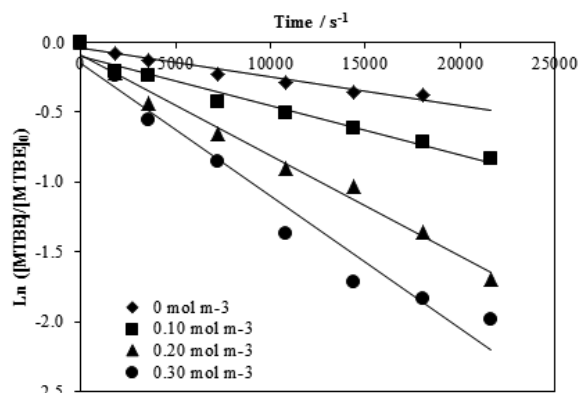


Fig. 1 Effect of concentrations of  $\text{Na}_2\text{S}_2\text{O}_8$  on MTBE degradation rate by persulfate with addition of 0.30  $\text{mol m}^{-3}$   $\text{Ag}^+$  at different concentration of  $\text{Na}_2\text{S}_2\text{O}_8$ .  $[\text{MTBE}]_0 = 1.14 \text{ mol m}^{-3}$ , Temperature = 20  $^{\circ}\text{C}$ .

Table 1. Rate constant of MTBE ( $[MTBE]_0 = 1.14 \text{ mol m}^{-3}$ ) degradation by persulfate catalyzed with  $Ag^+$  ions.

$[Na_2S_2O_8]_0$ $\text{mol m}^{-3}$	$[Ag^+]_0$ $\text{mol m}^{-3}$	Temperature $^{\circ}\text{C}$	$k \times 10^4$ $\text{s}^{-1}$	Half-life h	$R^2$
<b>5</b>	0.3	20	0.13	14.81	0.9877
<b>10</b>	0.3	20	0.33	5.83	0.9533
<b>18</b>	0.3	20	0.73	2.64	0.9917
<b>25</b>	0.3	20	0.95	2.03	0.9614
25	<b>0</b>	20	0.2	9.63	0.9553
25	<b>0.1</b>	20	0.35	5.5	0.9656
25	<b>0.2</b>	20	0.72	2.67	0.9858
25	<b>0.3</b>	20	0.95	2.03	0.9614
25	0.3	<b>20</b>	0.95	2.03	0.9614
25	0.3	<b>25</b>	1.45	1.28	0.9681
25	0.3	<b>30</b>	2.64	0.71	0.9732
25	0.3	<b>35</b>	3.77	0.51	0.9522
25	0.3	<b>40</b>	5.82	0.42	0.9289

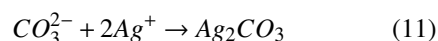
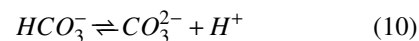
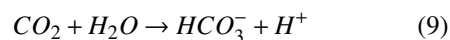
Fig. 2 Plot of  $k$  pseudo rate constant vs  $[Na_2S_2O_8]$  on MTBE degradation rate by persulfate with  $0.30 \text{ mol m}^{-3} Ag^+$ .  $[MTBE]_0 = 1.14 \text{ mol m}^{-3}$ , Temperature =  $20^{\circ}\text{C}$ .Fig. 3 Effect of concentrations of  $Ag^+$  ion on MTBE degradation rate by persulfate.  $[MTBE]_0 = 1.14 \text{ mol m}^{-3}$ ,  $[Na_2S_2O_8] = 25.00 \text{ mol m}^{-3}$ , Temperature =  $20^{\circ}\text{C}$ .

### 3.1.2 Effect of $Ag^+$ ions concentration

Fig. 3 shows the degradation of MTBE versus time at seven different  $Ag^+$  concentrations from 0 to  $0.30 \text{ mol m}^{-3}$ . The MTBE degradation rate increased as  $Ag^+$  concentration increased. Table 1 shows that the values of rate constant increased from  $0.20 \times 10^{-4}$  to  $0.95 \times 10^{-4} \text{ s}^{-1}$  as the initial  $Ag^+$  concentration increases.

