

Fractional-order modeling and experimental validation of levofloxacin degradation in wastewater treatment systems

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Abstract. This work develops and experimentally validates a Caputo fractional-order model for levofloxacin degradation and Chemical Oxygen Demand (COD) mineralization in Electro-Fenton wastewater treatment, capturing memory effects in long-time mineralization dynamics. Stability analysis using Lyapunov methods demonstrated asymptotic convergence to the equilibrium point. The system is solved using the Adams-Bashforth-Moulton (ABM) scheme, and parameters are calibrated via grid search over α with constrained kinetic optimization. The optimal orders indicate stronger memory in COD removal ($\alpha^* = 0.7$) than in levofloxacin decay ($\alpha^* = 0.9$), achieving high agreement with experiments ($R^2 = 0.9192$ for Levofloxacin and $R^2 = 0.9974$ for COD) across varying electrolyte, pH, catalyst, and biodegradability conditions. Relative to the integer-order model, the fractional model reduces residual error, and accurately predicts levofloxacin decay and COD mineralization under optimized conditions, highlighting the biodegradability potential of the treated wastewater. Finally, local sensitivity analysis identifies fractional order α and nonlinear reaction order n as the most influential parameters for predictive accuracy and process optimization.

Keywords: fractional Caputo model; electro-fenton; levofloxacin; COD; ABM scheme; sensitivity.

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1 Introduction

Water and sanitation are essential for public health and environmental protection. Efficient treatment processes are required to reduce contamination

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by pharmaceuticals and other chemicals in water bodies. Antibiotics such as levofloxacin are of particular concern due to their extensive use and adverse environmental effects [18, 19, 20, 24]. Levofloxacin, a widely used fluoroquinolone, is environmentally persistent, making its degradation a key objective in wastewater treatment research.

Mathematical modeling is widely used to analyze and optimize water treatment processes. Traditional pollutant degradation models are commonly based on ordinary differential equations (ODEs) with constant-rate assumptions, which often fail to capture complex environmental dynamics. Fractional calculus overcomes these limitations by accounting for memory effects and non-local interactions, providing a more accurate representation of natural systems.

Numerous studies highlight the increasing importance of fractional calculus in environmental modeling [5, 8, 9, 11, 14, 16, 21]. Fractional-order models offer enhanced flexibility and accuracy for describing complex, memory-dependent biological, chemical, and physical processes. In wastewater treatment, fractional models and controllers have outperformed integer-order approaches in handling nonlinear aeration and nutrient removal, leading to improved efficiency and reduced energy consumption [2, 4, 13, 15, 17, 22]. Recent applications include kinetic modeling of biochemical methane potential tests [23] and improved wastewater monitoring using chaos-driven fractional laser systems [12]. In particular, Caputo-type derivatives effectively capture nonlocal and hereditary effects in pollutant degradation, establishing fractional calculus as a robust framework for complex environmental systems.

Furthermore, fractional calculus has become a powerful tool for modeling systems with memory and anomalous dynamics, showing remarkable success not only in environmental but also in epidemiological applications. In wastewater treatment, fractional-order models outperform integer-order ones in managing nonlinear processes and improving efficiency [6, 7]. Similarly, in epidemiology, Caputo and fractal-fractional models effectively capture memory-driven disease dynamics [1, 3, 10].

In this study, we propose a fractional mathematical model to improve water and sanitation technology, focusing on the degradation of levofloxacin and the mineralization of COD under treatment conditions. The model is described by the following system of FDEs

$$\begin{aligned}D^\alpha C(t) &= -k_1 C(t)^n, \\D^\alpha \text{COD}(t) &= -k_2 \text{COD}(t), \\D^\alpha S(t) &= k_3 C(t),\end{aligned}$$

where D^α denotes the Caputo fractional derivative, and α is the fractional order parameter (with $0 < \alpha < 1$), capturing the memory effects and non-locality of the process. Here, $C(t)$ represents the concentration of levofloxacin, $\text{COD}(t)$ represents the COD (a measure of the mineralization of contaminants), and $S(t)$ is the effective activation of the Electro-Fenton environment (influenced by operating conditions such as electrolytes or catalysts). Incorporating fractional derivatives into water treatment models is motivated by many environmental systems exhibiting long-term effects, delays, and interactions that traditional

models cannot capture. In particular, recent studies have shown that fractional models can provide more accurate predictions of pollutant dynamics and treatment efficiency in systems with non-linear and memory-dependent processes.

Electro-Fenton treatment of pharmaceutical residues often exhibits a fast initial removal, followed by a slow long-time mineralization tail, which is difficult to represent accurately with classical integer-order kinetics. This mismatch motivates a fractional-order formulation: Caputo derivatives provide a compact way to encode history dependence (memory) in the reaction dynamics, yielding relaxation profiles consistent with the observed non-exponential behavior of COD and improving interpretability and prediction under changing operating conditions.

Although fractional calculus is used in wastewater studies to design control devices or sensing tasks (such as whole-plant stability control [15] and laser-based detection [12]), their work focuses on process kinetics, whereas in our work, we develop a fractional multicomponent model that directly describes levofloxacin degradation, COD extraction, and treatment agents in an electro-Fenton system. The proposed framework is numerically solved via an ABM scheme, calibrated against experimental measurements, and benchmarked under a fair $\alpha = 1$ versus $\alpha < 1$ protocol. In addition, we quantify operating-condition effects through an effective mineralization rate, track biodegradability, and use local sensitivity indices to identify the dominant parameters driving model outputs and optimization.

The objective of this study is to develop and validate a fractional mathematical model to improve water and sanitation technologies, specifically targeting the degradation of levofloxacin and the mineralization of COD. By incorporating Caputo-type fractional derivatives, this model aims to capture the complex, memory-dependent dynamics of pollutant removal and the interaction between contaminants and treatment agents. The central research question we address is: Can a Caputo-type FDE model outperform classical integer-order ODE models in simulating and optimizing levofloxacin degradation and COD mineralization under variable treatment conditions? This work seeks to answer this by integrating experimental data for calibration and validation, conducting rigorous stability analysis, and performing a comparative performance assessment. Ultimately, this research is expected to contribute to the development of more efficient and environmentally sustainable water treatment processes by providing insights into the role of fractional dynamics in pollutant degradation and treatment optimization.

This paper is structured as follows: In Section 2, we present the mathematical formulation of the model, defining the key variables and deriving the governing fractional differential equations. Section 3 integrates experimental data, where we calibrate and validate the model based on levofloxacin degradation and COD evolution under various treatment conditions. In Section 4, we investigate the positivity of solutions, equilibrium points, and Lyapunov stability analysis. Section 5 describes the experimental setup and analytical procedures used to measure levofloxacin, COD, and BOD₅. Section 6 discusses the numerical simulation based on the ABM predictor-corrector scheme. Section 7 summarizes the calibration protocol for α and kinetic parameters and

the corresponding model validation results, including residual-based fit metrics and a fair comparison between the fractional ($\alpha < 1$) and classical ($\alpha = 1$) benchmarks. Moreover, provides an operating-condition comparison and local sensitivity analysis identifying the most influential parameters. Finally, Section 8 concludes the study and highlights directions for future work.

