Supplementary Materials

Low-temperature transformation of florfenicol mediated by δ-MnO_2: The role of Mn(III) and reactive oxygen species

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florfenicol.

Table S2. Toxicity Category.

Text S1. Materials.

Sodium pyrophosphate (Na-PP, 99.0%), and tertiary butanol (TBA, 99.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd. P-benzoquinone (P-BQ, 97.0%) were supplied by Shanghai Macklin Biochemical Technology Co., Ltd. Catalase (CAT, 200000 unit·g^{-1}), and 2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5- carboxanilide (XTT, 90.0%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Titanium sulfate ($Ti(SO_4)_2$, ≥ 96.0%), terephthalic acid ($C_7H_6O_3$, 99.5%), 2-hydroxyterephthalic acid (C_8H_6O, ≥ 96.0%), and p-benzoquinone (P-BQ, 97.0%) were supplied by Shanghai Macklin Biochemical Technology Co., Ltd.

Text S2. Determination of free Mn(II) and adsorbed Mn(II) contents.

After the δ-MnO_2 suspension and FF solution were reacted for 2.0 h, they were centrifuged at 5000.0 rpm for 10 min. The supernatant was taken, and the precipitate was washed with deionized water 3.0 times to ensure that the free Mn(II) was completely eluted. The free Mn(II) was directly determined by atomic absorption spectrometry after filtration through a 0.2 μm filter membrane. The precipitate was added to 5.0 mL of 50.0 mmol·L^{-1} $CuSO_4$ solution (pH 5.0). It was placed in a constant-temperature incubator and oscillated at 200.0 rpm for 1.0 h. The displaced adsorbed Mn(II) in the supernatant was determined after centrifugation.

Text S3. Determination of ·OH.

A NaOH solution with a concentration of 2.0 mmol·L^{-1} was prepared, and an appropriate amount of sodium terephthalate was dissolved therein to obtain a solution with a sodium terephthalate concentration of 0.5 mmol·L^{-1}. Three reaction tubes were taken, and 5.0 mL of the prepared sodium terephthalate solution was added to each tube. Then, the filtered sample solution was introduced into the tubes, and the mixtures were reacted at 5.0 ℃ temperature for 30 minutes. A standard solution of 2-hydroxyterephthalic acid with concentrations ranging from 0.0 to 2.0 mmol·L^{-1} was prepared. [1] Six different concentrations (0.0, 0.2, 0.5, 1.0, 1.5, and 2.0 mmol·L^{-1}) were selected to construct a calibration curve. The aforementioned samples were analyzed using a fluorescence spectrophotometer. Prior to measurement, the pH of the samples was adjusted to 7.5 using a phosphate buffer solution. The excitation wavelength was set to 315.0 nm, and the emission wavelength was set to 425 nm.

Text S4. Determination of H_2O_2.

The hydrogen peroxide (H_2O_2) content in the samples was determined by the titanium sulfate spectrophotometric method. The specific operation steps were as follows. First, 0.5 mL of the filtered sample solution was pipetted into a 20.0 mL brown glass bottle. Then, 5.0 mL of 3.0 $mol \cdot L^{-1}$ sulfuric acid and 0.5 mL of 0.05 $mol \cdot L^{-1}$ titanium sulfate solution were added to the bottle in sequence. In order to obtain a suitable concentration for determination, the above-mentioned mixed solution was transferred to a volumetric flask and diluted to 10 mL with ultrapure water. After being kept at 5.0 ℃ for color development for 20.0 minutes, the absorbance of the sample solution was measured at a wavelength of 400.0 nm using a UV-visible spectrophotometer. Finally, based on the pre-drawn standard curve, the concentration of H_2O_2 in the samples was accurately calculated.

Text S5. Determination of $O_2^{\bullet-}$.

The content of $O_2^{\bullet-}$ in the system was determined by the XTT method.[2] Firstly, an XTT solution with an initial concentration of 0.05 mM was prepared. Three reaction tubes were taken, and 5.0 mL of the XTT solution and the filtered sample solution were added to each tube and allowed to react for 30 min. Then, the content of XTT formazan formed was measured by a UV spectrophotometer at 475.0 nm. The concentration of the formed $O_2^{\bullet-}$ was quantified based on this measurement. The extinction coefficient of XTT formazan was 23800.0 $M^{-1}\cdot cm^{-1}$.

