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Kinetically simulation of photo-Fenton process in removal of sulfamethazine, ciprofloxacin, sulfathiazole and amoxicillin by Monte Carlo modeling

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RESEARCH ARTICLE

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ABSTRACT

Kinetic Monte Carlo modeling was employed to investigate the kinetics and photodecomposition mechanism of sulfamethazine, ciprofloxacin, sulfathiazole, and amoxicillin antibiotics by the photo-Fenton process (iron(III) citrate/hydrogen peroxide in the presence of UV irradiation). The reaction kinetic mechanisms of each photo-Fenton degradation mentioned above have been achieved. The rate constants values for each step of the reaction mechanisms (including photo-Fenton process of antibiotics) were obtained as adjustable parameters by kinetic Monte Carlo simulation. The optimized values of iron(III) citrate and hydrogen peroxide were investigated through the obtaining the effect of their initial amounts on the rate of antibiotic elimination utilizing kinetic Monte Carlo simulation. The perfect agreement is observed between the simulation results and the experimental photo-Fenton data for the systems above.

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1. Introduction

Antibiotics are generally consumed for the treatment of bacterial infections in humans and animals and are also used in the production of livestock animals as growth promoters [1]. Many antibiotics are negligibly metabolized in the body [2,3], are excreted with their main component, and are transferred to wastewater. The existence of antibiotics in aquatic systems has become a main concern of scientists to discover efficient ways to eliminate these pollutants from water.

Several treatment methods have been proposed for the removal of dyes from contaminated waters which include photodecomposition, electrolysis, adsorption, oxidation, biodegradation, and coagulation flocculation [4-8].

Elimination of antibiotics and dyes has been investigated on various platforms of water treatment. Recently, the advanced oxidation processes (AOPs) that are based on hydroxyl radical production have been widely developed as suitable methods for the removal of non-biodegradable organic pollutants from water [9,10]. In order to decomposition of antibiotics most studies have been done according to AOPs including photocatalytic oxidation [11,12], ozonation [13], Fenton and Photo-Fenton processes [14-16]. In the Fenton process hydroxyl radicals are created from a solution of hydrogen peroxide and Fe(II) ions in an acidic medium [17]. This method can be improved by the assistant of UV-Vis irradiation (Photo-Fenton process) in which the reduction of Fe(III) to Fe(II) ions is hastened [18]. For example, degradation of sulfamethazine (SMZ), ciprofloxacin (CIP), sulfathiazole (STZ), and amoxicillin (AMX) in aqueous systems has been carried out by photo-Fenton process (Iron(III) citrate (FeCit)/H_2O_2/UV irradiation) [19].

Monte Carlo (MC) modeling has been broadly used in different science, such as engineering, physics, materials science and chemistry [20]. The MC method was used to study structural properties in condensed phases comprising magnetic reactivity, thermophysical and mechanical properties [21-30]. Kinetic Monte Carlo (kMC) simulation has been widely employed as an excellent method to study kinetic parameters in plentiful chemical process [31-38]. Kinetic Monte Carlo method has been magnificently developed to overcome some drawbacks of conventional deterministic modeling which can contain atomic surface structure and reaction conditions as a function of time [39-42]. When more accuracy is required in modeling, kMC simulation with outstanding efficiency is excellent for quick scans in diverse situations. In the kMC method, different mechanisms can be switched "*on*" and "*off*" *via* varying the diverse parameters and the influences of various

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factors on the output results can be easily investigated. By the analysis of different mechanistic states in this method and by comparing the consequences of kMC with the experimental results studied, perception of the mechanisms is afforded. The kMC method has numerous of superiorities to traditional method in solving numerically differential equations, which are more rapidly calculations for each step, facility of data handling, modeling of long-time scales and temperature programing [43].