2 Fundamentals

2.1 Fractional calculus

DEFINITION 1. [11] Riemann-Liouville fractional integral of a function $f(t)$ of order $\alpha > 0$ is defined as:

$$I^\alpha f(t) = \frac{1}{\Gamma(\alpha)} \int_0^t \frac{f(\tau)}{(t-\tau)^{1-\alpha}} d\tau,$$

where $\Gamma(\cdot)$ is the Gamma function.

DEFINITION 2. [11] The Caputo fractional derivative of a function $f \in C[0, T]$ of order $\alpha \in (0, 1)$ is defined as:

$$D^\alpha f(t) = \frac{1}{\Gamma(1-\alpha)} \int_0^t \frac{f'(s)}{(t-s)^\alpha} ds.$$

For $\alpha = 1$: $D^\alpha f(t) \rightarrow f'(t)$ as $\alpha \rightarrow 1$.

DEFINITION 3. [11] The series form of the ML function $E_{a,\beta}(z)$ is defined as:

$$E_{a,\beta}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(ak + \beta)}, \quad a > 0, \beta > 0.$$

And for $\beta = 1$:

$$E_{a,1}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(ak + 1)}.$$

Theorem 1. [8] For a given function where $\mathbf{X}(t) : [0, T] \rightarrow \mathbb{R}$, and $0 < \alpha < 1$. The following system

$${}_0^C D_t^\alpha \mathbf{X}(t) = \mathbf{F}(t, \mathbf{X}(t)), \quad \mathbf{X}(0) = \mathbf{X}_0$$

has the following solution

$$\mathbf{X}(t) = \mathbf{X}_0 + \frac{1}{\Gamma(\alpha)} \int_0^t (t-\sigma)^{\alpha-1} \mathbf{F}(\sigma, \mathbf{X}(\sigma)) d\sigma, \quad t \in [0, T],$$

where $\mathbf{X}(t) = [C(t), \text{COD}(t), S(t)]^\top$ and

$$\mathbf{F}(t, \mathbf{X}(t)) = \begin{bmatrix} -k_1 C(t)^n \\ -k_2 \text{COD}(t) \\ k_3 C(t) \end{bmatrix}.$$

2.2 Model formulation

The mathematical representation of the Caputo fractional order model is presented as follows:

$$\begin{aligned} D^\alpha C(t) &= -k_1 C(t)^n, \\ D^\alpha \text{COD}(t) &= -k_2 \text{COD}(t), \\ D^\alpha S(t) &= k_3 C(t), \end{aligned} \quad (2.1)$$

subject to the initial conditions $C(0) \geq 0$, $\text{COD}(0) \geq 0$, $S(0) \geq 0$, where D^α is the Caputo fractional derivative of order α ($0 < \alpha < 1$) and $k_1, k_2, k_3 > 0$. The state variables and parameters have the following interpretations: $C(t)$ denotes the concentration of levofloxacin (mg/L), $\text{COD}(t)$ represents the Chemical Oxygen Demand (COD) (mg/L), which measures the mineralization of contaminants, $S(t)$ denotes an effective treatment-activation state or activation proxy (dimensionless or in model units) that aggregates the cumulative action of the Electro-Fenton environment (e.g., oxidant generation/activation) and is driven by the presence of the parent compound $C(t)$, k_1 is the degradation rate constant of levofloxacin, $n \geq 1$ is the nonlinear reaction order, k_2 is the mineralization rate constant, and k_3 is the treatment-agent activation rate constant.

The first equation in (2.1) describes the fractional n th-order decay of levofloxacin concentration $C(t)$. The second models mineralization via the reduction of $\text{COD}(t)$ as a lumped measure of oxidative removal, while the third represents treatment intensity through the auxiliary state $S(t)$, characterizing the Electro-Fenton environment. Operating conditions (electrolyte and catalyst) are treated as exogenous effects embedded in k_2^{eff} , RMSE, and removal efficiency, whereas BOD_5/COD is reported as an experimentally derived biodegradability indicator.

2.3 Experimental context

The study monitors levofloxacin and COD degradation under varying electrolytes, pH, and catalysts, using the resulting data to calibrate k_1, k_2, k_3, n , and α , ensuring realistic model dynamics.

3 Experimental data integration

Experimental levofloxacin and COD data under varying electrolytes, pH, and catalysts are used to calibrate and validate the model, serving as benchmarks for accuracy and treatment effectiveness.

3.1 Chemicals

Levofloxacin (purity > 97%) was procured from Sigma Aldrich. Catalysts used in the experiments included copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) from Merck, and manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) from Scharlau. Also, Ultra-pure water for all solution preparations was obtained using a Millipore Milli-Q system.

3.2 Electrochemical setup

Electrochemical experiments were performed using a Voltalab Potentiostat/Galvanostat in a 230 mL open cell. A platinum anode with an active area of 5 cm^2 and a Carbone-Lorraine carbon felt cathode ($12\text{ cm} \times 8\text{ cm}$) were employed, with the anode centrally positioned in the electrolyte and facing the cathode.

3.3 Methods of analysis

Electrochemical mineralization was evaluated by monitoring COD reduction after sample digestion with potassium dichromate at 150°C for 120 min using a Lovibond® COD VARIO photometer, with concentrations determined colorimetrically by a DR/125 spectrophotometer (Hach, USA). Levofloxacin concentrations were analyzed using a Waters 2695 HPLC system equipped with a 2997 photodiode-array detector at 295 nm, employing a Thermo Hypersil C18 column ($5\text{ }\mu\text{m}$, $24\text{ cm} \times 4.6\text{ mm}$) operated at 45°C and a mobile phase of methanol, tetrabutylammonium hydrogen sulfate, potassium dihydrogen phosphate, and phosphoric acid (27:73, v/v) at a flow rate of 1.2 mL min^{-1} ; data were acquired using Empower 2 software. BOD measurements were conducted with an Oxidirect BOD Lovibond system at 20°C , with sample pH adjusted to 6–7.5 using bacterial seed and nutrients, and continuous aeration applied to ensure oxygen saturation.

4 Fractional model analysis

In this section, we analyze the mathematical properties of the proposed model to ensure physical validity and dynamical stability. The analysis establishes positivity, equilibrium behavior, and stability using both linearization and Lyapunov methods.

4.1 Well-posedness and positivity

The Caputo fractional derivative is appropriate for modeling systems with memory effects and physical initial conditions. The right-hand sides of system (2.1) are locally Lipschitz and quasi-positive in $\mathbb{R}_+^3$. Consequently, we prove that all state variables (levofloxacin, COD, and treatment agents) remain positive for all $t \geq 0$, given non-negative initial conditions.

