



Mineralization of aliphatic acids by solar mediated iron processes

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ABSTRACT

The mineralization of aliphatic acids in aqueous solution by solar mediated iron processes have been explored using acetic acid, oxalic acid and malonic acid as model compounds. Experiments were performed in batch mode under natural sunlight at optimum conditions. In solar-Fenton process, almost complete mineralization was observed for oxalic acid, 88% and 62% for malonic and acetic acid respectively while in solar-Ferric ion process, the mineralization efficiency was around 99%, 30% and 26% for oxalic acid, malonic acid and acetic acid respectively. The acids follow pseudo-first-order kinetics for solar-Fenton process and zero-order kinetics for solar-Ferric process. The kinetic rate constant for dicarboxylic acids like oxalic acid is higher than for monocarboxylic acid, acetic acid with the same number of carbon atoms. The results of the study provide an insight into the photochemical red-ox reactions of Fe^{3+}/Fe^{2+} ions which plays an important role in mineralizing the acids.

Keywords: Aliphatic acids, solar-Fenton, solar-Ferric, mineralization, photo-decarboxylation.

INTRODUCTION

Aliphatic acids are organic carboxylic acids which include monocarboxylic acid like formic acid, acetic acid, propanoic acid, dicarboxylic acids like oxalic acid, malonic acid and their derivatives. These compounds are commonly found in wastewater from various industries like petrochemical, pharmaceutical, pesticide, paints, dyes and pigments in varying concentration. The aliphatic acids are also present in wastewater treatment processes apart from industrial effluents as a byproduct formed during the degradation of macro organic molecules in aqueous solution by advanced oxidation process (AOP). These acids were found to be refractory and tend to lower the mineralization rate of AOPs during the final stages of the treatment process [1]. The presence of these compounds restricts the zero discharge limit of AOPs. The acids formed during AOPs are low molecular weight compounds like acetic acid, formic acid, oxalic acid, malonic acid, propanoic acid, maleic acid, fumaric acid and so on [2]. Some of the aliphatic acids and their derivatives are proved to be toxic as chloroacetic acid, carcinogenic and teratogenic in nature like valproic acid, 2-ethyl hexanoic acid [3]. It is, therefore, imperative to treat these acids before its discharge into the waterways.

Treatment methods employed for degradation of acids include photocatalysis using either TiO_2 [4-5] or immobilized TiO_2 [6], UV/H_2O_2 [7] and $Fe(III)/UV$ [8]. Studies have been conducted to understand the influence of these acids on the degradation of phenol [9], Rhodamine B[10]. Most of the researchers reported the usage of iron polycarboxylates in UV-visible region which results in oxidative degradation of carboxylate ligand [11-12]. Mailhot et al [13] have studied the degradation of diethyl phthalate by $Fe(III)$ -solar light in aqueous solutions. Hence, an attempt has been made to utilize the viability of Fe^{2+}/Fe^{3+} ions in the presence of solar light for photo degradation studies.

The present study aims at exploiting the behavior of photochemical red-ox cycling of Fe^{2+}/Fe^{3+} ions in the removal of recalcitrant aliphatic compounds by using solar light. The possibility of exploiting solar light as a substitute for

UV light is examined which would pave a new way in wastewater treatment processes. The mineralization of these acids is compared for solar-Fenton and solar-Ferric process in order to assess the predominance role of photochemical redox reactions. The kinetics for solar mediated process is proposed to understand the dynamics of the reactions.

EXPERIMENTAL SECTION

Analytical grade reagents, sodium acetate, malonic acid and sodium oxalate were purchased from CDH. The concentration of the acids used during the experimental run was 200mg/L. Ferrous sulphate hepta hydrate [CDH] was used as a source of iron for Fenton and solar-Fenton processes while anhydrous Ferric chloride [CDH] is used as a source for solar-Ferric process. Experiments were conducted in a shallow glass trough (23.5 cm x14 cm) at a depth of 2.2 cm both at room and solar conditions in a batch mode. The initial pH of the experimental run solution was adjusted to $\text{pH } 3.0 \pm 0.2$ using 0.05M H_2SO_4 or 1M NaOH. The reaction was initiated by adding either peroxide or ferrous/ferric ions to the acid solution. The solar-mediated processes were conducted at Anna University campus building under clear sky conditions. The intensity of the solar radiation was measured using Kipp and Zonen CC20 radiation indicator and was found to be in the range of 680-726 Wm^{-2} during the experimental run. Samples were withdrawn from the batch reactor at selected time intervals during the reaction and analyzed for the removal and mineralization of acids. The acids concentration was monitored using ion-chromatographic system Dionex DX120 equipped with Ionpac AS-14 column with sodium carbonate and sodium bicarbonate as eluent. The peaks were detected at 2.68, 6.83 and 7.85 min for acetic acid, malonic acid and oxalic acid respectively. The mineralization of acids was determined by decrease in dissolved organic content (DOC) in Analytic Jena Model 1997 equipped with liquid auto sampler ALSC-104. The removal efficiency was calculated by monitoring the parent compound as,