The main purpose of ongoing research is to study kinetic parameters and mechanisms of photo-Fenton process ($FeCit/H_2O_2/UV$) for removing antibiotics including SMZ, CIP, STZ and AMX from wastewater. Simulated concentration curves *versus* time were obtained for antibiotics mentioned above, and the effects of various factors comprising initial concentrations of iron(III) citrate and H_2O_2 on the rate of antibiotic degradation were also investigated by kMC simulation.

In this method, the effect of different parameters on the output data can be examined and various mechanisms can be switched on and off by changing the parameters. By testing various mechanistic situations in the kMC method and comparing the results with experimental data, we can gain insight into the mechanisms. Compared with traditional methods for solving numerically differential equations, this method has many advantages, such as faster computation for each attempted step, easier data handling, temperature programming, and simulation of long-time scales.

2. Experimental

In the present study, the kinetics and mechanism of elimination of some antibiotics from wastewater were assayed by the photo-Fenton process. Perini *et al.* studied the degradation of STZ, AMX, CIP, and SMZ using a photo-Fenton system containing iron(III) citrate/H_2O_2 at the present UVC irradiation and the concentration curves of each antibiotic mentioned *versus* time were obtained [19]. Through these experimental curves, the degradation of STZ, AMX, CIP and SMZ by $FeCit/H_2O_2/UV$ was modelled using kMC simulation. To perform the kMC simulation, experimental information such as initial antibiotic concentrations (FeCit and H_2O_2) and also temperature should be placed in CKS software as input data. The resultants of CKS simulation are concentration curves of antibiotics as a function of time should be in well agreement with existing experimental data.

The photo-Fenton process in removal of antibiotics including sulfathiazole, amoxicillin, sulfamethazine and ciprofloxacin [19] was kinetically simulated by the stochastic algorithm of Monte Carlo technique [44]. Chemical Kinetic Simulator (CKS) software [45] was applied for kinetic Monte Carlo (kMC) modeling.

In the algorithm of simulation, the reaction mechanism consists of several reactions including:

$$nN + mM + ... \rightarrow \text{Products} \quad (1)$$

The input information for the kMC simulation is the steps of the supposed mechanism, the rate constants of each step (k_i), and the initial number of molecules in the reaction (C_i). Thus, we have [44]:

$$a_i = k_i \times C_i \; (I = 1, 2, ..., M) \quad (2)$$

$$a = \sum_{i=1}^{M} a_i = \sum_{i=1}^{M} k_i \times C_i \quad (3)$$

The reaction probability density function, $P(\tau,i)$, plays an important role in the algorithm of kMC modelling. $P(\tau,i)$ is calculated by Master equation [44]:

$$P(\tau,i) = k_i \times C_i \times exp\{-\Sigma k_i \times C_i \times \tau\} \quad (4)$$

A random amount of τ (Time of each step in mechanism) is achieved by drawing a random value (r_1) from the constant distribution in the unit distance:

$$\tau = \left[\frac{1}{a}\right] \ln\left[\frac{1}{r_1}\right] \quad (5)$$

Moreover, a random value i can be caused by drawing a random amount (r_2) from the uniform distribution in the unit interval by captivating i to be the value for which,

$$\sum_{v=1}^{i-1} a_v < r_2 a \leq \sum_{v=1}^{i} a_v \quad (6)$$

In this technique, r_1 and r_2 are created to compute τ and i using Equations (5) and (6) [44].

The Monte Carlo simulation was extended by repeatedly randomly selecting among the probability-weighted steps in the suitable mechanism and updating the populations of reactants, substrates and products with the stoichiometric ratios for each step, state variables, and reaction rates. Final resultants of the kMC modeling are curves of concentration *vs* time. This stochastic numerical approach has been utilized to study various chemical systems [30-37]. In ongoing research, the kMC simulation method was applied to investigate the kinetics of the degradation of STZ, AMX, CIP and SMZ by the photo-Fenton (Iron(III) citrate and H_2O_2 in the current UVC irradiation) process.

