

Kinetic Monte Carlo Simulation of Oxalic Acid Ozonation over Lanthanum-based Perovskites as Catalysts

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Kinetic Monte Carlo simulation was applied to investigate the kinetics and mechanism of oxalic acid degradation by direct and heterogeneous catalytic ozonation. La-containing perovskites including LaFeO₃, LaNiO₃, LaCoO₃ and LaMnO₃ was studied as catalyst for oxalic acid ozonation. The reaction kinetic mechanisms of each abovementioned catalytic systems have been achieved. The rate constant values for each step of the reaction mechanisms were obtained as adjustable parameters by kinetic Monte Carlo simulation. Comparison of the direct and catalytic ozonation simulation results proves that the lanthanum-based perovskites catalysts display significant roles during oxalic acid ozonation by increasing the reactivity of ozone and oxalic acid on the surface of catalyst. Also, the effect of inlet ozone concentration and initial amount of LaMO₃ (M = Fe, Ni, Co, Mn) on the rate of oxalic acid decomposition has been studied. The kinetic Monte Carlo simulation results of this research have suitable agreement with the available experimental data for the oxalic acid ozonation.

Keywords: Monte Carlo, Kinetic simulation, Ozonation, Lanthanum-based perovskites, Oxalic acid, Degradation

INTRODUCTION

Ozone is used extensively in water treatment owing to its powerful oxidation [1-3]. Ozonation is an interesting technique for destruction of organic pollutants in aqueous solution. However, it has been reported that the ozonation cannot completely degrade organic compounds in most cases and sometimes generate toxic intermediates. In such cases, the efficiency of oxidation can be enhanced by applying ozone together with H₂O₂ or UV irradiation to produce free radicals, mainly hydroxyl radicals (HO•) with high oxidation potential [4,5]. However, they present some disadvantages such as the residual of H₂O₂ [6], the shorter life and higher energy consumption of UV lamp [7]. As a promising development in treatment of drinking water and wastewater field [8], heterogeneous catalytic ozonation has attracted the increasing interest because of its potentially higher effectiveness in the degradation and mineralization

of organic contaminants and lower negative effect on water quality [9-12]. The main advantages of this process are the ability to enhance the rate of organic compounds oxidation and especially to improve the mineralization degree attained at the end of the method [13]. Carbon materials, metal oxides (*e.g.* MgO [14], Co₃O₄ [15,16], ZnO [17], TiO₂ [18], Al₂O₃ [19]) and supported metal oxides (*e.g.* Pr/Al₂O₃, [20] Co/Al₂O₃ [21], Au/Bi₂O₃ [22], MnOx/MWCNT [12], TiO₂/silicagel [23], TiO₂/Al₂O₃ [24]) have been reported as efficient heterogeneous ozonation catalytic systems. Moreover, a few studies proposed the catalytic activity of perovskites in ozonation methods. General formula of perovskite is ABO₃, where A is commonly a rare earth cation and B a transition metal cation [25]. In the recent years, a perovskite comprising copper was employed as a very effective catalyst to improve TOC removal in the ozonation of sulfamethoxazole, a sulfonamide type synthetic antibiotic [26]. A wide range of La-containing perovskites were used to investigate the catalytic ozonation of oxalic acid by Orgeetal [27].

In this research kinetic parameters and mechanism of

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oxalic acid ozonation over lanthanum-based perovskites catalysts was studied using computational technique. Kinetic Monte Carlo method has demonstrated an important application as an advanced device in simulating of different reactions [28-35]. In this investigation, an effective technique has been applied for identification of kinetic degradation mechanism of oxalic acid by O_3 , $O_3/LaFeO_3$, $O_3/LaNiO_3$, $O_3/LaCoO_3$ and $O_3/LaMnO_3$ using kinetic Monte Carlo simulation. The kinetic mechanisms and the rate constant of each step of the mechanism are obtained for aforementioned catalytic systems. Furthermore, the curves of oxalic acid concentration versus time are drawn for the above systems by simulation. According to the simulated results, the effect of inlet ozone concentration and initial amount of $LaMO_3$ ($M = Fe, Ni, Co, Mn$) on the rate of oxalic acid decomposition are investigated.