$$\text{Removal efficiency in \%} = (C_t - C_o / C_o) \times 100 \quad (1)$$

where C_t is the concentration of the acids at time t in minutes and C_o is the initial concentration of the acid. The mineralization efficiency was computed by measuring the DOC content of the solution as,

$$\text{Mineralization efficiency in \%} = (\text{DOC}_t - \text{DOC}_0 / \text{DOC}_0) \times 100 \quad (2)$$

where DOC_t is the DOC content of the solution at time t in minutes and DOC_0 is the initial DOC of the solution at time 0 minute.

RESULTS AND DISCUSSION

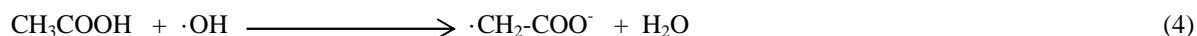
Degradation studies were conducted for acetic acid, malonic acid and oxalic acid by maintaining a pH of 3.0 ± 0.2 and optimum conditions of acid: peroxide at 1:14 and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ at 20. When peroxide was added to acid solution containing iron solution, the solution remained colourless for all the acids studied at room conditions. In solar-mediated process, the reacting solution remained colorless for acetic acid and malonic acid while for oxalic acid solution, the color changed to green during the initial stages of the reaction. As the reaction continues, the green colour changes to colorless at the end of the reaction.

3.1 Fenton process

When peroxide is added to ferrous ion at acidic pH, hydroxyl ($\cdot\text{OH}$) radicals are generated as shown in eq.3



The removal efficiency of acetic acid, oxalic acid and malonic acid by Fenton process is shown in Fig.1. These acids are highly resistant to Fenton oxidation [2] as indicated by meager removal efficiency of around 6%. The $\cdot\text{OH}$ radical generated attacks the acetic acid at ' α ' hydrogen atom through hydrogen abstraction with a very low rate constant of $7.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [14].



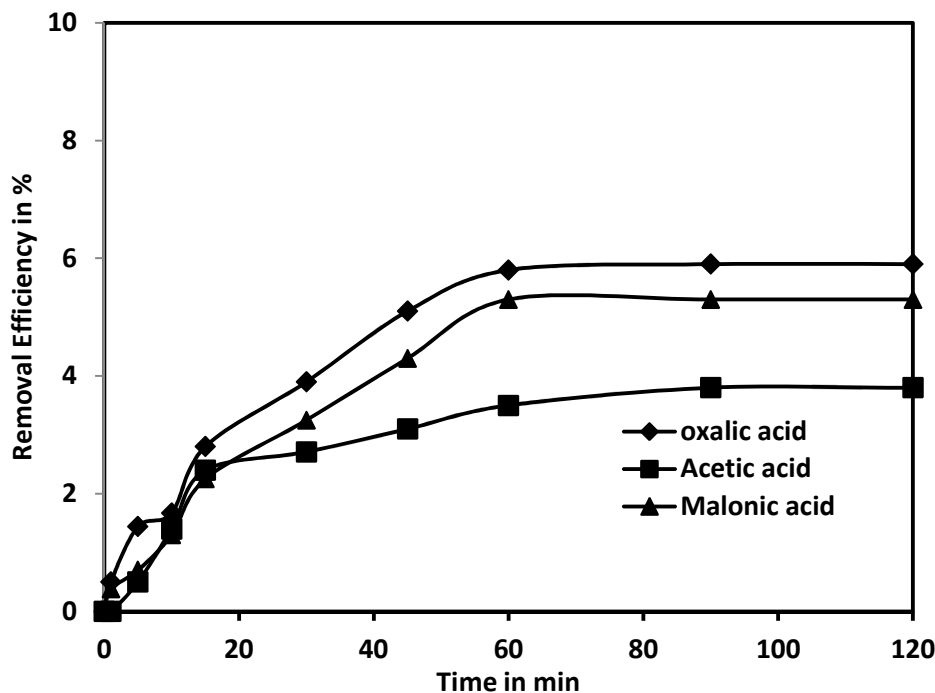
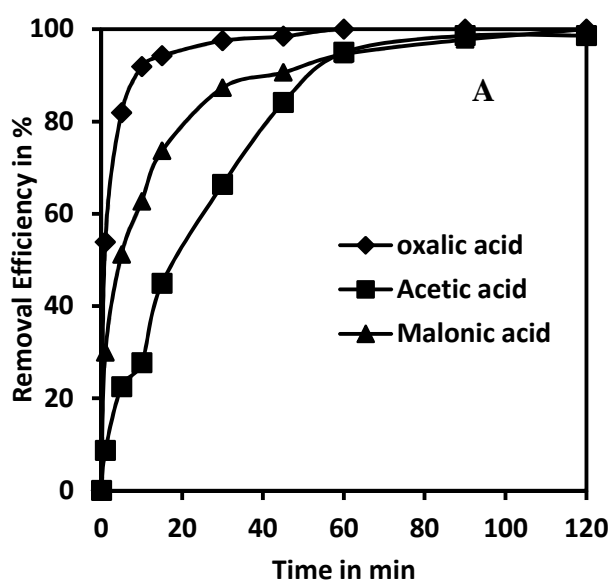