3. Results and discussion

In order to find the appropriate kinetic mechanism for antibiotic elimination by the photo-Fenton system, the kMC modeling of the experimental data was first performed for the degradation of SMZ by $FeCit/H_2O_2/UV$. The input data for the simulation are the steps of the recommended mechanism, the rate coefficients of each step, and the experimental reaction conditions (Temperature = 298.15 K, initial SMZ concentration = 7.19×10^{-1} μM, initial FeCit concentration = 10 μM and initial H_2O_2 concentration = 500 μM). Various mechanisms which have been proposed for antibiotic degradation by photo-Fenton system were simulated by kMC method. The most adjustable mechanism with existing experimental results was presented in this research.

In the mechanism which has a perfect fitting with the experimental kinetic data, iron(III) citrate is broken by UV irradiation and Fe^{2+} ions are created. Then, the oxidation of Fe^{2+} ions by H_2O_2 produces hydroxyl radicals and Fe^{3+} ions. Produced Fe^{3+} ions react with hydrogen peroxide and Fe^{2+} ions are again generated so that Fe^{2+}/Fe^{3+} cycle is established. The SMZ antibiotic degrades by created OH. These reactions are defined as follows:

$$\text{Fe(III)-Cit} \xrightarrow{h\upsilon,\ k_1} Fe^{2+} + {}^{\bullet}OOC\text{-}C(OH)(CH_2COO)_2^{2-} \quad (7)$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k_2} Fe^{3+} + {}^{-}OH + {}^{\bullet}OH \quad (8)$$

$$Fe^{3+} + H_2O_2 \xrightarrow{k_3} Fe^{2+} + HOO^{\bullet} + H^{+} \quad (9)$$

$$SMZ + {}^{\bullet}OH \xrightarrow{k_4} \text{Degradation products} \quad (10)$$

Accurate rate constants were determined by varying the rate determination step. Also, the values of the rate constants of the aforementioned mechanism were changed up to a reasonable fitting between the simulated and experimental results [19] was found.

Table 1. Rate constants of the simulated photo-Fenton mechanism for the removal of antibiotics.

Entry	Antibiotic	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	k_4 (min^{-1})
1 [a]	SMZ	2.16×10^{1}	4.21×10^{3}	1.54×10^{3}	4.52×10^{2}
2 [b]	CIP	2.16×10^{1}	4.21×10^{3}	1.54×10^{3}	4.63×10^{2}
3 [c]	AMX	2.16×10^{1}	4.21×10^{3}	1.54×10^{3}	9.97×10^{2}
4 [d]	STZ	2.16×10^{1}	4.21×10^{3}	1.54×10^{3}	1.44×10^{3}

[a] Simulation condition: $[SMZ]_\circ$ = 0.719 µM, $[FeCit]_\circ$ = 10 µM, $[H_2O_2]_\circ$ = 500 µ, T = 298.15 K, and pH = 7.4.
[b] Simulation condition: $[CIP]_\circ$ = 0.604 µM, $[FeCit]_\circ$ = 10 µM, $[H_2O_2]_\circ$ = 500 µ, T = 298.15 K, and pH = 7.4.
[c] Simulation condition: $[AMX]_\circ$ = 0.547 µM, $[FeCit]_\circ$ = 10 µM, $[H_2O_2]_\circ$ = 500 µ, T = 298.15 K, and pH = 7.4.
[d] Simulation condition: $[STZ]_\circ$ = 0.783 µM, $[FeCit]_\circ$ = 10 µM, $[H_2O_2]_\circ$ = 500 µ, T = 298.15 K, and pH = 7.4.