KINETIC MONTE CARLO METHOD

The stochastic simulation algorithm *via* Monte Carlo methods developed by Gillespie [36] was used to simulate the experimental data for the ozonation of oxalic acid over lanthanum-based perovskites [27]. Kinetic simulations were carried out by the assistance of the Chemical Kinetic Simulator software, version 1.01 [37]. In this algorithm of simulation the reaction mechanism is considered as a series of several reactions:



The input data for the simulation are the steps of the rate constants of each step (k_i), temperature (T) and number of molecules (C_i). The algorithm of this modelling is founded on the reaction probability density function ($P(\tau, i)$) which is gained by Master equation:

$$P(\tau, i) = k_i C_i \exp\{-\sum k_i C_i \tau\} \quad (2)$$

Indeed, the reaction probability density function is a two-variable probability density function that can be described as the product of two one-variable probability density functions:

$$P(\tau, i) = P(\tau).P(i) \quad (3)$$

where, $P(\tau d\tau)$ is the probability of occurrences of the next reaction between times $t+\tau$ and $t+\tau+d\tau$, irrespective of which reaction could be, and $P(i)$ represents the probability that the next reaction may be R_i reaction occurring at time $t+\tau$.

By the addition theory for probabilities, $P(\tau d\tau)$ is achieved by summation of $P(\tau, i) d\tau$ on overall i -values:

$$p(t) = \sum_{i=1}^M P(\tau, i) \quad (4)$$

at which $P(i)$ is obtained by substituting Eq. (4) in Eq. (3) as:

$$p(i) = P(\tau, i) / \sum_{i=1}^M P(\tau, i) \quad (5)$$

These two equations clearly define the two one-variable density functions in Eq. (3) that give two-variable density function $P(\tau, i)$. By substitution of Eq. (2) in Eqs. (4) and (5) $P(\tau)$ and $P(i)$ are as follows:

$$P(\tau) = a \exp(-a\tau) \quad 0 \leq \tau \leq \infty \quad (6)$$

$$P(i) = \frac{a_i}{a} \quad (i = 1, 2, \dots, M) \quad (7)$$

Therefore, we have in summary:

$$a_i = k_i C_i \quad (i = 1, 2, \dots, M) \quad (8)$$

$$a = \sum_{i=1}^M a_i = \sum_{i=1}^M k_i C_i \quad (9)$$

In this exceptional case, $P(i)$ is independent of τ . It is also noted that, both of these one-variable density functions are suitably standardized over their respective description:

$$\int_0^{\infty} P(\tau) d\tau = \int_0^{\infty} a \exp(-a\tau) d\tau = 1, \quad \sum_{i=1}^M P(i) = \sum_{i=1}^M \frac{a_i}{a} = 1$$

The idea of this technique is forming a random value of τ according to $P(\tau)$ in Eq. (6), then creating a random integer i according to $P(i)$ in Eq. (7). The result of random pair (τ, i) can be distributed according to $P(\tau, i)$.

A random value τ can be generated according to $P(\tau)$ in

Eq. (6) by apparently drawing a random number r_1 , from the uniform distribution in the unit interval and calculating

$$\tau = \left[\frac{1}{a} \right] \ln \left[\frac{1}{r_1} \right] \quad (10)$$

Finally a random integer i may be created according to $P(i)$ in Eq. (7) by drawing another random number r_2 from the uniform distribution in the unit interval by taking i to be that integer for which,

$$\sum_{v=1}^{i-1} a_v < r_2 a \leq \sum_{v=1}^i a_v \quad (11)$$

In this method, two random numbers r_1 and r_2 are formed, τ and i are calculated by Eq. (10) and Eq. (11), respectively. The simulation was extended by frequently choosing at random among the probability weighted steps in the reaction mechanism and updating the substrates and products populations according to stoichiometry of the designated step, system state variables and reaction rate constants. The results were attained as curves of concentration versus time. This stochastic method has been used to simulation of numerous chemical reactions [28-34]. In the present work kinetic Monte Carlo simulation has been applied to kinetic study of the ozonation of oxalic acid over LaFeO₃, LaNiO₃, LaCoO₃ and LaMnO₃.

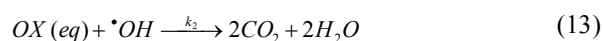
RESULTS AND DISCUSSION

In this research, the kinetics and ozonation mechanism of oxalic acid over lanthanum-based perovskites catalysts are investigated. Orge and his coworkers have studied the removal of oxalic acid by O₃, O₃/LaFeO₃, O₃/LaNiO₃, O₃/LaCoO₃ and O₃/LaMnO₃ [27]. The concentration of oxalic acid versus time curves was attained for each abovementioned catalytic systems. In the present study, kinetics modelling of the oxalic acid ozonation over the lanthanum-based perovskites performed using kinetic Monte Carlo simulation.

