

Simulation removal of sulfamethazine, ciprofloxacin, sulfathiazole and amoxicillin *via* photo-Fenton process in by Monte Carlo modeling

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Received Date : July 21, 2022
Accepted Date : Aug 25, 2022
Published Date : Sep 08, 2022
Archived : www.jcmimagescasereports.org
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2022

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Abstract

Kinetic Monte Carlo modeling was employed as a powerful tool to kinetically investigate of antibiotics removal by photo-Fenton process (iron(III) citrate/ hydrogen peroxide in the presence of UV irradiation). Sulfamethazine, ciprofloxacin, sulfathiazole and amoxicillin are the antibiotics which were studied in this investigation. The kinetic mechanism of the photo-Fenton degradation was found by Monte Carlo simulation for several studied antibiotics including sulfamethazine, ciprofloxacin, sulfathiazole and amoxicillin. Also the rate constants values of each step in the suggested mechanism were acquired for these antibiotics through the simulation. Optimized values of Fe(III) citrate and hydrogen peroxide were attained through obtaining the effect of their initial amounts on the rate of antibiotics elimination by utilizing kinetic Monte Carlo simulation. The perfect agreement is observed between the simulation results and the experimental photo-Fenton data for the systems above.

Keywords: Kinetic; Monte Carlo; Antibiotic; Photo-Fenton; Simulation; Degradation.

Introduction

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

The elimination of antibiotics has been investigated in various platforms of water treatment. Recently advanced oxidation processes (AOPs) which are based on the hydroxyl radicals production, have been widely developed as the suitable methods for removing of non-biodegradable organic pollutants from water [4,5]. To the decomposition of antibiotics most studies have been done according to AOPs including photocatalytic oxidation [6,7], ozonation [8], Fenton and photo-Fenton [9-11]. In the Fenton process hydroxyl radicals is created from a solution of hydrogen peroxide and Fe (II) ions in an acidic media [12]. This method can be improved by the assistant of UV-vis irradiation (photo-Fenton process) that the reduction

of Fe(III) to Fe(II) ions is hastened [13]. For example, degradation of sulfamethazine (SMZ), ciprofloxacin (CIP), sulfathiazole (STZ) and amoxicillin (AMX) in aqueous systems has been performed by photo-Fenton process (iron (III) citrate (FeCit)/ H₂O₂/ UV irradiation) [14].

Monte Carlo (MC) modeling has been broadly used in different science such as engineering, physics, materials science and chemistry [15]. The MC method was used to study of structural properties in condensed phases comprising magnetic reactivity, thermophysical and mechanical properties [16–25]. Kinetic Monte Carlo (kMC) simulation has been widely employed as an excellent method to study of kinetic parameters in plentiful chemical process [26-33]. Kinetic Monte Carlo method has been magnificently developed to overcome some drawbacks of conventional deterministic modeling which can clearly contain atomic surface structure and reaction conditions as a function of time [34-37]. When a 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 factors

Citation: Hamid Dezhampannah. Simulation removal of sulfamethazine, ciprofloxacin, sulfathiazole and amoxicillin *via* photo-Fenton process in by Monte Carlo modeling. J Clin Med Img Case Rep. 2022; 2(5): 1237.

on the output results can be easily investigated. By analysis different mechanistic states in this method and comparing the kMC consequences with studied experimental results, perception of the mechanisms is afforded. The kMC method has numerous 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 [38].

The main purpose of ongoing research is study kinetic parameters and mechanism of photo-Fenton process (FeCit/H₂O₂/UV) for removing antibiotics including SMZ, CIP, STZ and AMX from wastewater. The simulated concentration curves versus time were obtained for systems above of antibiotics and also the effects of various factors comprising such as initial concentrations of iron (III) citrate and H₂O₂ on the rate of antibiotics degradation were evaluated by kMC simulation.

Kinetic Monte Carlo modeling

The photo-Fenton process in removal of antibiotics including sulfathiazole, amoxicillin, sulfamethazine and ciprofloxacin [13] was kinetically simulated by the stochastic algorithm of the Monte Carlo technique [39]. Chemical Kinetic Simulator (CKS) software [40] was applied for the kinetic Monte Carlo (kMC) modeling.