Fig. 1. Removal efficiency of acetic acid, oxalic acid and malonic acid by Fenton process

Hence, acetic acid was resistant to oxidation and their removal efficiency is around 3.5% which is in accordance with the results reported by Sinha et al [15] for low concentration of acetic acid. In dicarboxylic acids like oxalic acid and malonic acid, the $\cdot\text{OH}$ radical attack either the carboxylate ion or methylene group as shown in eq.5 and 6 with a low rate constant [16].



Moreover, the cleavage of C-C bond by $\cdot\text{OH}$ radical is very low contributing for only 6% removal efficiency. In addition, the ferric ion formed reacts with the acids resulting in stable complexes which further deactivate the oxidation process [17].



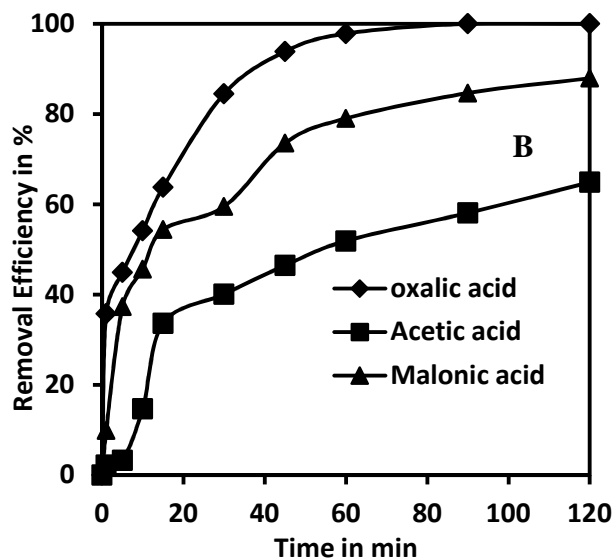


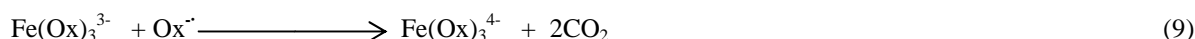
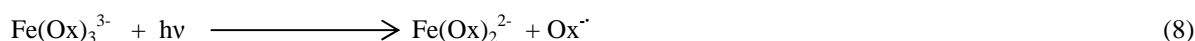
Fig 2. Removal efficiency of acids by solar-mediated processes. A: solar-Fenton process; B: solar-Ferric process

3.2 Solar-assisted process

The removal efficiency of acetic acid, oxalic acid and malonic acid by solar-mediated processes is represented in Fig.2. In solar-Ferric process, around 90-99% of dicarboxylic acid was removed while in monocarboxylic acid only 65% of acetic acid was removed. Increase in removal efficiency compared to Fenton process may be attributed to 1) photolysis of Fe(III) hydroxyl complex at pH 2.5-5.0 which yield $\cdot\text{OH}$ radical, effective for the degradation of organic compounds [18].