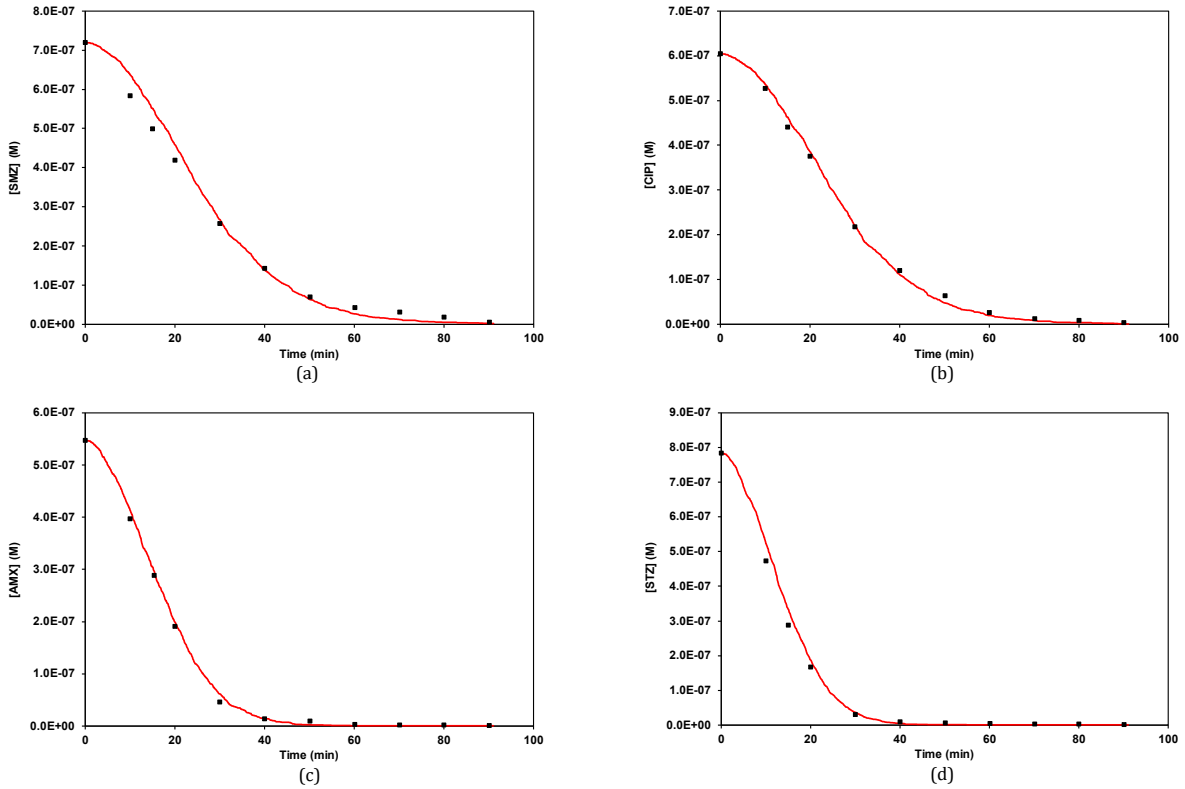

Figure 1. Kinetic data for removal of (a) SMZ, (b) CIP, (c) AMX, and (d) STZ by photo-Fenton process. Experimental (Filled markers) and kMC simulation (Solid line) results. Simulation condition: $[SMZ]_\circ$ = 0.719 µM, $[CIP]_\circ$ = 0.604 µM, $[AMX]_\circ$ = 0.547 µM, $[STZ]_\circ$ = 0.783 µM, $[FeCit]_\circ$ = 10 µM, $[H_2O_2]_\circ$ = 500 µ, T = 298.15 K and pH = 7.4.

The rate constants k_1-k_4 of reactions 7-10 were achieved as variable parameters by Monte Carlo simulation as inserted in Table 1 (Entry 1). Using the offered mechanism and the kMC simulation, we also obtained the kinetic parameters for the degradation of STZ, AMX, and CIP by the photo-Fenton process. The adjustable rate coefficients of four steps for photo-Fenton decomposition of STZ, AMX and CIP antibiotics were recorded in Entries 2 and 3 of Table 1. As observed in this table, Step 1 with the rate constant k_1 (Reaction 7) is the rate determining step in the destruction of all drugs studied by FeCit/H_2O_2/UV. Consequently, k_1 is more significant than k_3-k_4 in the rate of the photo-Fenton process. As expected, the amounts of the rate constants k_1-k_3 are equal for the removal of SMZ, STZ, AMX and CIP but k_4 is different in various antibiotics.