Theorem 2. *For the fractional-order system (2.1) with the initial conditions $C(0) \geq 0$, $COD(0) \geq 0$, $S(0) \geq 0$, the solutions $C(t)$, $COD(t)$, $S(t)$ remain non-negative for all $t \geq 0$.*

Proof. For $C(t)$ we have

$$D^\alpha C(t) = -k_1 C(t)^n, \quad k_1 > 0, \quad n \geq 1.$$

The Caputo derivative $D^\alpha C(t)$ for $0 < \alpha < 1$ depends on the history of $C(t)$. Since $C(0) \geq 0$, the term $-k_1 C(t)^n$ is non-positive whenever $C(t) \geq 0$. Therefore, the derivative $D^\alpha C(t)$ ensures that $C(t)$ cannot increase. By the properties of FDEs, the solution $C(t)$ remains non-negative for all $t \geq 0$. For COD(t) we have

$$D^\alpha \text{COD}(t) = -k_2 \text{COD}(t), \quad k_2 > 0.$$

The right-hand side $-k_2 \text{COD}(t)$ is non-positive whenever $\text{COD}(t) \geq 0$. The general solution is given by

$$\text{COD}(t) = \text{COD}(0)E_\alpha(-k_2 t^\alpha),$$

where $E_\alpha(\cdot)$ is the Mittag-Leffler function, which is positive and decreasing for $k_2 > 0$ and $t \geq 0$. Since $\text{COD}(0) \geq 0$ and $E_\alpha(-k_2 t^\alpha) > 0$, the solution $\text{COD}(t)$ remains non-negative for all $t \geq 0$.

Finally, for $S(t)$, we have

$$D^\alpha S(t) = k_3 C(t), \quad k_3 > 0.$$

Using Theorem 1, we have

$$S(t) = S(0) + \frac{k_3}{\Gamma(\alpha)} \int_0^t (t - \tau)^{\alpha-1} C(\tau) d\tau. \quad (4.1)$$

Since $S_0 \geq 0$, $k_3 > 0$, and $C(\tau) \geq 0$ for all $\tau \in [0, t]$, and noting that $(t - \tau)^{\alpha-1} > 0$ for $t > \tau$ and $\Gamma(\alpha) > 0$ for $\alpha > 0$, it follows that the integral term in (4.1) is non-negative. Therefore, $S(t)$ is non-decreasing and remains non-negative for all $t \geq 0$, which is consistent with its physical interpretation as an accumulated treatment-agent concentration.

Hence, we conclude that $C(t) \geq 0$, $\text{COD}(t) \geq 0$, and $S(t) \geq 0$, for all $t \geq 0$. $\square$

4.2 Equilibrium points and stability analysis

Consider the Caputo fractional-order system with $0 < \alpha < 1$:

$$\begin{cases} {}^C D^\alpha C = -k_1 C^n, \\ {}^C D^\alpha \text{COD} = -k_2 \text{COD}, \\ {}^C D^\alpha S = k_3 C, \end{cases} \quad (4.2)$$

where $k_1, k_2, k_3 > 0$ and $n \geq 1$.

Equilibrium Points: An equilibrium point $E_e := (C_e, \text{COD}_e, S_e)$ of system (4.2) satisfies

$${}^C D^\alpha C = {}^C D^\alpha \text{COD} = {}^C D^\alpha S = 0.$$

Setting the right-hand sides of (4.2) to zero yields

$$-k_1 (C_e)^n = 0, \quad -k_2 \text{COD}_e = 0, \quad k_3 C_e = 0.$$

Hence, $C_e = 0$, $\text{COD}_e = 0$, while S_e is arbitrary. Therefore, the equilibrium set is

$$E_e = (0, 0, S_e), \quad S_e \geq 0.$$

Linear Stability Analysis: Let $x_1 = C$, $x_2 = \text{COD}$, and $x_3 = S$. The Jacobian matrix of (4.2) is

$$J = \begin{pmatrix} -k_1 n C^{n-1} & 0 & 0 \\ 0 & -k_2 & 0 \\ k_3 & 0 & 0 \end{pmatrix}.$$

Case $n = 1$. Evaluating J at E_e gives

$$J(E_e) = \begin{pmatrix} -k_1 & 0 & 0 \\ 0 & -k_2 & 0 \\ k_3 & 0 & 0 \end{pmatrix},$$

whose eigenvalues are $\lambda_1 = -k_1$, $\lambda_2 = -k_2$, and $\lambda_3 = 0$. For a Caputo fractional system, local asymptotic stability holds if $|\arg(\lambda_i)| > \frac{\alpha\pi}{2}$. Hence, the equilibrium is asymptotically stable in the (C, COD) -subsystem and neutrally stable in the S -direction.

Case $n > 1$. In this case, the equilibrium is non-hyperbolic, and linearization alone is insufficient to conclude stability.

Lyapunov Stability Analysis: To establish stability beyond linearization, we employ a Lyapunov approach.

Theorem 3. *The equilibrium set $E_e = (0, 0, S_e)$ of model (4.2) is globally asymptotically stable with respect to the variables $C(t)$ and $\text{COD}(t)$.*

Proof. Consider the Lyapunov function $V(C, \text{COD}) = \frac{1}{2}C^2 + \frac{1}{2}\text{COD}^2$, which is positive definite. Using the property of Caputo derivatives for $0 < \alpha \leq 1$, we obtain

$${}^C D^\alpha V = C {}^C D^\alpha C + \text{COD} {}^C D^\alpha \text{COD}.$$

Substituting from (4.2) gives

$${}^C D^\alpha V = -k_1 C^{n+1} - k_2 \text{COD}^2 \leq 0.$$

Moreover,

$${}^C D^\alpha V = 0 \iff C = 0, \text{COD} = 0.$$

By the fractional Lyapunov direct method and the invariance principle, the equilibrium set E_e is globally asymptotically stable in the (C, COD) -components.

□

Remark 1. Model (2.1) has a continuum of equilibria $E_e = (0, 0, S_e)$ with $S_e \geq 0$. Linear and Lyapunov fractional stability analyses show the system is dissipative: $C(t)$ and $\text{COD}(t)$ decay asymptotically. Meanwhile $S(t)$ changes monotonically according to the history of $C(t)$, acting as an auxiliary, $C(t)$ -driven variable with no feedback on the dynamics.

The stability properties of the system are illustrated in Figure 1. Figure 1(a) presents the 3D surface of the Lyapunov function $V(C, COD)$, which is convex and attains its unique minimum at the origin $(0, 0)$, thereby confirming global stability of the states $C(t)$ and $COD(t)$. Figure 1(b) depicts the equilibrium manifold $E_e = \{(0, 0, S) : S \geq 0\}$, indicating that once degradation and mineralization are complete, the system settles at equilibrium for any non-negative value of $S(t)$.