In Fig. 4,  $k$  is plotted against initial  $Ag^+$  concentration and shows a slope of  $3 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . At higher  $Ag^+$  concentration the rate constant increase, but the slope value is lower than  $3 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , suggesting a change in the mechanism of the reaction. The change in reaction mechanism can be caused by the precipitation of the insoluble  $Ag_2CO_3$ ,

since  $CO_3^{2-}$  is generated from oxidation of MTBE in aqueous medium as described by Félix-Navarro et al. (2013) (Eq. (9)-Eq. (11)):



Another possibility is the generation of  $Ag_2SO_4$  as a precipitate from the sulfate produced from the reduction of persulfate when this oxidizes MTBE.

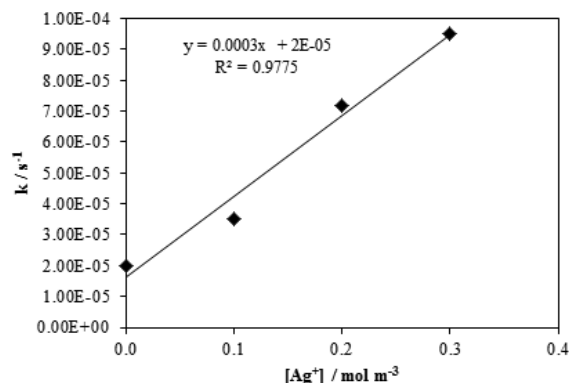


Fig. 4 Plot of  $k$  vs  $[Ag^+]$  on MTBE degradation rate by persulfate.  $[MTBE]_0 = 1.14 \text{ mol m}^{-3}$ ,  $[Na_2S_2O_8]_0 = 25.00 \text{ mol m}^{-3}$ , Temperature = 20 °C.

An UV visible absorption spectrum showed that at concentrations of  $0.60 \text{ mol m}^{-3} Ag^+$  or greater (not shown), the baseline gave values greater than zero absorbance, which can be due to the formation of a dispersion of precipitated silver salts (invisible to the eye but detectable by the spectrophotometer).

### 3.1.3 Effect of temperature on degradation of MTBE by persulfate with $Ag^+$

The effect of temperature upon MTBE degradation was studied in the range of 20 °C to 40 °C, since the boiling point of MTBE at atmospheric pressure is 55 °C. Fig. 5 shows that the reaction rate is significantly influenced by temperature. At higher temperature, faster MTBE is degraded. Table 1 shows that the pseudo-first-order rate constants ( $k$ ) of MTBE degradation increased from  $0.95 \times 10^{-4} \text{ s}^{-1}$  (at 20 °C) to  $5.82 \times 10^{-4} \text{ s}^{-1}$  (at 40 °C).

Fig. 6 shows an Arrhenius type plot of  $\ln k$  versus  $1/T$  for determination of the activation energy. The activation energy was determined using Arrhenius equation (Eq. 12):

$$k = Ae^{-E_a/RT} \quad (12)$$

where  $A$  is the frequency factor,  $E_a$  is the activation energy,  $R$  is the universal gas constant and  $T$  is the temperature. From slope of the plot  $\ln k$  vs  $1/T$  the obtained value of activation energy is  $E_a = 69.89 \times 10^3 \text{ J mol}^{-1}$  for the reaction of MTBE by persulfate with presence of  $Ag^+$  ions in low concentration ( $0.3 \text{ mol m}^{-3}$ ).

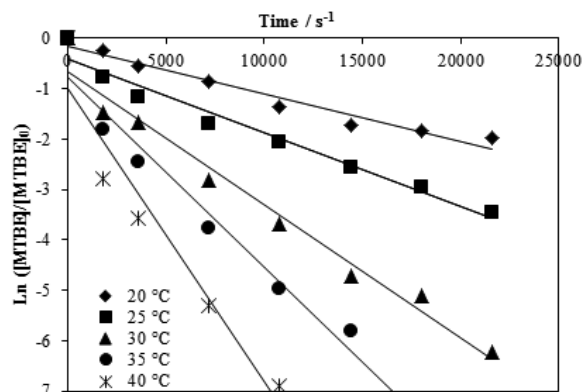


Fig. 5 Effect of temperature on the degradation of MTBE by persulfate with  $Ag^+$ .  $[MTBE]_0 = 1.14 \text{ mol m}^{-3}$ ,  $[Na_2S_2O_8]_0 = 25.00 \text{ mol m}^{-3}$ ,  $[Ag^+]_0 = 0.30 \text{ mol m}^{-3}$ .