Concentrations of STZ, AMX, SMZ, and CIP *vs* time curves were gained as output results of CKS software for the simulated photo-Fenton (FeCit/H_2O_2/UV) process (Figure 1). As a result of this figure, the simulated data shown as solid lines are in correct conformity with the experimental results [19], which were displayed as filled markers for all drugs studied. These agreements prove that the advised mechanism can be proper for kinetically study of antibiotics degradation by the photo-Fenton systems.

The effects of different conditions including initial amounts of FeCit and H_2O_2 on the removal rate of STZ, AMX, SMZ, and CIP by the photo-Fenton process were investigated using the obtained kinetic parameters by kinetic Monte Carlo simulation.

With the aim of study, the effect of initial FeCit concentration on the rate of this process, different inlet iron(III) citrate concentrations (0.5, 1, 5, 10, 50, and 100 µM) were designated for simulations and inserted in CKS software as input data. Other data inserted for these simulations are temperature (298.15 K), initial antibiotic concentration (200 µg/L), and initial amount of H_2O_2 (500 µM) [19], the mechanism steps gained (reactions 7-10) and the step rate constants (rate constants k_1-k_4, Table 1). Figure 2 represents the kMC simulation curves of concentration *versus* times for the photo-Fenton degradation of STZ, AMX, SMZ and CIP by various initial FeCit concentrations. The rate of antibiotic degradation increases with the increase in the initial FeCit amount as revealed in these curves. It can be said that the optimized value of FeCit for the photo-Fenton removal of STZ, AMX, SMZ, and CIP is 50 µM. In the presence of FeCit values greater than 50 µM, no significant increase in the photo-Fenton process rate was observed.

Furthermore, the influence of the initial value of H_2O_2 on the degradation rate of STZ, AMX, SMZ, and CIP was investigated using the kinetic mechanism and parameters obtained using kMC modeling. The initial amounts of hydrogen peroxide which were selected for this purpose are 1×10^{-5}, 5×10^{-5}, 1×10^{-4}, 5×10^{-4}, 1×10^{-3}, 5×10^{-3}, and 1×10^{-2} mol/L.