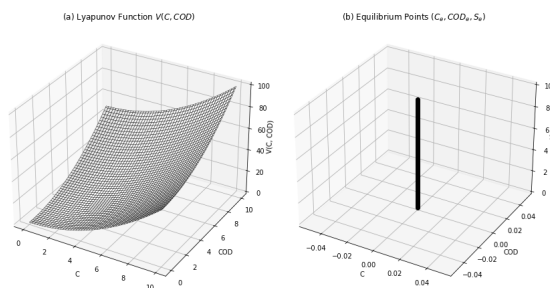


Figure 1. Stability analysis of the system: (a) Lyapunov function surface showing a global minimum at $(0, 0)$; (b) Equilibrium manifold $E_e = \{(0, 0, S) : S \geq 0\}$.

5 Experimental results

The experimental results are summarized in Tables 1–5. The degradation kinetics of levofloxacin are presented in Table 1. The influence of key operational parameters on COD removal was investigated, including the type of supporting electrolyte (Table 2), initial solution pH (Table 3), and the catalyst used (Fe^{2+} , Mn^{2+} , or Cu^{2+}) (Table 4). Furthermore, to assess the evolution of biodegradability during the treatment process, the BOD_5 and COD values were monitored over time. The resulting BOD_5/COD ratio, a key indicator of biodegradability, is presented in Table 5, showing a significant increase from 0.00 to 0.296 after 300 min of treatment.

5.1 Tables and experimental trends

The model can be validated and calibrated using experimental data obtained from the Electro-Fenton treatment process. The experimental data are as shown in Tables 1–5.

Table 1. Concentration of Levofloxacin over time.

Time (min)	Concentration of Levofloxacin (mg/L)
0 (1)	49.88 (47.70)
2 (3)	46.62 (42.64)
4 (5)	35.41 (31.80)
6 (8)	27.83 (19.88)
10 (11)	16.98 (13.73)
13 (15)	9.76 8.67

Table 2. COD levels under different electrolytes.

Time (min)	COD with Na ₂ SO ₄ (mg/L)	COD with NaCl (mg/L)
0 (30)	160 (101)	160 (121)
60 (120)	79 (56)	100 (88)
180 (240)	45 (41)	70 (60)

Table 3. COD levels under different pH conditions.

Time (min)	COD at pH2 (mg/L)	COD at pH3 (mg/L)	COD at pH4 (mg/L)
0 (30)	160 (117)	160 (101)	160 (101)
60 (120)	97 (68)	79 (56)	84 (61)
180 (240)	60 (56)	45 (41)	52 (48)

Table 4. COD Levels (mg/L) over time under the influence of different catalysts.

Time (min)	COD Fe ²⁺ (mg/L)	COD Mn ²⁺ (mg/L)	COD Cu ²⁺ (mg/L)
0 (30)	160 (101)	160 (111)	160 (117)
60 (120)	79 (56)	84 (61)	97 (68)
180 (240)	45 (41)	52 (48)	60 (56)

Table 5. Evolution of COD, BOD₅, and biodegradability ratio during treatment.

Time (min)	COD (mg/L)	BOD ₅ (mg/L)	BOD ₅ /COD Ratio
0	160	0.00	0.00
15	130	0.00	0.00
30	101	0.00	0.00
60	79	0.00	0.00
120	56	1.39	0.025
180	45	3.31	0.074
240	41	5.62	0.137
300	18	5.32	0.296

Figure 2(a) shows the unit-standardized levofloxacin decay data, while Figures 2(b)–2(d) summarize the COD behavior under different electrolytes, pH, and catalysts. Figure 2(e) reports the biodegradability index BOD_5/COD .

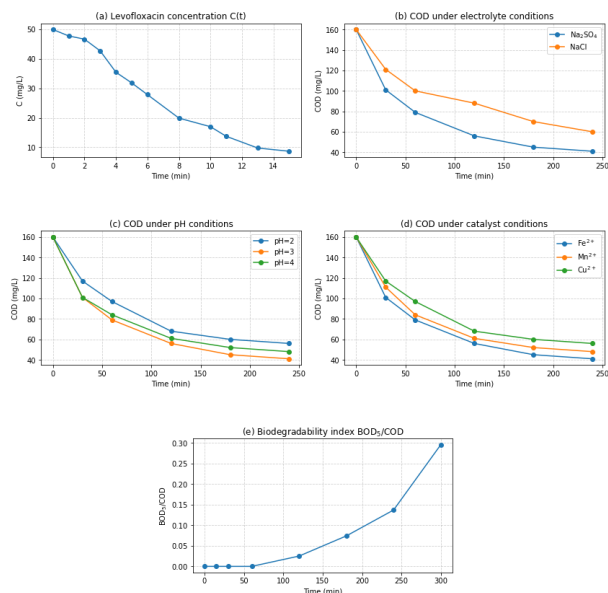


Figure 2. Experimental raw data used for model calibration.

6 Numerical simulation

This section presents the numerical solution of the model (2.1) and compares simulated results with experimental data to evaluate the predictive capability and robustness.

6.1 Numerical scheme

The model (2.1) is solved using the ABM scheme [8], ensuring numerical stability and accuracy. Accordingly, the fractional-order problem can be expressed as

$$\begin{cases} D^\alpha z(t) = \mathcal{H}(t, z(t)), & t \in [0, T], \\ z(0) = z_0. \end{cases}$$

where $\mathcal{H}: [0, T] \times \mathbb{R} \rightarrow \mathbb{R}$. So that according to the Theorem 1, we have

$$z(t) = z_0 + \frac{1}{\Gamma(\alpha)} \int_0^t (t - \sigma)^{\alpha-1} \mathcal{H}(\sigma, z(\sigma)) d\sigma, \quad t \in [0, T]. \quad (6.1)$$

We use the discretization for (6.1) as $h = \frac{T}{N}$, $t_r = rh$, $r = 0, 1, 2, \dots, N \in \mathbb{Z}^+$, we obtain

$$z(t_{r+1}) = z_0 + \frac{h^\alpha}{\Gamma(\alpha+2)} \mathcal{H}(t_{r+1}, z^P(t_{r+1})) + \sum_{j=0}^r \frac{h^\alpha \Delta_{j,r+1}}{\Gamma(\alpha+2)} \mathcal{H}(t_j, z(t_j)), \quad (6.2)$$

where

$$z^P(t_{r+1}) = z_0 + \frac{1}{\Gamma(\alpha)} \sum_{j=0}^r \Delta_{j,r+1} \mathcal{H}(t_j, z(t_j)). \quad (6.3)$$