The reaction occurs both in sunlight and UV light. In the presence of the acids studied, the hydroxyl complex is highly unstable as seen from their stability constants. The stability constant of $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{ac})_3^{3-}$, $\text{Fe}(\text{Ox})_3^{3-}$, $\text{Fe}(\text{mal})_3^{3-}$ are -7.1, 18.5, 18.4 and 20.4 respectively where ac, ox and mal represents acetate, oxalate and malonate ions [19]. Hence the contribution of above equation towards removal efficiency is negligible. 2) Photo decarboxylation of ferric polycarboxylates, the acids forms outer sphere stable complex with ferric ion at acidic pH of 2-4. The ferric complexes are photo-active in nature. Absorption of photon in the wavelength range of 250-400 nm by these complexes undergoes a series of chemical reactions by transferring its electron from organic ligand to Fe(III) by ligand to metal charge transfer (LMCT). The photochemical reactions are shown below[20].



The above eq.8 suggests that photo decarboxylation reaction plays an important role for removal of the acids by solar-Ferric ion process. In solar-Fenton process, almost complete removal of acids is observed which can be assigned to photo decarboxylation of ferric complexes as well as photolysis of hydrogen peroxide. The added peroxide generates additional oxidants like $\cdot\text{OH}$, HO_2^{\cdot} , H_2O_2 and Fe^{3+} ions [21] which contributes to increase in removal efficiency.

The mineralization efficiency of the acids by solar-mediated process is depicted in Fig.3. In solar-Ferric process, 73%, 30% and 25% mineralization was noted for oxalic acid, malonic acid and acetic acid respectively. As seen in eq.9-10, the carboxylate radical undergoes decarboxylation to form either CO_2 or react with O_2 to form oxidized intermediate compounds. Depending on the nature of carboxylic acid ligand, the mineralization efficiency is varied which can be explained from the quantum yield of Fe^{2+} ion from Fe(III)-polycarboxylate eq.8. The decrease in mineralization efficiency for malonic acid compared to oxalic acid is due to low quantum yield of Fe^{2+} ion for malonic acid (2.7%) than oxalic acid [11]. As seen in Fig.3, the mineralization efficiency of the acids studied was increased for solar-Fenton process. Increased mineralization is due to photolysis of peroxide and photo decarboxylation reaction. The photolysis of peroxide contributes to increase in mineralization efficiency of 60% and

35% for malonic and acetic acid respectively. Hence, it may be suggested that photo decarboxylation and photolysis of hydrogen peroxide plays a significant role in mineralizing the acids by solar-Fenton process.