Kinetic Monte Carlo Simulation of Oxalic Acid Degradation by Ozone

At first, kinetic Monte Carlo method was carried out for

simulation of experimental data for oxalic acid ozonation in the absence of perovskites catalysts [27]. The input information for this simulation are temperature of reaction (298 K), initial concentration of oxalic acid ([OX]₀ = 1 × 10⁻³ M), initial concentration of ozone (50 g m⁻³) [27], the steps of proposed mechanism and rate constants of each step. The values of rate constants were adjusted until a perfect agreement was attained between the simulated and the experimental ozonation data. Several mechanisms have been examined for the ozonation of oxalic acid using kinetic Monte Carlo simulation. The mechanism which has a reasonable fitting with the experimental results can be written as:



In the above mechanism, hydroxyl radical is produced by reaction between ozone and water (reaction 12, rate constant = k_1). Consequently oxalic acid is oxidized by hydroxyl radical with the rate constant k_2 (reaction 13). The rate constant of two steps were obtained as adjustable parameters using kinetic Monte Carlo simulation (Table 1, entries 1,2). It is shown in this table that the first step (reaction (12)) is the rate-determining step. Thus, k_1 is more significant than k_2 in the direct ozonation process.

The curves of oxalic acid concentrations versus time have been obtained for the ozonation reaction using kinetic Monte Carlo simulation. There is well agreement between simulated and experimental [27] destruction curves as presented in Fig. 1.

Kinetic Monte Carlo Simulation of Oxalic Acid Ozonation over Lanthanum-based Perovskites Catalysts

Also, the kinetic Monte Carlo simulation has been applied to identify the suitable mechanism for ozonation of oxalic acid in the presence of lanthanum-based perovskites catalysts. The investigation was performed to modelling of oxalic acid ozonation ([OX]₀ = 1 × 10⁻³ M, [O₃]₀ = 50 g m⁻³) over LaFeO₃ (100 mg) at room temperature [27]. The aforementioned initial condition, steps of proposed

Table 1. Rate Constants of the Simulated Mechanism for Direct and Heterogeneous Catalytic Ozonation of Oxalic Acid

Entry	Reactions	Rate constants (min ⁻¹)
1	$O_3 + H_2O \longrightarrow O_2 + 2 \cdot OH$	$k_1 = 5 \times 10^{-2}$
2	$\cdot OH + OX \longrightarrow 2CO_2 + 2H_2O$	$k_2 = 4.95$
3	$O_3(aq) + LaFeO_3 \longrightarrow O_3(ad)^a$	$k_1 = 2.58 \times 10^1$
4	$O_3(aq) + LaNiO_3 \longrightarrow O_3(ad)^b$	$k_1 = 1.06 \times 10^2$
5	$O_3(aq) + LaCoO_3 \longrightarrow O_3(ad)^c$	$k_1 = 1.22 \times 10^2$
6	$O_3(aq) + LaMnO_3 \longrightarrow O_3(ad)^d$	$k_1 = 1.47 \times 10^2$
7	$O_3(ad) + H_2O \longrightarrow 2 \cdot OH + LaFeO_3^a$	$k_2 = 1.23$
8	$O_3(ad) + H_2O \longrightarrow 2 \cdot OH + LaNiO_3^b$	$k_2 = 1.21$
9	$O_3(ad) + H_2O \longrightarrow 2 \cdot OH + LaCoO_3^c$	$k_2 = 1.22$
10	$O_3(ad) + H_2O \longrightarrow 2 \cdot OH + LaMnO_3^d$	$k_2 = 1.20$
11	$OX(aq) + LaFeO_3 \longrightarrow OX(ad)^a$	$k_3 = 1.85 \times 10^1$
12	$OX(aq) + LaNiO_3 \longrightarrow OX(ad)^b$	$k_3 = 8.04 \times 10^1$
13	$OX(aq) + LaCoO_3 \longrightarrow OX(ad)^c$	$k_3 = 1.07 \times 10^2$
14	$OX(aq) + LaMnO_3 \longrightarrow OX(ad)^d$	$k_3 = 1.23 \times 10^2$
15	$OX(ad) + \cdot OH \longrightarrow 2CO_2 + 2H_2O^a$	$k_4 = 2.01 \times 10^2$
16	$OX(ad) + \cdot OH \longrightarrow 2CO_2 + 2H_2O^b$	$k_4 = 2.02 \times 10^2$
17	$OX(ad) + \cdot OH \longrightarrow 2CO_2 + 2H_2O^c$	$k_4 = 2.02 \times 10^2$
18	$OX(ad) + \cdot OH \longrightarrow 2CO_2 + 2H_2O^d$	$k_4 = 2.03 \times 10^2$