The coefficients $\Delta_{j,r+1}$, $\Delta_{j,r+1}$ in (6.2), and (6.3) are described as

$$\Delta_{j,r+1} = \begin{cases} r^{\alpha+1} - (r-\alpha)(r+1)^\alpha, & j=0, \\ (r-j-2)^{\alpha+1} + (r-j)^{\alpha+1} - 2(r-j+1)^{\alpha+1}, & 1 \leq j \leq r, \\ 1, & j=r+1, \end{cases}$$

and $\Delta_{j,r+1} = (r-j+1)^\alpha - (r-j)^\alpha$. With the preceding numerical investigation formula in mind, we can now determine the intended numerical scheme for the suggested model (2.1) as

$$C(t_{r+1}) = C_0 + \frac{h^\alpha}{\Gamma(\alpha+2)} \left[\mathbf{U}_1(t_{r+1}, C^P(t_{r+1})) + \sum_{j=0}^r \Delta_{j,r+1} \mathbf{U}_1(t_j, C(t_j)) \right], \quad (6.4)$$

$$\begin{aligned} \text{COD}(t_{r+1}) = & \text{COD}_0 + \frac{h^\alpha}{\Gamma(\alpha+2)} \left[\mathbf{U}_2(t_{r+1}, \text{COD}^P(t_{r+1})) \right. \\ & \left. + \sum_{j=0}^r \Delta_{j,r+1} \mathbf{U}_2(t_j, \text{COD}(t_j)) \right], \end{aligned} \quad (6.5)$$

$$S(t_{r+1}) = S_0 + \frac{h^\alpha}{\Gamma(\alpha+2)} \left[\mathbf{U}_3(t_{r+1}, S^P(t_{r+1})) + \sum_{j=0}^r \Delta_{j,r+1} \mathbf{U}_3(t_j, S(t_j)) \right], \quad (6.6)$$

where

$$\begin{aligned} C^P(t_{r+1}) = & C_0 + \frac{h^\alpha}{\Gamma(\alpha+1)} \sum_{j=0}^r \Delta_{j,r+1} \mathbf{U}_1(t_j, C(t_j)), \\ \text{COD}^P(t_{r+1}) = & \text{COD}_0 + \frac{h^\alpha}{\Gamma(\alpha+1)} \sum_{j=0}^r \Delta_{j,r+1} \mathbf{U}_2(t_j, \text{COD}(t_j)), \\ S^P(t_{r+1}) = & S_0 + \frac{h^\alpha}{\Gamma(\alpha+1)} \sum_{j=0}^r \Delta_{j,r+1} \mathbf{U}_3(t_j, S(t_j)), \end{aligned}$$

and $\mathbf{U}_1(t, C(t)) = -k_1 C(t)^\alpha$, $\mathbf{U}_2(t, \text{COD}(t)) = -k_2 \text{COD}(t)$, $\mathbf{U}_3(t, S(t)) = k_3 C(t)$. We use various fractional orders to simulate the outcomes of our proposed model (2.1) with the aid of the aforementioned relations (6.4), (6.5) and (6.6).

6.2 Simulation results

The numerical simulations of the Caputo fractional-order system (2.1) are performed through the numerical solutions obtained using the ABM predictor–corrector scheme given by Equations (6.4)–(6.6), with the parameter set in Table 6. The simulations provide important insights into the dynamic behavior of the key state variables $C(t)$, $COD(t)$, and $S(t)$ for different fractional orders α in the range $0.5 \leq \alpha \leq 1$. The resulting figures illustrate how variations in α influence degradation kinetics, mineralization efficiency, and treatment proxy dynamics, thereby enabling a systematic assessment of memory effects and facilitating validation of the proposed fractional-order model against experimental observations. The experimental and simulated $C(t)$ and $COD(t)$ are expressed in mg/L, hence the error metrics reported below are also in mg/L.

Table 6. Values used in the numerical simulation.

Symbol	Description	Value	Units
C_0	Initial concentration of Levofloxacin	49.88	mg/L
COD_0	Initial COD	160	mg/L
S_0	Initial activation treatment proxy	0	model units
k_1	Reaction rate constant for $C(t)$	0.1196	$(\text{mg/L})^{1-n} \cdot \text{min}^{-\alpha}$
k_2	Reaction rate constant for $COD(t)$	0.0127	$\text{min}^{-\alpha}$
k_3	Reaction rate constant for $S(t)$	0.0500	$\text{min}^{-\alpha}$
n	Reaction order for $C(t)$	1.2	dimensionless
α	Fractional-order derivative	0.5 – 0.9	dimensionless
h	Step size for numerical simulation	0.1	min
T	Total simulation time	300	min

6.2.1 System-level simulation of (C, COD, S)

Using nominal parameters, we simulate the full system and plot the trajectories in Figures 3–4. Smaller α (stronger memory) slows the relaxation of $C(t)$ and $COD(t)$. For $S(t)$, fractional memory spreads the input $k_3 C(t)$ over time: $\alpha = 1$ rises quickly and then saturates, while $\alpha < 1$ yields slower early growth (especially for smaller α) and can produce higher late-time levels.

6.2.2 Fractional-order effects

To assess memory effects on degradation, (k_1, n) are calibrated for fixed α values and the resulting model curves are compared to the standardized $C(t)$ data.

Figure 5 shows the effect of fractional order α on $C(t)$ (a) and COD (b). Smaller α enhances memory effects, slowing decay, while larger α approaches classical kinetics. The best COD fit occurs at $\alpha = 0.7$, capturing both early and long-time behavior.

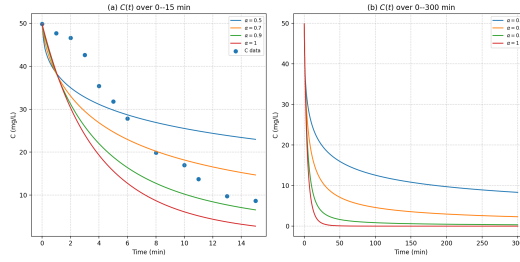


Figure 3. System simulation of $C(t)$ (mg/L) (a) over (0-15 min) and (b) over (0-300 min) for $\alpha \in \{0.5, 0.7, 0.9, 1\}$.

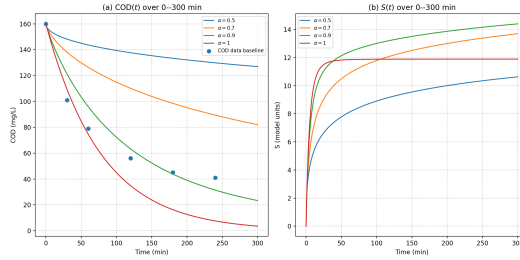


Figure 4. System simulation of the (a) COD (mg/L) over (0-300 min) and (b) activation proxy $S(t)$ over (0-300 min) for $\alpha \in \{0.5, 0.7, 0.9, 1\}$.

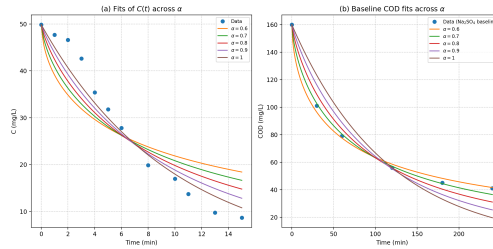


Figure 5. $C(t)$ (mg/L) and COD (mg/L) under Na_2SO_4 : data (markers) and fractional fits (curves) for several α .

7 Model calibration and parameter optimization

This section describes calibrating the fractional model (2.1), including a grid search over α coupled with constrained kinetic-parameter fitting, using ABM-based numerical solutions.