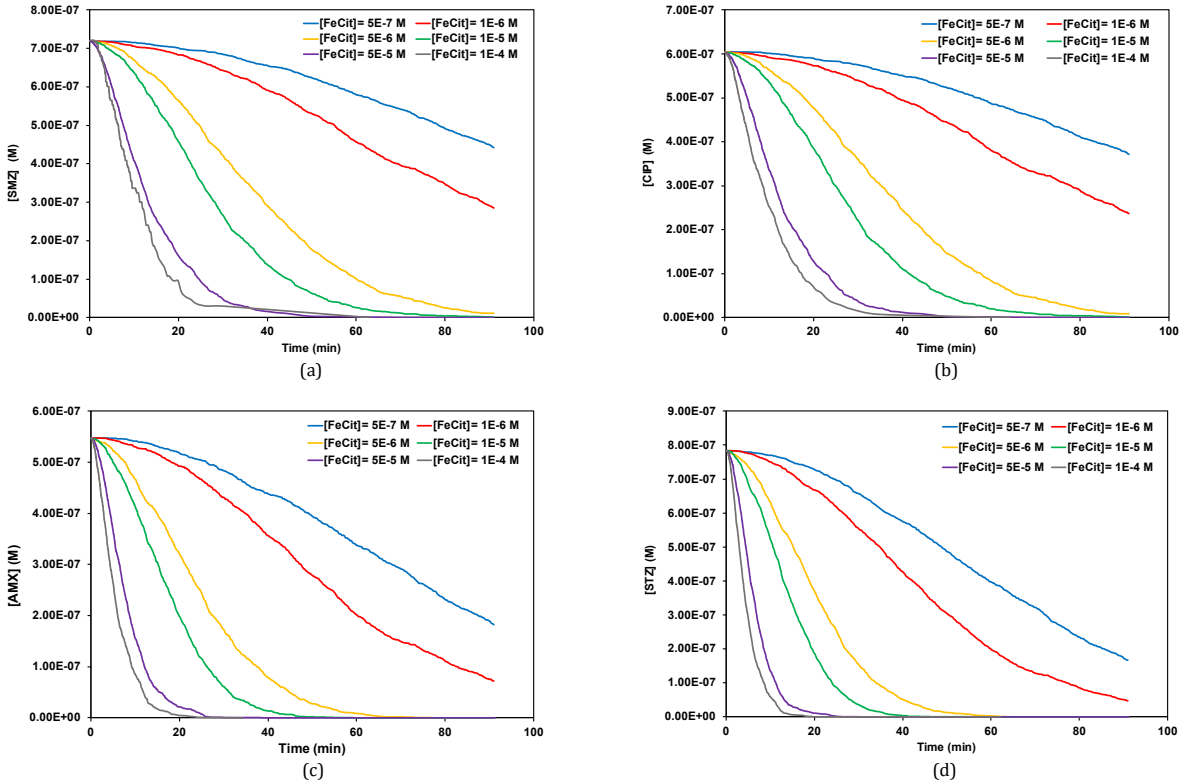

Figure 2. The removal rate of (a) SMZ, (b) CIP, (c) AMX, and (d) STZ by various inlet concentrations of FeCit. Simulation condition: $[SMZ]_{\circ}$ = 0.719 µM, $[CIP]_{\circ}$ = 0.604 µM, $[AMX]_{\circ}$ = 0.547 µM, $[STZ]_{\circ}$ = 0.783 µM, $[H_2O_2]_{\circ}$ = 500 µ, T = 298.15 K and pH = 7.4.