^aOxalic acid ozonation over LaFeO₃ (simulation condition: [OX]_o = 1 × 10⁻³ M, [O₃]_o = 50 g m⁻³, T = 273 K, pH = 3.0). ^bOxalic acid ozonation over LaNiO₃ (simulation condition: [OX]_o = 1 × 10⁻³ M, [O₃]_o = 50 g m⁻³, T = 273 K, pH = 3.0). ^cOxalic acid ozonation over LaCoO₃ (simulation condition: [OX]_o = 1 × 10⁻³ M, [O₃]_o = 50 g m⁻³, T = 273 K, pH = 3.0). ^dOxalic acid ozonation over LaMnO₃ (simulation condition: [OX]_o = 1 × 10⁻³ M, [O₃]_o = 50 g m⁻³, T = 273 K, pH = 3.0).

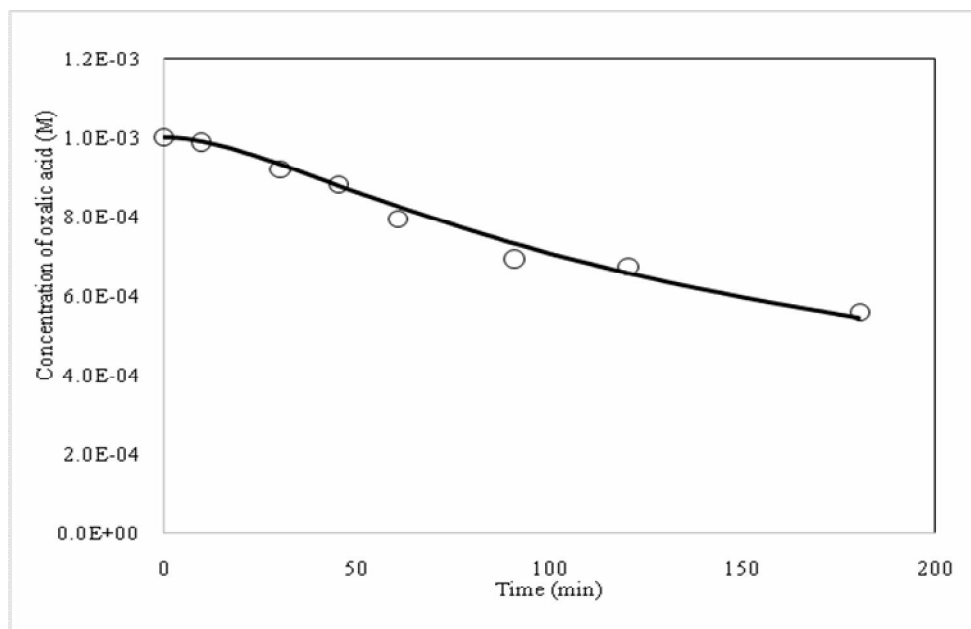
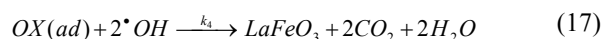
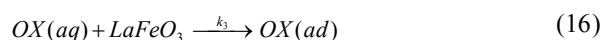
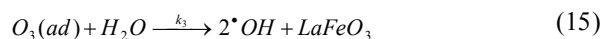
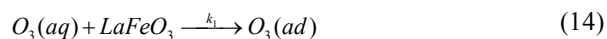


Fig. 1. Kinetics of oxalic acid ozonation. Experimental data (open circles) and simulated data (solid line). Initial concentration of oxalic acid = 1×10^{-3} M, initial concentration of ozone = 50 g m^{-3} and temperature (298 K), pH = 3.0.

mechanism and rate constants of each step are input data for the simulation.