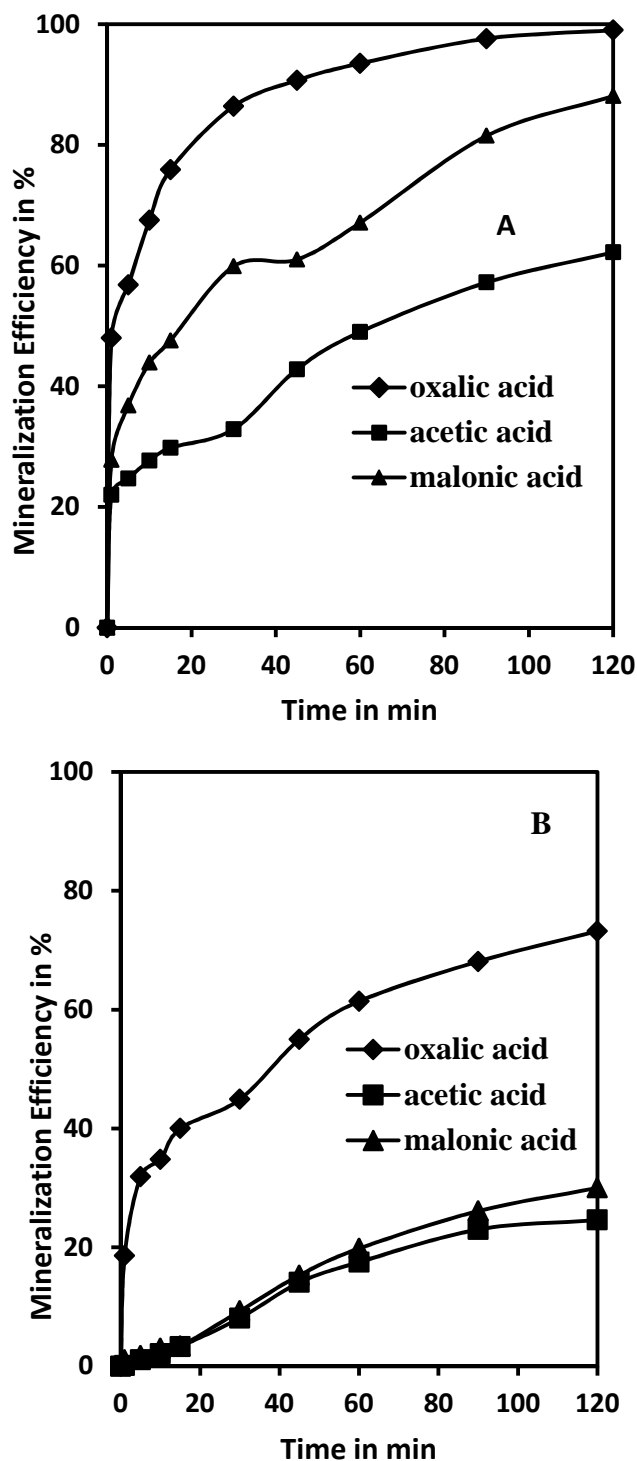


Fig.3. Mineralization efficiency of acids by solar-mediated processes. A:solar-Fenton process; B: solar-Ferric process

3.3 Kinetics for aliphatic acid oxidation

The kinetics of aliphatic acid oxidation follows different order of reaction based on the solar mediated process.

3.3.1 Solar-Ferric process

The overall mineralization of the process is attributed to photolysis of Ferric polycarboxylates as shown below



The kinetics for acid oxidation can be represented as follows,

$$dC_{\text{acid}}/dt = -k_{\text{acid}} \quad (12)$$

where C_{acid} is the concentration of acid and k_{acid} is the zero-order rate constant. When $t = 0$, C_{acid} is equal to $C_{\text{acid}0}$, the eq. 12 on integration becomes,

$$C_{\text{acid}0} - C_{\text{acid}} = k_{\text{acid}}t \quad (13)$$

During the reaction, the acids were completely removed with the formation of organic intermediates. Thus, it would be appropriate to assess the overall rate constant with respect to DOC rather than the acid. The eq.13 can be rewritten as,

$$C_{\text{DOC}0} - C_{\text{DOC}} = k_1t. \quad (14)$$

$$\tau_{(1/2)} = C_{\text{DOC}0}/2. k_1 \quad (15)$$

Zero-order rate constant (k_1) can be obtained through a linear least-square fit for the acid data to eq.14. The zero-order kinetic plots for acetic, oxalic and malonic acid is shown in Fig 4 with regression greater than 0.98. The rate constant for acetic acid, oxalic acid and malonic acid are 2.7616×10^{-3} , 3.045×10^{-3} , $1.730 \times 10^{-3} \text{ mM min}^{-1}$ respectively. Half-life ($\tau_{1/2}$) values for acids was determined by applying the rate constant values to eq.15 and was found to be 602.9, 364.5 and 554.9 min for acetic, oxalic and malonic acid respectively.