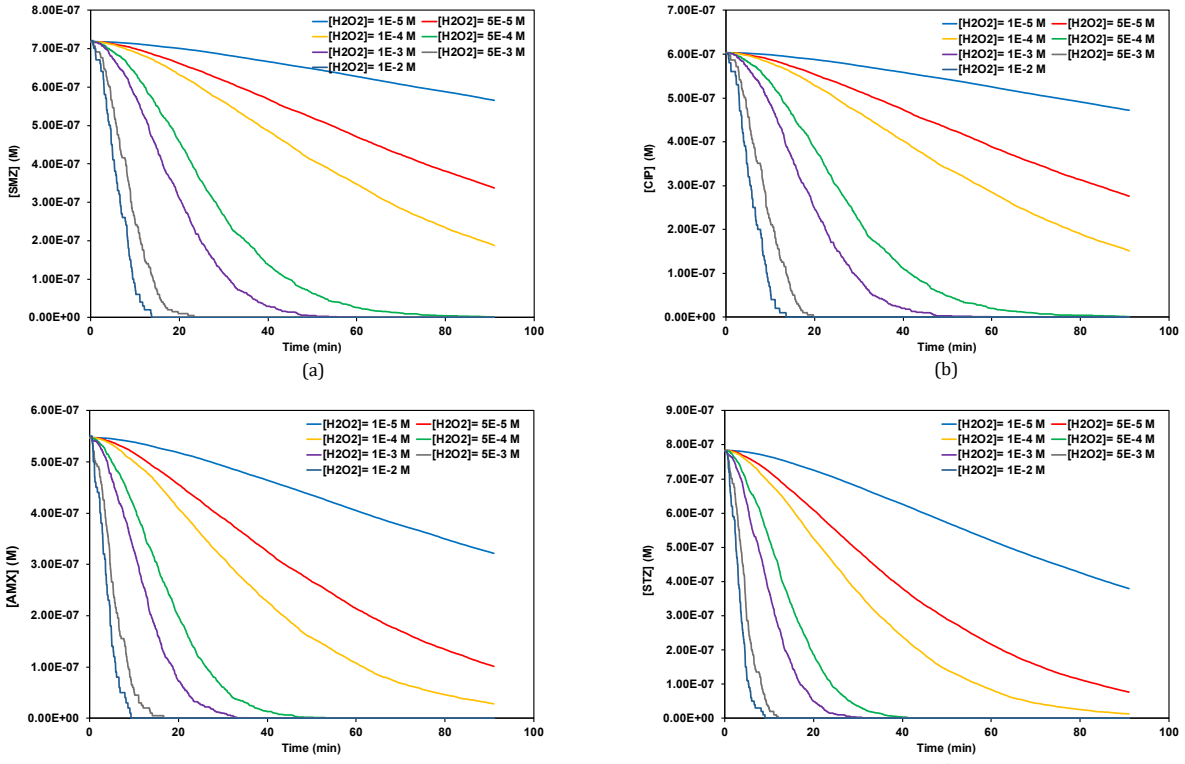

Figure 3. KMC simulation data for photo-Fenton degradation of (a) SMZ, (b) CIP, (c) AMX, and (d) STZ by different initial concentrations of H_2O_2. Simulation condition: $[SMZ]_{\circ}$ = 0.719 µM, $[CIP]_{\circ}$ = 0.604 µM, $[AMX]_{\circ}$ = 0.547 µM, $[STZ]_{\circ}$ = 0.783 µM, $[FeCit]_{\circ}$ = 10 µM, T = 298.15 K and pH = 7.4.

For these simulations, the input information in the CKS software is temperature (T = 298.15 K), the reactions of the obtained mechanism (Reaction 7-10), the rate constants k_1-k_4 in Table 1, initial antibiotics concentration (200 µg/L), initial

concentration of FeCit (10 μM) and initial amount of H_2O_2 and the results are concentration of antibiotics as a function of times which depicted in Figure 3. Clearly, the rate of photo-Fenton process increases with an increase in the amount of H_2O_2.

4. Conclusions

The kinetics of photo-Fenton destruction for antibiotics containing sulfamethazine, ciprofloxacin, sulfathiazole, and amoxicillin was studied by kMC simulation. Kinetic factors such as the photo-Fenton mechanism and rate constants were obtained *via* kMC simulation. The effects of various parameters, including initial concentrations of iron(III) citrate and H_2O_2, on the rate of degradation of antibiotics above were investigated by simulation. One of the advantages of this kMC study is obtaining an optimized condition for photo-Fenton decay of antibiotics *via* a low-cost technique. The simulated outcomes show a perfect fit with the experimental photo-Fenton data for all antibiotics studied. Thus, the offered mechanism is applicable to the kinetic investigation of photo-Fenton systems in pollutant removal from wastewater.

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Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered.

CRediT authorship contribution statement

Conceptualization: Hamid Dezhampanah, Hamed Moradmand Jalali; Methodology: Hamid Dezhampanah, Hamed Moradmand Jalali; Software: Hamid Dezhampanah, Hamed Moradmand Jalali; Validation: Hamid Dezhampanah, Hamed Moradmand Jalali; Formal Analysis: Hamid Dezhampanah, Hamed Moradmand Jalali; Investigation: Hamid Dezhampanah, Hamed Moradmand Jalali; Resources: Hamid Dezhampanah, Hamed Moradmand Jalali; Data Curation: Hamed Moradmand Jalali; Writing - Original Draft: Hamid Dezhampanah, Hamed Moradmand Jalali; Writing - Review and Editing: Hamid Dezhampanah; Visualization: Hamid Dezhampanah, Hamed Moradmand Jalali; Funding acquisition: Hamed Moradmand Jalali; Supervision: Hamid Dezhampanah; Project Administration: Hamid Dezhampanah.

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