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

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

The input information for 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 [39]:

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

$$a_i = k_i C \quad (i = 1, 2, \dots, M) \quad (3)$$

The reaction probability density function, $P(\tau, i)$, plays an important role in the algorithm of kMC modeling. $P(\tau, i)$ is calculated by Master equation [39]:

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

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:

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

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 that value for which,

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

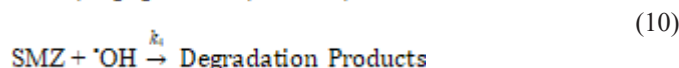
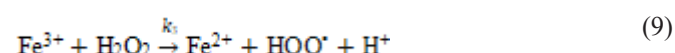
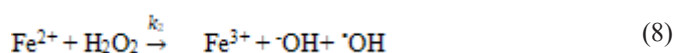
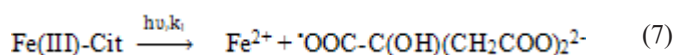
In this technique, r_1 and r_2 are created to compute τ and i through equations (5) and (6) [39].

The Monte Carlo simulation was extended via repeatedly random selecting among the probability-weighted steps in the suitable mechanism and updating the populations of reactants, and products according to the stoichiometric ratios for each step, state variables and reaction rates. Final resultants of the kMC modeling are curves of concentrations versus time. This stochastic numerical approach has been utilized to study various chemical systems [25-32]. In the ongoing research, kMC method was employed to kinetically simulation of STZ, AMX, CIP and SMZ degradation by photo-Fenton process.

Results and Discussion

Perini and his colleagues were researched degradation of STZ, AMX, CIP and SMZ using photo-Fenton system containing iron (III) citrate/H₂O₂ at present UV irradiation and the concentration curves of each mentioned antibiotics versus time were attained [13]. By means of these experimental curves, a kinetically simulation of STZ, AMX, CIP and SMZ degradation by FeCit/H₂O₂/UV were performed. To perform kMC simulation, experimental information such as initial concentrations of antibiotics, FeCit and H₂O₂ and also temperature should be placed into 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.

In order to find the appropriate kinetic mechanism for antibiotics elimination by photo-Fenton system, at first the kMC modeling of experimental data were performed for SMZ degradation by FeCit/H₂O₂/UV. The input data for the simulation are steps of recommended mechanism, rate coefficients of each step and experimental reaction conditions (temperature= 298.15 K, initial concentration of SMZ=7.19×10⁻¹ μM, initial concentration of FeCit =10 μM and initial concentration of H₂O₂=500 μM). Various mechanisms which have been proposed for antibiotic degradation by photo-Fenton system were simulated by kMC method. Most adjustable mechanism with existing experimental results were 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 Fe²⁺ is created. Then oxidation of Fe²⁺ by H₂O₂ produces hydroxyl radicals and Fe³⁺. Produced Fe³⁺ reacts with hydrogen peroxide and Fe²⁺ is again generated that Fe²⁺/Fe³⁺ cycle is established. SMZ antibiotic degrades by created •OH. These reactions are defined as below:



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Table 1: Rate constants of 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

aSimulation condition: [SMZ]₀= 0.719 μM, [FeCit]₀= 10 μM, [H₂O₂]₀= 500 μ, T=298.15 K and pH=7.4.

bSimulation condition: [CIP]₀= 0.604 μM, [FeCit]₀= 10 μM, [H₂O₂]₀= 500 μ, T=298.15 K and pH=7.4.

cSimulation condition: [AMX]₀= 0.547 μM, [FeCit]₀= 10 μM, [H₂O₂]₀= 500 μ, T=298.15 K and pH=7.4.

dSimulation condition: [STZ]₀= 0.783 μM, [FeCit]₀= 10 μM, [H₂O₂]₀= 500 μ, T=298.15 K and pH=7.4.