Various mechanisms proposed for ozonation of oxalic acid by LaFeO_3 were simulated by the kinetic Monte Carlo method. Most adjustable mechanism with existing experimental results are presented in this research. In the mechanism which has a perfect fitting with the experimental kinetic data, ozone ($\text{O}_3(\text{aq})$) is adsorbed on the LaFeO_3 surface ($\text{O}_3(\text{ad})$) and subsequently reacts with water to produce hydroxyl radicals. Oxalic acid is also adsorbed on the catalyst surface and combines with created hydroxyl radicals resulting in formation of CO_2 and H_2O . These steps can be described as below:



The right rate constants were determined by changing rate determining step. Also, the values of the rate constants were changed until a reasonable fitting between the calculated and existing experimental data [27] was found. The rate constants k_1 - k_4 were achieved as adjustable parameters by kinetic Monte Carlo simulation as listed in Table 1 (entries 3, 7, 11, 15). Furthermore, the proposed mechanism was applied for modelling the ozonation reaction over various lanthanum-based perovskites catalysts including LaNiO_3 , LaCoO_3 and LaMnO_3 . The input data are $[\text{OX}]_0 = 1 \times 10^{-3}$ M, $[\text{O}_3]_0 = 50 \text{ g m}^{-3}$, 100 mg initial amount of catalyst, temperature (298 K), [27] the steps of aforementioned mechanism and rate constants of each step. The values of the rate constants were adjusted until a reasonable agreement was observed between the calculated and experimental ozonation data [27].

Table 1 represents the values of rate constants for the ozonation of oxalic acid by these perovskites catalysts. It is shown in this table that the second step (reaction (15)) is the rate-determining step. Therefore, k_2 is more significant than other rate coefficients in the abovementioned process. Comparison of the direct and catalytic ozonation simulated

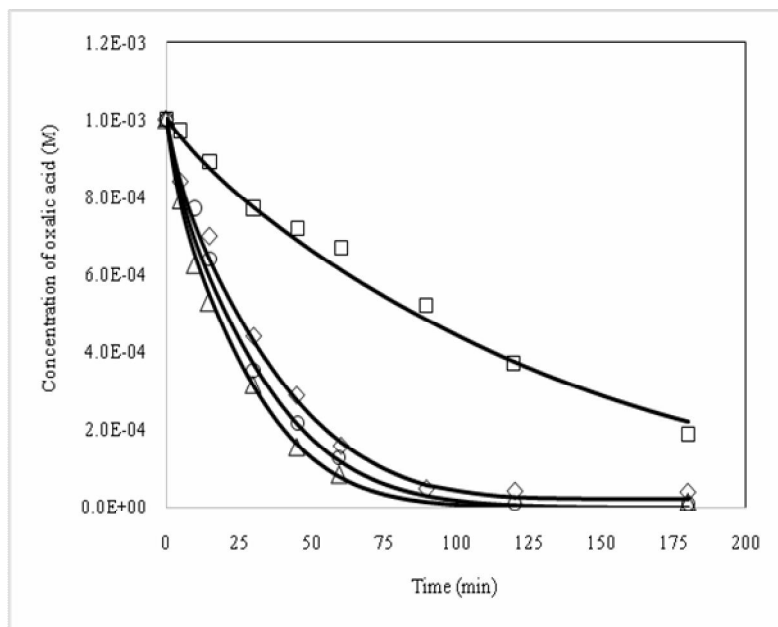
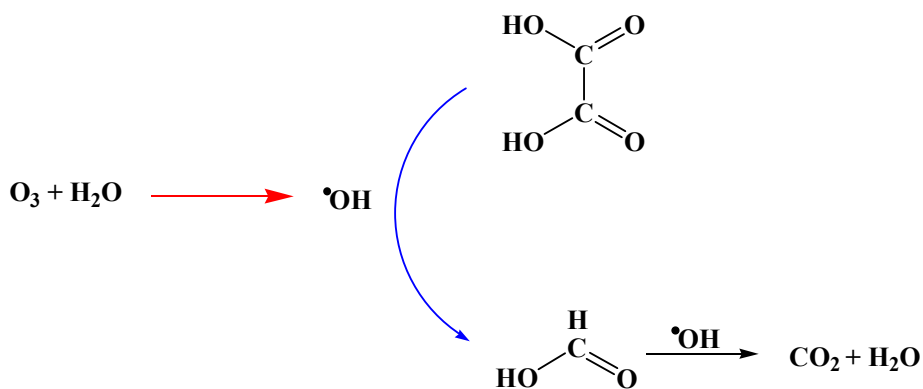


Fig. 2. Kinetic data for decomposition of oxalic acid by (\square) $\text{O}_3/\text{LaFeO}_3$, (\diamond) $\text{O}_3/\text{LaNiO}_3$, (\circ) $\text{O}_3/\text{LaCoO}_3$ and (Δ) $\text{O}_3/\text{LaMnO}_3$. Experimental data (open circles) and theoretical data (solid line). Initial concentration of oxalic acid = 1×10^{-3} M, $[\text{O}_3]_0 = 50 \text{ g m}^{-3}$ over 100 mg LaFeO_3 and $T = 298 \text{ K}$, $\text{pH} = 3.0$.