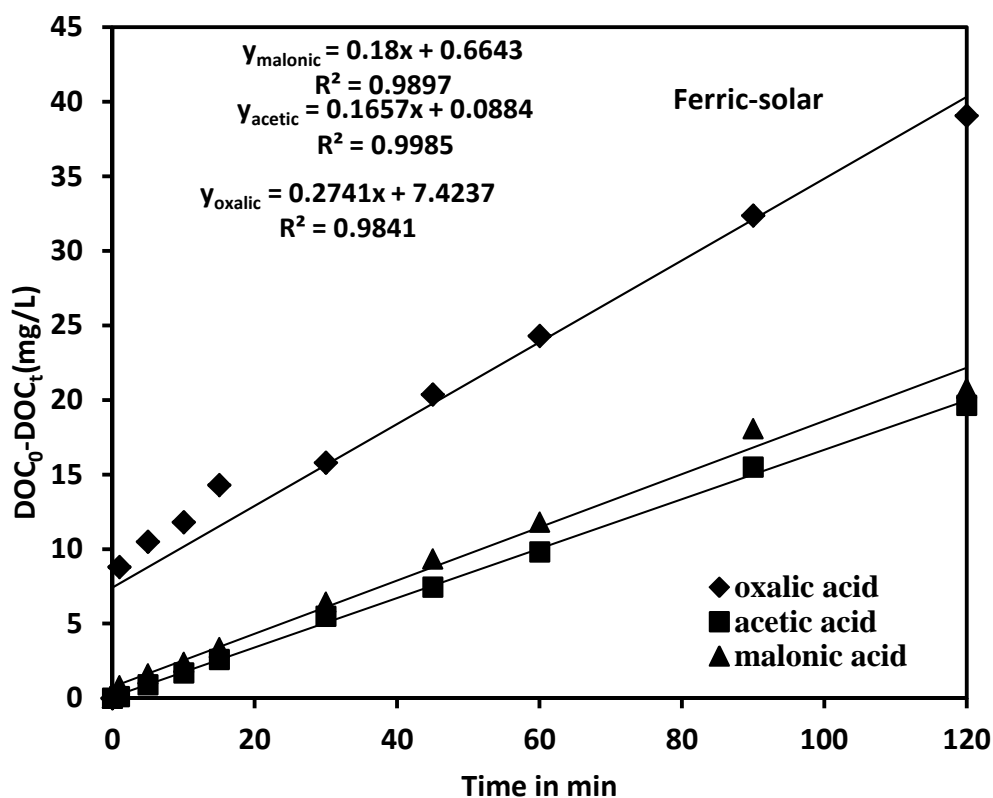


Fig.4. Zero-order kinetic plot for mineralization of acid by solar-Ferric process

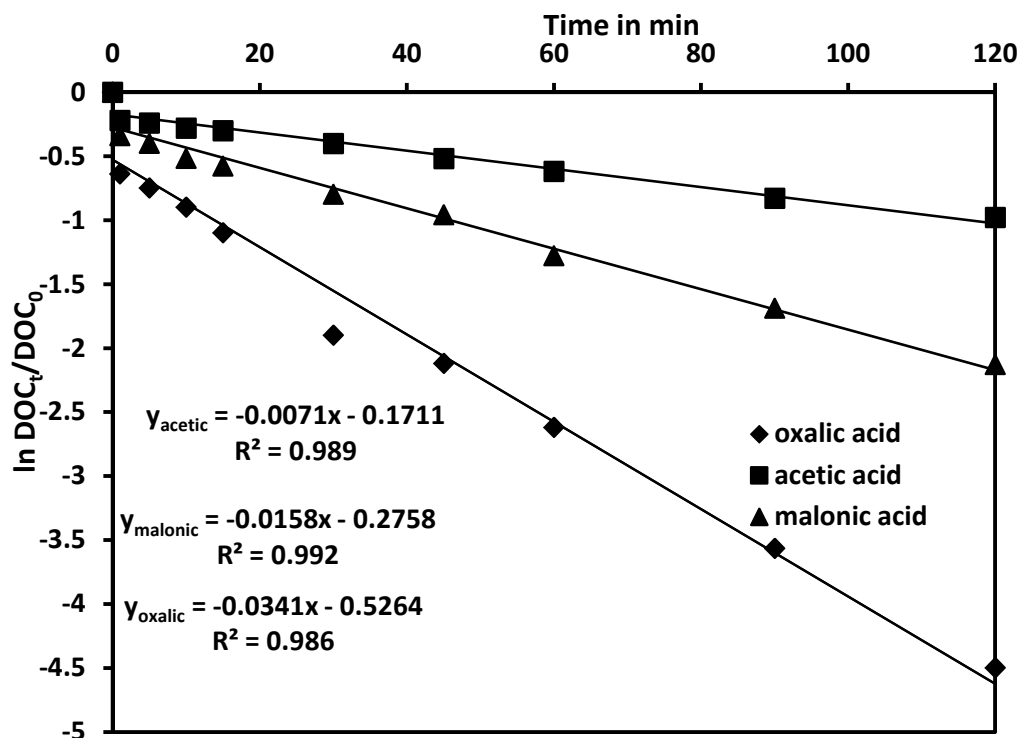


Fig. 5. Pseudo-First-order kinetic plot for mineralization of acids by solar-Fenton process