7.1 Objective function

Let $\theta = (k_1, k_2, n, \alpha)$ with $k_1, k_2 > 0$, $n \geq 1$, and $0 < \alpha \leq 1$. The parameter k_3 is fixed since $S(t)$ does not affect $C(t)$ or COD and is not identifiable from the data. Calibration uses $C_{\text{exp}}(t_i)$ and $\text{COD}_{\text{exp}}(t_j)$ and minimizes the sum of

squared residuals:

$$\mathcal{J}(\theta) = \sum_{i=1}^{N_C} (C_{\text{exp}}(t_i) - C_{\text{sim}}(t_i; \theta))^2 + \sum_{j=1}^{N_{\text{COD}}} (\text{COD}_{\text{exp}}(t_j) - \text{COD}_{\text{sim}}(t_j; \theta))^2.$$

Alternatively, the objective can be expressed as RMSE for both $C(t)$ and COD:

$$\mathcal{J}_{\text{RMSE}} = \text{RMSE}_C^2 + \text{RMSE}_{\text{COD}}^2.$$

To account for different scales in the data, we use a normalized objective:

$$\mathcal{J}_{\text{std}} = \left(\frac{\text{RMSE}_C}{\sigma_C} \right)^2 + \left(\frac{\text{RMSE}_{\text{COD}}}{\sigma_{\text{COD}}} \right)^2,$$

where σ_C and σ_{COD} are the sample standard deviations of the experimental C and COD data, respectively. A grid search over $\alpha \in [0.5, 1]$ selects α^* by minimizing the objective. With the unweighted cost $\mathcal{J}_{\text{unw}}$, $\alpha^* = 0.7$ (driven by the lowest COD RMSE). With the normalized cost $\mathcal{J}_{\text{std}}$, $\alpha^* = 0.9$, yielding a better fit to $C(t)$ due to scale normalization. The calibrated parameters clarify the kinetics: k_1 drives nonlinear levofloxacin decay with $n > 1$ (non-first-order), while k_2 controls COD mineralization and is dominated by long-time behavior. The shift in α^* with the objective suggests near-classical degradation for $C(t)$ ($\alpha \approx 0.9$) but stronger memory in COD decay ($\alpha \approx 0.7$).

7.2 Residual-based statistical metrics and goodness-of-fit

To quantitatively assess model performance, we employ residual-based metrics such as the sum of squared errors (SSE), RMSE, and (R^2). These metrics compare experimental data $y_{\text{exp}} := \{y_i\}_{i=1}^N$ with model predictions $y_{\text{sim}} := \{\hat{y}_i\}_{i=1}^N$ at the same sampling times, are defined as $\text{SSE} = \sum_{i=1}^N e_i^2$, $\text{RMSE} = \sqrt{\text{SSE}/N}$, $e_i = y_i - \hat{y}_i$, $\text{MAE} = \frac{1}{N} \sum_{i=1}^N |e_i|$, $R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \bar{y})^2}{\sum_{i=1}^N (y_i - \bar{y})^2}$, $\bar{y} = \frac{1}{N} \sum_{i=1}^N y_i$, where $\bar{y}$ is the sample mean of the observations and $N = 12$ data points for levofloxacin and $N = 6$ for baseline COD, consistent with the experimental tables used. For levofloxacin degradation ($\alpha = 0.9$), the calibrated model yields an RMSE of 4.165 mg/L and $R^2 = 0.9192$, indicating strong agreement despite mild deviations at later times. For COD mineralization ($\alpha = 0.7$), RMSE is 2.090 mg/L, with $R^2 = 0.9974$, confirming the fractional model's superior fit for long-term dynamics. The full residual tables and breakdowns of fit metrics are summarized in Tables 7–9.

7.3 Predictive validation (train–test split for baseline COD)

To evaluate predictive capability, k_2 is fitted using only early-time baseline COD measurements $\{0, 30, 60\}$ min and then used to predict $\{120, 180, 240\}$ min. Note that, the classical case ($\alpha = 1$) tends to overestimate mineralization at late times (too-fast exponential decay), whereas fractional models preserve a slower, memory-driven tail that more closely matches the observed long-term

Table 7. $C(t)$ residuals (mg/L) for $\alpha = 0.9$: $e_i = C_{\text{exp}} - C_{\text{sim}}$, with e_i^2 and $|e_i|$.

t (min)	C_{exp}	C_{sim}	e_i	e_i^2	$ e_i $
0	49.880	49.880	0.000	0.000	0.000
1	47.700	43.832	3.868	14.959	3.868
2	46.620	39.246	7.374	54.381	7.374
3	42.640	35.385	7.255	52.638	7.255
4	35.410	32.054	3.356	11.260	3.356
5	31.800	29.145	2.655	7.051	2.655
6	27.830	26.581	1.249	1.560	1.249
8	19.880	22.285	-2.405	5.783	2.405
10	16.980	18.853	-1.873	3.507	1.873
11	13.730	17.393	-3.663	13.419	3.663
13	9.760	14.888	-5.128	26.291	5.128
15	8.670	12.833	-4.163	17.328	4.163

Table 8. Baseline COD mineralization residuals (Na_2SO_4 , mg/L) for the fractional fit $\alpha = 0.7$.

t (min)	COD_{exp}	COD_{sim}	e_i	e_i^2	$ e_i $
0	160.000	160.000	0.000	0.000	0.000
30	101.000	102.564	-1.564	2.445	1.564
60	79.000	80.477	-1.477	2.180	1.477
120	56.000	57.099	-1.099	1.208	1.099
180	45.000	44.471	0.529	0.279	0.529
240	41.000	36.518	4.482	20.085	4.482

Table 9. Summary of residual-based fit metrics (SSE, RMSE, R^2 , MAE in mg/L).

Variable (case)	N	SSE	RMSE (mg/L)	MAE (mg/L)	R^2
$C(t)$ ($\alpha = 0.9$)	12	208.178	4.165	3.582	0.9192
COD (Na_2SO_4 , $\alpha = 0.7$)	6	26.198	2.090	1.525	0.9974

behavior. Figure 6 shows that fractional models (especially $\alpha \approx 0.7$) maintain better predictive accuracy than the classical exponential model $\alpha = 1$. This train-test result supports the use of $\alpha < 1$ for predictive COD modeling.

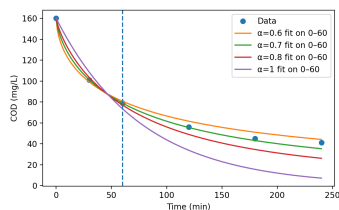


Figure 6. Predictive validation for baseline COD (mg/L).

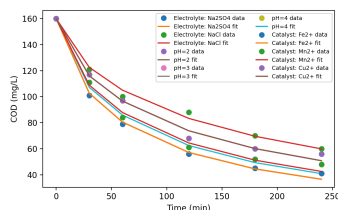


Figure 7. COD (mg/L) under different operating conditions at $\alpha = 0.7$.