Scheme 1. The possible pathway for ozonation of oxalic acid

results of Table 1 indicates that $\text{O}_3(\text{ad})$ is combined with H_2O much faster than $\text{O}_3(\text{eq})$. Additionally, adsorbed oxalic acid on the perovskites catalysts ($\text{OX}(\text{ad})$) is more reactive than $\text{OX}(\text{eq})$ and reacts with hydroxyl radical about 40 times faster than $\text{OX}(\text{eq})$. As a result, the lanthanum-based perovskites catalysts display significant roles during oxalic acid ozonation by increasing reactivity of ozone and oxalic

acid on the surface of catalyst. Furthermore, comparison of the rate constants k_1 - k_4 of the recent mechanism between the different lanthanum-based perovskites catalysts demonstrates that the adsorption rates of ozone (k_1) and oxalic acid (k_3) increase as $\text{LaMnO}_3 > \text{LaCoO}_3 > \text{LaNiO}_3 > \text{LaFeO}_3$, while the reaction rates of $\text{O}_3(\text{ad})$ (k_2) and $\text{OX}(\text{ad})$ (k_3) are almost constant for four perovskites catalysts.

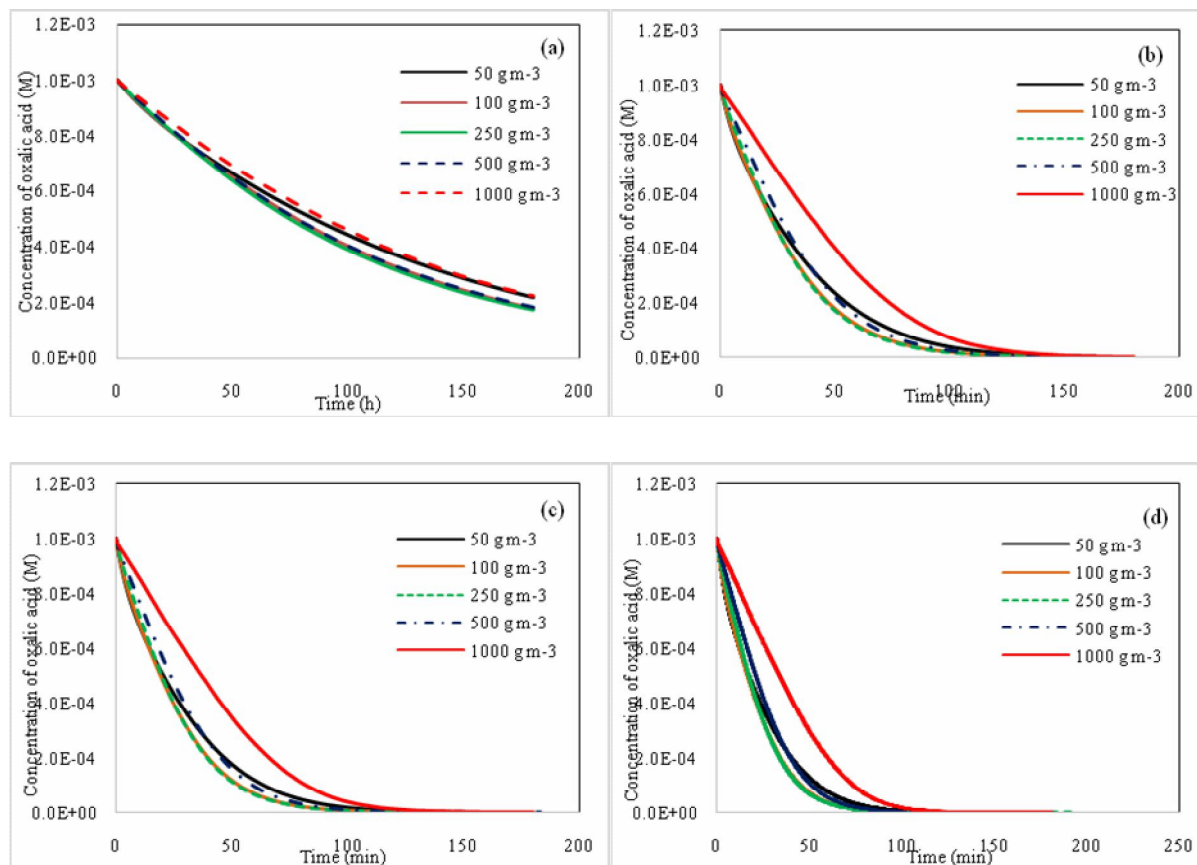


Fig. 3. Effect of inlet ozone concentration on the rate of oxalic acid degradation over (a) LaFeO_3 , (b) LaNiO_3 , (c) LaCoO_3 , (d) LaMnO_3 . Initial concentration of oxalic acid = 1×10^{-3} M, initial amount of LaMO_3 (100 mg) and $T = 298$ K, $\text{pH} = 3.0$.