3.3.2 Solar-Fenton process

In solar-Fenton process, photolysis of hydrogen peroxide and ferric polycarboxylates play a significant role in mineralizing the acids studied. The reaction rate depends directly on the concentration of acid and $\cdot\text{OH}$ radical generated resulting in second-order rate equation as follows,

$$dC_{\text{acid}}/dt = -k_{\text{acid}}C_{\text{acid}}C_{\cdot\text{OH}} \quad (16)$$

where C_{acid} and $C_{\cdot\text{OH}}$ are the concentration of acid and hydroxyl radical respectively and k_{acid} is the second-order rate constant. In the presence of high concentration of $\cdot\text{OH}$ radical, the eq can be deduced to pseudo-first-order rate equation,

$$dC_{\text{acid}}/dt = -k_{\text{acid}}C_{\text{acid}} \quad (17)$$

On integrating the above eq.17,

$$\ln C_{\text{acid}}/\ln C_{\text{acid}0} = -k_2t \quad (18)$$

$$\tau_{(1/2)} = 0.693/k_2 \quad (19)$$

The above equation can be applied for overall mineralization of acid by incorporating the residual DOC. Pseudo-first order rate constant (k_2) for acids can be obtained through a linear least-square fit of mineralization data to eq.18 and is illustrated in Fig.5 with regression greater than 0.98. The rate constant for acetic, oxalic and malonic acid is 0.0158, 0.0341 and 0.0071 min^{-1} respectively. Half-life ($\tau_{(1/2)}$) values for acids can be measured by applying the rate constant to eq.19 and found to be in the range of 20 to 98 min.

Rate constant and Half-lives for acids by solar-mediated process is presented in Table1. As seen from the values, the rate constant for dicarboxylic acid is higher than the monocarboxylic acid with the same carbon atoms which is consistent with the results obtained by Chen et al [22]. The mineralization rate constant for solar mediated process follows the order of oxalic acid > acetic acid > malonic acid. The rate constant for the acids studied by solar-Fenton process is greater than solar-ferric ion process by a factor of 10. The half-lives of acids for solar-Fenton process are in the range of 20 to 98 min while 365- 603 min was observed for solar-Ferric process. From the values, it can be deduced that the half-lives of acids by solar-ferric process is reduced by a factor of 5-18 compared to solar-Fenton

process. Increased mineralization rate and reduced half-life for acids by solar-Fenton process was witnessed compared to solar-ferric process. The acids take longer time to degrade by solar-Ferric process.

Table 1. Rate constant and their Half-lives ($\tau_{1/2}$) for mineralization of acids by solar mediated Process

Acid	Solar-Ferric			Solar-Fenton			Increased efficiency $\tau_{1/2}(\text{sol-ferric}) / \tau_{1/2}(\text{sol-fenton})$
	$k_1 \times 10^{-3}$ mM min ⁻¹	$\tau_{1/2}$ min	r^2	k_2 min ⁻¹	$\tau_{1/2}$ min	r^2	
Acetic	2.76	602.9	0.9985	0.0158	43.86	0.989	13.74
Oxalic	3.045	364.5	0.9841	0.0341	20.32	0.986	17.93
Malonic	1.73	554.9	0.9841	0.0071	97.60	0.992	5.68

CONCLUSION

The foregoing study suggests that the acids were completely removed by solar-mediated processes. On the basis of the study, the following implications are obtained:

- Acetic, oxalic and malonic acids were removed meagerly up to 6% by Fenton process while almost complete removal is achieved in solar-mediated process except for acetic acid, accounts for 68% removal in solar-Ferric process.
- The mineralization efficiency of acetic, oxalic and malonic acid by solar-Fenton process was 62%, 99% and 88% respectively while only 25%, 73% and 30% was observed for solar-Ferric process.
- The acids follows pseudo- first-order kinetic model for solar-Fenton process while a zero-order model was obeyed for solar-Ferric process. The mineralization rate constant for the acids by both processes conforms with the following sequence: oxalic acid > acetic acid > malonic acid.
- The rate constant for dicarboxylic acid, oxalic acid is higher than for monocarboxylic acid, acetic acid with same carbon atoms.
- Half-life of acids by solar-Fenton process were in the range of 20-97.6 min whereas the half-life observed for solar-ferric process ranges from 365 to 603 min.
- Even though, solar-Fenton offers a promising treatment technology for complete mineralization of acids studied, solar-Ferric process could also be a viable alternate technology for mineralizing the acids at low cost (without the usage of oxidants like peroxide) for tropical countries like India, where sunlight is available throughout the year.

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