Figure 8 shows that COD RMSE strongly depends on α , reaching a minimum at $\alpha^* = 0.7$, while $C(t)$ RMSE varies mildly (often favoring $\alpha \approx 0.9$; Table 9). Figure 9 indicates improved early-time $C(t)$ decay for $\alpha^* = 0.7$ compared with $\alpha = 1$, with minor late-time bias (Figure 10). Figure 11 shows that $\alpha^* = 0.7$ captures both the rapid drop and slow tail of COD, whereas $\alpha = 1$ decays too quickly at long times; residuals remain small and near zero (Figure 12, Table 9).

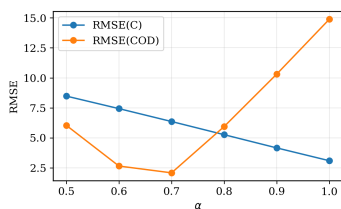


Figure 8. RMSE vs α for C and COD.

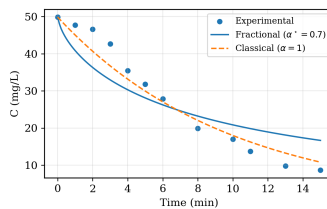


Figure 9. Best-fit overlay for $C(t)$: fractional vs classical.

7.4 Operating-condition comparison using an effective mineralization rate

Operating conditions (electrolyte, pH, and catalyst) were compared using an effective mineralization rate k_2^{eff} estimated for each COD dataset at the fixed fractional order $\alpha = 0.7$. The BOD_5/COD ratio was also used as a biodegradability indicator, where higher values imply improved suitability for downstream biological treatment. Table 10 reports k_2^{eff} , RMSE, COD removal at 240 min, and the corresponding BOD_5/COD ratio, while Figures 7 and 13 present the model fits and ratio trends. Larger k_2^{eff} values indicate faster mineralization. Overall, Na_2SO_4 , pH 3, and Fe^{2+} show the best performanc.

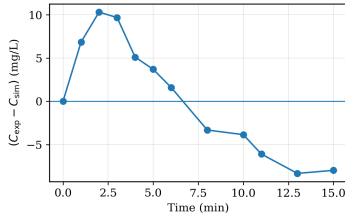


Figure 10. Residuals for $C(t)$ at $\alpha^* = 0.7$.

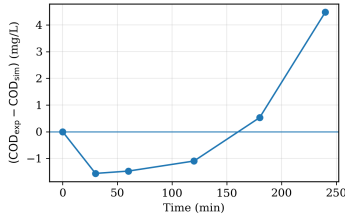


Figure 12. Residuals for COD at $\alpha^* = 0.7$.

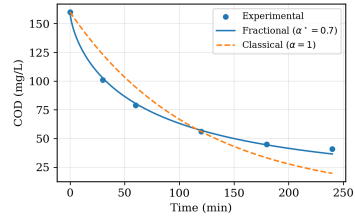


Figure 11. Best-fit overlay for COD: fractional vs classical.

Table 10. Effective COD mineralization parameter k_2^{eff} (fixed $\alpha = 0.7$) across operating conditions, with BOD_5/COD ratio at 240 min.

Condition	k_2^{eff} ($\text{min}^{-\alpha}$)	RMSE (mg/L)	Removal (%)	BOD_5/COD Ratio
Na_2SO_4	0.040470	2.089610	74.375	0.137
NaCl	0.023488	2.876430	62.500	0.101
pH 2	0.028598	3.212176	65.000	0.074
pH 3	0.040470	2.089610	74.375	0.145
pH 4	0.036155	4.122427	70.000	0.120
Fe^{2+}	0.040470	2.089610	74.375	0.145
Mn^{2+}	0.034676	3.207175	70.000	0.111
Cu^{2+}	0.028598	3.212176	65.000	0.084

7.5 Comparison with the classical model ($\alpha = 1$)

Here, we compare the fractional-order model ($\alpha < 1$) against its classical integer-order ($\alpha = 1$) using an identical protocol: (i) the same datasets and time points ($N = 12$ for $C(t)$ and $N = 6$ for baseline COD), (ii) the same initial conditions, and (iii) the same residual metrics (SSE/RMSE/MAE and R^2). Moreover, we fix the kinetic nonlinearity to the same reaction order $n = 1.2$ in both models, ensuring that any differences are not caused by changing the reaction order. Setting $\alpha = 1$ reduces (2.1) to the classical integer-order system

$$\frac{dC}{dt} = -k_1 C^n, \quad \frac{d\text{COD}}{dt} = -k_2 \text{COD}, \quad \frac{dS}{dt} = k_3 C,$$

where the levofloxacin equation is nonlinear ($n > 1$) and COD follows an exponential decay. In this subsection, we use the same numerical values of $(C_0, \text{COD}_0, S_0, k_1, k_2, k_3, n)$ reported in Table 6, and only change the derivative order to $\alpha = 1$ as shown in Table 11. For the fractional model, we use the same parameter values in Table 6 and the selected fractional orders consistent with Table 9, where $\alpha = 0.9$ for $C(t)$ and $\alpha = 0.7$ for baseline COD (Na_2SO_4).

Table 11. Parameter-matched setup for the fractional and classical models.

Quantity	Fractional model	Classical model
Levofloxacin order	$\alpha = 0.9$	$\alpha = 1$
COD order (baseline Na_2SO_4)	$\alpha = 0.7$	$\alpha = 1$
Reaction order	$n = 1.2$	$n = 1.2$
C_0 (mg/L)	49.88	49.88
COD_0 (mg/L)	160	160
S_0 (model units)	0	0
k_1	0.1196	0.1196
k_2	0.0127	0.0127
k_3	0.0500	0.0500

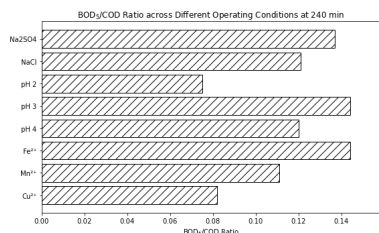


Figure 13. BOD₅/COD ratio across different operating conditions at 240 min.

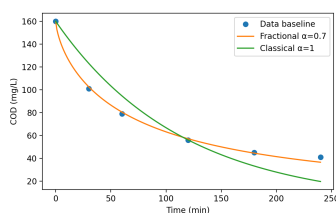


Figure 14. fractional model ($\alpha = 0.7$) vs classical model ($\alpha = 1$).

Figure 14 compares the baseline COD trajectory for the fractional model ($\alpha = 0.7$) against the parameter-matched classical decay ($\alpha = 1$). The classical model decays too rapidly at long times, while the fractional model yields a slower relaxation profile consistent with memory effects. This explains the improved predictive validation performance of fractional orders in Figure 6. To report a transparent quantitative gap between models, we compute the RMSE reduction (%) achieved by the fractional model relative to the classical benchmark:

$$\% \Delta \text{RMSE} = 100 \times \frac{\text{RMSE}_{\alpha=1} - \text{RMSE}_{\alpha < 1}}{\text{RMSE}_{\alpha=1}}. \quad (7.1)$$

A positive value indicates that the fractional model reduces error; a negative value indicates that the fractional model increases error.