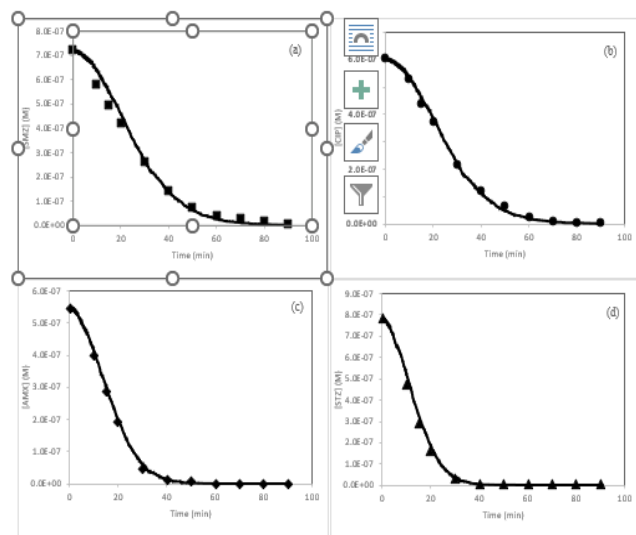


Figure 1: Kinetic data for removal of (a) SMZ, (b) CIP, (c) AMX and (d) STZ by photo-Fenton process. Experimental (Filled markers) and kMC simulation (solid line) results. Simulation condition: [SMZ]₀= 0.719 μM, [CIP]₀= 0.604 μM, [AMX]₀= 0.547 μM, [STZ]₀= 0.783 μM, [FeCit]₀= 10 μM, [H₂O₂]₀= 500 μ, T=298.15 K and pH=7.4.

Concentrations of STZ, AMX, SMZ and CIP versus time curves were shown as output results of CKS software for the simulated photo-Fenton (FeCit/H₂O₂/UV) process (Figure 1). As a result of this figure, simulated data shown as solid lines are in correct conformity with the experimental results [13] which

were displayed as filled markers for all studied drugs. This Consistency proves that the advised mechanism can be proper for kinetically study of antibiotics degradation by photo-Fenton systems.

Effects of different conditions including initial amounts of FeCit and H₂O₂ on the removal rate of STZ, AMX, SMZ and CIP by the photo-Fenton process were investigated using the obtained kinetic parameters via kinetic Monte Carlo simulation. With the aim of the 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 inserted data for these simulations are temperature (298.15 K), initial concentration of antibiotics (200 μg/L), initial amount of H₂O₂ (500 μM) [13], the gained steps of mechanism (reactions 10- 13) and the rate constants of steps (rate constants k₁-k₄, 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 diverse initial FeCit concentrations. The rate of antibiotics degradation enhances by enhancement of initial FeCit amount as revealed in these curves. It can be said that 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 increasing on the rate of photo-Fenton process was observed.

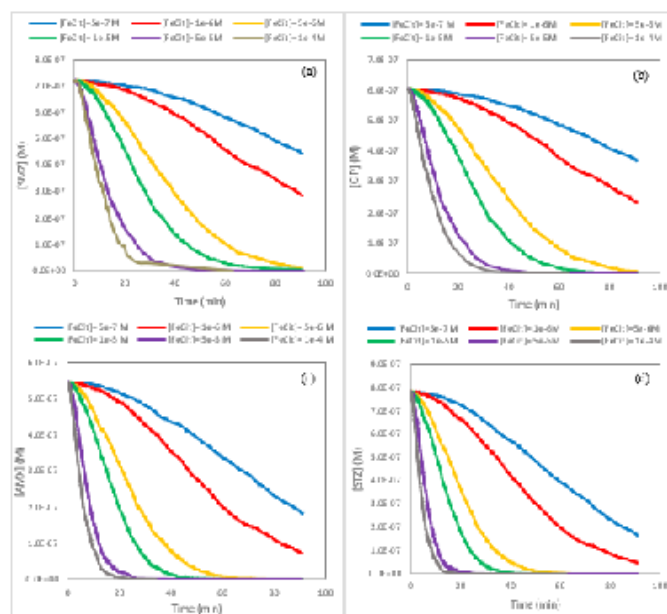


Figure 2: The removal rate of (a) SMZ, (b) CIP, (c) AMX and (d) STZ by various inlet concentration of FeCit. Simulation condition: [SMZ]₀= 0.719 μM, [CIP]₀= 0.604 μM, [AMX]₀= 0.547 μM, [STZ]₀= 0.783 μM, [H₂O₂]₀= 500 μ, T=298.15 K and pH=7.4.