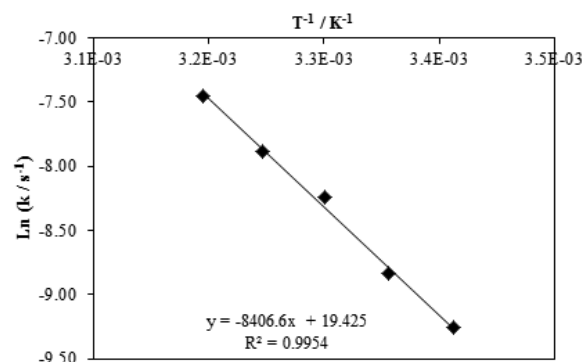


Fig. 6 Plot of  $\ln k$  vs  $1/T$  for  $E_a$  estimation using Arrhenius equation.  $[MTBE]_0 = 1.14 \text{ mol m}^{-3}$ ,  $[Na_2S_2O_8]_0 = 25.00 \text{ mol m}^{-3}$ ,  $[Ag^+]_0 = 0.30 \text{ mol m}^{-3}$ .

Thermodynamic activation parameters like enthalpy ( $\Delta H^\ddagger$ ), Free Gibbs energy ( $\Delta G^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) were computed with the following equations (Eq. (13)-Eq. (15)) (Espenson 1995):

$$\Delta H^\ddagger = E_a - RT \quad (13)$$

$$\Delta G^\ddagger = RT \ln \frac{\kappa T}{k_1 h} \quad (14)$$

$$\Delta S^\ddagger = R \ln \frac{k_1 h}{\kappa T} + \frac{\Delta H^\ddagger}{T} \quad (15)$$

where  $T$  is the ambient temperature,  $k_1$  is the rate constant at ambient temperature,  $\kappa$  is the Boltzmann constant ( $1.381 \times 10^{-23} \text{ J K}^{-1}$ ) and  $h$  is the Planck constant ( $6.626 \times 10^{-34} \text{ J s}$ ). The results of parameters of transition state are:  $\Delta H^\ddagger = 67.45 \times 10^3 \text{ J mol}^{-1}$  (endothermic),  $\Delta G^\ddagger = 94.28 \times 10^3 \text{ J mol}^{-1}$  and  $\Delta S^\ddagger = -91.56 \text{ J mol}^{-1} \text{ K}^{-1}$ .

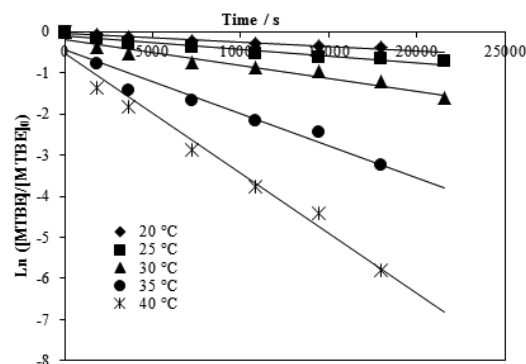


Fig. 7 Effect of temperature on the degradation of MTBE by persulfate without  $\text{Ag}^+$  ions.  $[\text{MTBE}]_0 = 1.14 \text{ mol m}^{-3}$ ,  $[\text{Na}_2\text{S}_2\text{O}_8]_0 = 25.00 \text{ mol m}^{-3}$ .

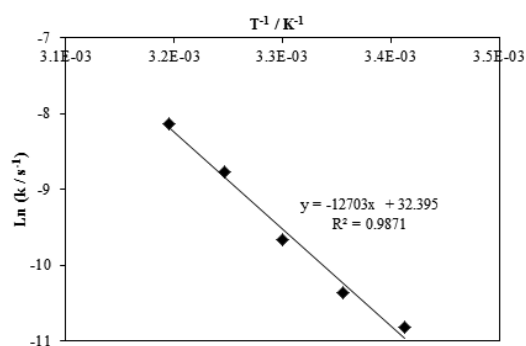


Fig. 8 Plot of  $\ln k$  vs  $1/T$  for  $E_a$  estimation using Arrhenius equation.  $[\text{MTBE}]_0 = 1.14 \text{ mol m}^{-3}$ ,  $[\text{Na}_2\text{S}_2\text{O}_8]_0 = 25.00 \text{ mol m}^{-3}$ .