Concentrations of oxalic acid versus time curves have been obtained for the ozonation reaction over LaFeO_3 , LaNiO_3 , LaCoO_3 and LaMnO_3 using kinetic Monte Carlo simulation and results were illustrated in Fig. 2. As shown in this figure, simulated data have perfect agreement with experimental ozonation data [27]. These agreements demonstrate that the proposed mechanism can be appropriate for studying kinetics of oxalic acid ozonation reaction over the perovskites catalysts.

A possible mechanism for ozonation of oxalic acid has been revealed in Scheme 1. Ozone reacts with water and generates hydroxide radicals. Subsequently formic acid is formed by $\bullet\text{OH}$ reaction with oxalic acid and produces carbon dioxide and water. It should be noted that these

processes are performed over surface of lanthanum-based perovskites catalysts.

Effect of Inlet Ozone Concentration on the Rate of Oxalic Acid Degradation over Lanthanum-Based Perovskites Catalysts

In order to investigate the effect of inlet ozone concentration on the rate of oxalic acid decomposition catalyzed by LaMO_3 ($M = \text{Fe, Ni, Co, Mn}$), various inlet ozone concentrations have been selected. Different initial concentrations of ozone used for simulations are 50, 100, 250, 500 and 1000 g m^{-3} . The input data for the simulations are temperature (298 K), initial concentration of ozone, initial concentration of oxalic acid ($[\text{OX}]_0 = 1 \times 10^{-3} \text{ M}$),