Table 12 reports the residual metrics for both model classes. The fractional metrics are taken directly from Table 9. The classical metrics are computed on the same time points using the $\alpha = 1$ solutions with the same parameter values in Table 6.

Table 12. Residual-based fit metrics for fractional vs. classical models (mg/L).

Dataset	Model	N	SSE	RMSE	MAE	R^2
$C(t)$	Fractional ($\alpha = 0.9$)	12	208.178	4.165	3.582	0.9192
$C(t)$	Classical ($\alpha = 1$)	12	1829.035	12.346	11.155	0.2900
COD (Na_2SO_4)	Fractional ($\alpha = 0.7$)	6	26.198	2.090	1.525	0.9974
COD (Na_2SO_4)	Classical ($\alpha = 1$)	6	2476.469	20.316	15.986	0.7563

Using Equation (7.1), Table 13 summarizes the performance difference. Under the parameter-matched setup (same (k_1, k_2, k_3, n) as Table 6), the fractional model reduces RMSE by 66.26% for $C(t)$ and by 89.71% for baseline COD, and it increases R^2 from 0.2900 to 0.9192 for $C(t)$ and from 0.7563 to 0.9974 for COD. Positive values indicate improvement by the fractional model.

Table 13. Quantitative difference of the fractional model relative to the classical model

Dataset	% Δ RMSE	% Δ MAE	% Δ SSE	$100 \times \Delta R^2$
$C(t)$	+66.26	+67.89	+88.62	+62.92
COD (Na_2SO_4)	+89.71	+90.46	+98.94	+24.11

Under identical benchmarking, the fractional model yields quantifiably superior fits, where COD RMSE decreases by 89.71% (R^2 improves from 0.7563 to 0.9974), and levofloxacin $C(t)$ RMSE decreases by 66.26% (R^2 from 0.2900 to 0.9192), indicating strong memory effects in both degradation dynamics.

7.6 Sensitivity analysis

A local sensitivity analysis is conducted to assess the robustness of the calibrated fractional-order model and to identify influential parameters $\{k_1, k_2, k_3, n, \alpha\}$ on $C(t)$ and COD(t). The analysis focused on the degradation, mineralization, and activation endpoints using the COD-driven calibrated parameter set.

Local sensitivities are computed by perturbing each parameter p by $\pm 1\%$ around its baseline value and evaluating a normalized sensitivity index

$$S_p = \frac{p}{y} \frac{\partial y}{\partial p}, \quad (7.2)$$

where y is a scalar model output. This metric is dimensionless and can be interpreted as an elasticity: $S_p = -2$ means a 1% increase in p yields an approximate 2% decrease in y .

Table 14. Local normalized sensitivities S_p (Equation (7.2)) at fractional fit $\alpha^* = 0.7$.

Parameter	S_p for $C(15 \text{ min})$	S_p for $COD(300 \text{ min})$	S_p for $S(300 \text{ min})$
k_1	-0.787	0.000	-0.823
n	-2.786	0.000	-1.854
k_2	0.000	-0.519	0.000
k_3	0.000	0.000	1.000
α	-1.992	-2.056	0.572

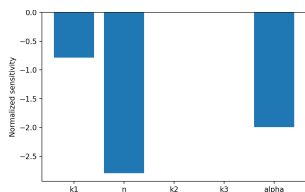


Figure 15. Local sensitivity indices S_p at $\alpha^* = 0.7$ for $C(15 \text{ min})$.

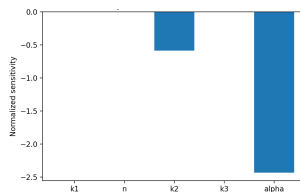


Figure 16. Local sensitivity indices S_p at $\alpha^* = 0.7$ for $COD(300 \text{ min})$.

Table 14 reports S_p for $y = C(15 \text{ min})$, $y = COD(300 \text{ min})$, and $y = S(300 \text{ min})$. Negative values indicate that increasing the parameter decreases the output. Figure 15 shows the local normalized sensitivity indices for the levofloxacin concentration $C(15 \text{ min})$ at the baseline fractional order $\alpha^* = 0.7$, indicating that $C(15)$ is most sensitive to the kinetic nonlinearity n and the fractional order α (both negative), while k_2 and k_3 have negligible influence due to the decoupled structure of the C -equation.

Figure 16 highlights the local sensitivity indices for $COD(300 \text{ min})$, where the response is dominated by k_2 and α (both negative), consistent with the exponential/mineralization dynamics in the COD equation, and showing essentially zero sensitivity to k_1 , n , and k_3 because COD is not directly driven by $C(t)$ or $S(t)$ in the present model.

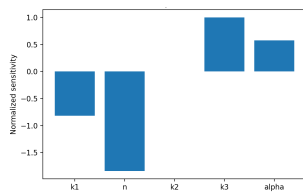


Figure 17. Local sensitivity indices S_p at $\alpha^* = 0.7$ for $S(300 \text{ min})$.

Figure 17 illustrates the local sensitivity indices for the effective activation state $S(300 \text{ min})$ (including k_3), revealing a strong positive sensitivity to k_3 (near-linear dependence through $D^\alpha S = k_3 C$), a moderate positive sensitivity to α , and negative sensitivities to k_1 and n because faster decay of $C(t)$ reduces the cumulative forcing term that drives $S(t)$.

From Table 14, the most sensitive parameters are α and n (largest $|S_p|$ across outputs), while k_1 , k_2 , and k_3 mainly affect their own subsystems (C , COD, and S , respectively).

8 Conclusions

A fractional-order model was developed and validated to describe levofloxacin degradation and COD mineralization in the Electro-Fenton process. Positivity of the state variables and Lyapunov-based analysis ensure convergence to the equilibrium $E_e = (0, 0, S_e)$, while ABM numerical simulations successfully capture the memory-dependent dynamics of the system.

Calibration results show that fractional dynamics significantly improve model accuracy, particularly for COD mineralization with the optimal order $\alpha^* = 0.7$, whereas levofloxacin degradation behaves closer to classical kinetics with $\alpha^* = 0.9$. The model demonstrates strong predictive capability, achieving $R^2 = 0.9974$ (RMSE = 2.090 mg/L) for COD and $R^2 = 0.9192$ (RMSE = 4.165 mg/L) for levofloxacin, outperforming integer-order models. Sensitivity analysis further identifies the fractional order α and the nonlinear reaction order $n > 1$ as key parameters for process optimization, while the BOD₅/COD ratio complements the effective mineralization rate as a biodegradability indicator.

Overall, the proposed framework provides an accurate and robust description of pollutant removal dynamics, with COD mineralization particularly well captured. Future work may incorporate mechanistic $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycling and alternative fractional operators to further enhance model realism.

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