### 3.2 Degradation kinetics of MTBE by persulfate

Typical reaction rate of persulfate oxidation of MTBE against time at various temperature are presented in Fig. 7. This figure shows the  $[\text{MTBE}]$  decay at five different temperatures (20, 25, 30, 35 and 40 °C) with constant initial  $[\text{MTBE}]$ , persulfate concentrations at  $1.14 \text{ mol m}^{-3}$  and  $25.00 \text{ mol m}^{-3}$  respectively.

Fig. 8 shows a plot of  $\ln k$  vs  $1/T$  for activation energy ( $E_a$ ) estimation using Arrhenius equation. The value of  $E_a$  for the reaction of MTBE with persulfate is  $105.61 \times 10^3 \text{ J mol}^{-1}$ . Thermodynamic activation parameters  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$  were computed:  $\Delta H^\ddagger = 103.17 \times 10^3 \text{ J mol}^{-1}$ ,  $\Delta G^\ddagger = 98.07 \times 10^3 \text{ J mol}^{-1}$  and  $\Delta S^\ddagger = 17.39 \text{ J mol}^{-1} \text{ K}^{-1}$ .

Huang *et al.* (2002) reported a value of  $102.51 \pm 6.7 \times 10^3 \text{ J mol}^{-1}$  for reaction of MTBE with persulfate, but other transition state thermodynamic parameters were not reported.

## Conclusion

In this study the degradation of MTBE by persulfate oxidation catalyzed with  $\text{Ag}^+$  ions is reported. MTBE degradation kinetic parameters were obtained and affecting factors were particularly examined. Degradation rate of MTBE was found to be pseudo-first order with respect to MTBE concentration. The experimental results indicate that degradation of MTBE with  $\text{Ag}^+$ -catalyzed persulfate is favored by temperature, increase in concentration of the oxidizing agent and also on catalyst concentration.

The  $\text{Ag}^+$  ions acts as a catalyst to accelerate the reaction decreasing the energy barrier to initiate the reaction, which is reflected in the values of activation energy, being of  $69.89 \times 10^3 \text{ J mol}^{-1}$ , for the catalyzed reaction and  $105.61 \times 10^3 \text{ J mol}^{-1}$ , for the uncatalyzed reaction. In order to find the optimal concentration of  $\text{Ag}^+$  ions during reaction is necessary to carry out experiments in the concentration range of 0.3 to  $0.6 \text{ mol m}^{-3}$   $\text{Ag}^+$ , thus at  $0.6 \text{ mol m}^{-3}$   $\text{Ag}^+$  and higher concentration precipitate in solution is formed, suggesting a change in the oxidation mechanism.

The activation thermodynamic parameters calculated at 20 °C, for both the catalyzed reaction and the uncatalyzed, indicate that  $\Delta H^\ddagger$  is  $35.72 \times 10^3 \text{ J mol}^{-1}$  lower in the catalyzed reaction, this indicates that the reaction requires to absorb less energy from the surrounding to be carried out.  $\Delta G^\ddagger$  values are similar:  $98.07 \times 10^3 \text{ J mol}^{-1}$  for the uncatalyzed reaction and  $94.28 \times 10^3 \text{ J mol}^{-1}$  for the catalyzed reaction.

The value of  $\Delta S^\ddagger$  is  $17.39 \text{ J mol}^{-1} \text{ K}^{-1}$  for the uncatalyzed reaction, while for the catalyzed reaction is  $-91.56 \text{ J mol}^{-1} \text{ K}^{-1}$ , which indicates a reaction of global order two, i.e. first order with respect to the concentration of MTBE and first order with respect to the concentration of  $\text{Ag}^+$  under the condition of an excess in  $\text{Na}_2\text{S}_2\text{O}_8$  concentration.

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