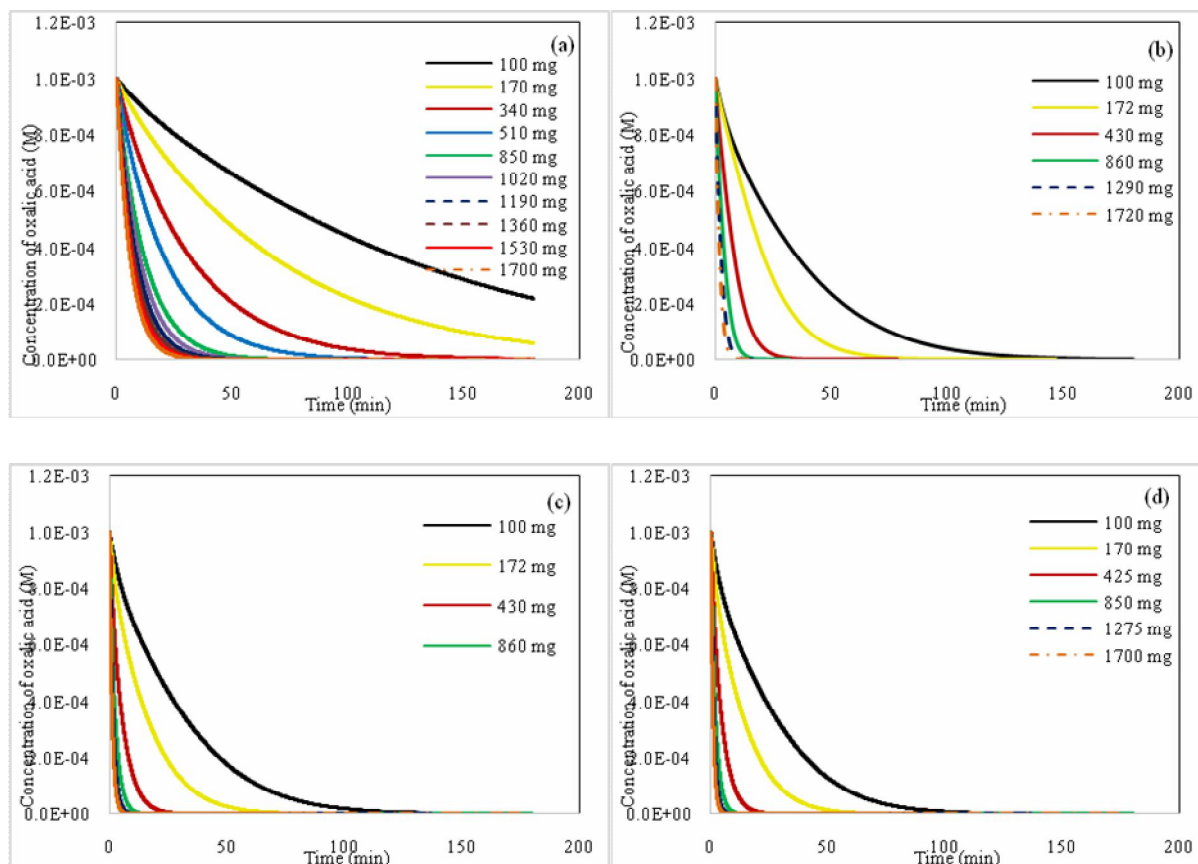


Fig. 4. Effect of initial LaMO₃ amount on the rate of oxalic acid ozonation (a) LaFeO₃, (b) LaNiO₃, (c) LaCoO₃, (d) LaMnO₃. Initial concentration of ozone = 50 g m⁻³, initial concentration of oxalic acid = 1 × 10⁻³ M and T = 298 K, pH = 3.0.

initial amount of LaMO₃ (100 mg) [27], the obtained steps of mechanism and rate constants of them (Table 1). Figure 3a represents the simulated values of oxalic acid concentration as a function of time for different inlet ozone concentrations over LaFeO₃ obtained by kinetic Monte Carlo method. Generally, there is no considerable effect on the oxidation rate of oxalic acid by enhancing inlet ozone concentration. The rate of oxalic acid degradation increases by increasing ozone concentration up to 100 g m⁻³, and the rate is constant until 250 g m⁻³ ozone inlet but it decreases by increasing ozone concentration more than 250 g m⁻³. Therefore, optimized concentration of inlet ozone can be 100 g m⁻³. The oxalic acid concentration from 50, 100, 250, 500 and 1000 g m⁻³ O₃ over LaFeO₃ after 180 min are

obtained as 2.20×10^{-4} , 1.82×10^{-4} and 1.82×10^{-4} , 1.82×10^{-4} , 2.20×10^{-4} M, respectively. This treatment was also observed for the reaction over LaNiO₃, LaCoO₃ and LaMnO₃ (Figs. 3b-3d).

Effect of Initial LaMO₃ amount on the Rate of Oxalic Acid Ozonation

Using the proposed mechanism and kinetic parameters, the simulation has been carried out for different initial amounts of lanthanum-based perovskites catalysts. To study the effect of initial amount of the catalysts on the rate of oxalic acid ozonation, different initial amounts of catalysts have been chosen. The input data for the simulations are temperature (298 K), initial concentration of ozone (50

g m^{-3}), initial concentration of oxalic acid ($1 \times 10^{-3} \text{ M}$) [27], initial amount of LaMO_3 , the mechanism and the obtained rate constants for each step (Table 1). Figure 4a illustrates the effect of initial amount of LaFeO_3 on the rate of oxalic acid ozonation. As seen in this figure, the rate of oxalic acid ozonation increases by enhancing initial amount of LaFeO_3 catalyst. However, there is no significant effect on the oxalic acid ozonation by increasing initial LaFeO_3 amount more than 850 mg. This treatment was also observed for the ozonation reaction over LaNiO_3 , LaCoO_3 and LaMnO_3 (Figs. 4b-4d).

CONCLUSIONS

Kinetic Monte Carlo simulation was used as an efficient method to investigate the kinetics and mechanism of oxalic acid degradation by O_3 , $\text{O}_3/\text{LaFeO}_3$, $\text{O}_3/\text{LaNiO}_3$, $\text{O}_3/\text{LaCoO}_3$ and $\text{O}_3/\text{LaMnO}_3$. The rate constant of mechanism steps were obtained by the simulation. Comparison of the direct and catalytic ozonation simulation results demonstrates that the lanthanum-based perovskites catalysts display significant roles during oxalic acid ozonation by increasing the reactivity of ozone and oxalic acid on the surface of catalyst. The effect of inlet ozone concentration and initial amount of LaMO_3 ($\text{M} = \text{Fe}, \text{Ni}, \text{Co}, \text{Mn}$) on the rate of oxalic acid degradation was studied. The kinetic Monte Carlo simulation results demonstrate qualitative agreement with the experimental kinetic data of oxalic acid ozonation for each aforementioned catalytic system. Therefore, the obtained mechanisms can be suitable for the kinetic study of pollutant removal by direct and heterogeneous catalytic ozonation.

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