Also the influence of initial H₂O₂ value on the rate of STZ, AMX, SMZ and CIP degradation was investigated by obtained kinetic mechanism and parameters 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⁻¹. For these simulations, the input information in CKS software are temperature (T=298.15 K), the reactions of obtained mechanism (reaction 7-10), the rate constants k₁-k₄ in (Table 1), initial concentration of antibiotics (200 μg/L), initial concentration of FeCit (10 μM) and initial

H2O2 amount and output results are antibiotics concentration as a function of times which depicted in (Figure 3). Clearly the rate of photo-Fenton process increases by increment of H2O2 amount.

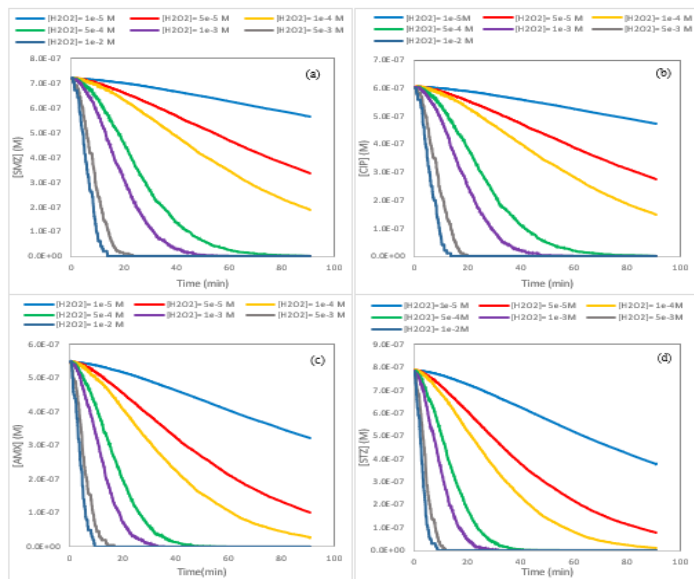


Figure 3: KMC simulation data for photo-Fenton degradation of (a) SMZ, (b) CIP, (c) AMX and (d) STZ by different initial concentration of H₂O₂. Simulation condition: [SMZ]₀= 0.719 μM, [CIP]₀= 0.604 μM, [AMX]₀= 0.547 μM, [STZ]₀= 0.783 μM, [FeCit]₀= 10 μM, T=298.15 K and pH=7.4.

Conclusions

To investigate the kinetics of photo-Fenton destruction was studied for antibiotics containing sulfamethazine, ciprofloxacin, sulfathiazole and amoxicillin by means of kMC simulation. The kinetic factors such as photo-Fenton mechanism and constant rate value of each step were determined using the kMC simulation. The effects of various parameters including initial concentrations of iron (III) citrate and H₂O₂ on the rate of above antibiotics degradation were investigated by the simulation. One of the advantages of this kMC study is obtaining optimized condition for photo-Fenton decay of antibiotics via a low-cost technique. The simulated outcomes show perfect fitting with the experimental photo-Fenton data for all studied antibiotics. Thus the offered mechanism is applicable for the kinetically research of photo-Fenton systems in pollutant removal from wastewater.

Acknowledgments

We gratefully acknowledge the graduate office of University of Guilan for supporting of this work.

Declarations

Funding: The authors declare no funding about this research.

Conflicts of interest/Competing interests: The authors declare that they have no conflict of interest.

Availability of data and material: The authors declare that there are data transparency.

Code availability: The authors declare that they have no software application or custom code.

Authors' contributions: All the authors have read and approved the final version (include appropriate statements).

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