Text S6. Determination of florfenicol degradation products.

The degradation products of florfenicol in the samples were collected by solid-phase extraction (SPE). The SPE operation was as follows: The Oasis HLB solid-phase extraction column (3.0 cc, 60.0 mg) was activated successively with 6.0 mL of methanol and 6 mL of primary water. Then, 5.0 mL of the filtered target solution was added and allowed to pass through the Oasis HLB solid-phase extraction column at a filtration rate of 3.0-5.0 $mL \cdot min^{-1}$ for enrichment. After enrichment, the column was rinsed with 6.0 mL of primary water. Subsequently, it was eluted with 5.0 mL of methanol (chromatographic grade), and the elution flow rate was less than or equal to 1.0 $mL \cdot min^{-1}$. The obtained eluate was blown to dryness under a nitrogen stream, and the residue was reconstituted with 1 mL of methanol. The oxidized products after SPE were qualitatively analyzed by LC-MS/MS. The gradient elution table is as follows.

Gradient elution table

Time (min)	Mobile Phase A (%)	Mobile Phase B (%)
0	95	5
2	95	5
5	80	20
8	60	40
10	40	60
12	20	80
15	5	95
15.01	95	5
20	95	5

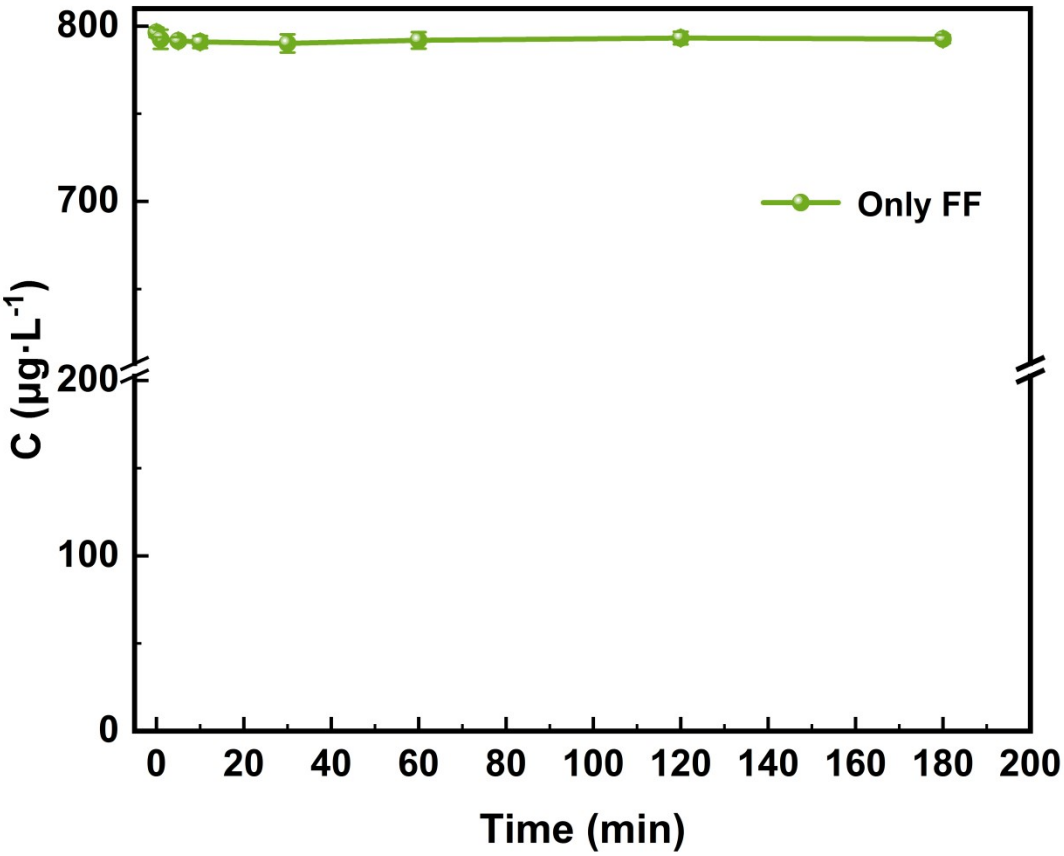

Fig. S1. Concentration change of florfenicol in the absence of δ-MnO_2. Experimental conditions: [FF] = 800 μg·L^{-1}, and pH = 7.0.

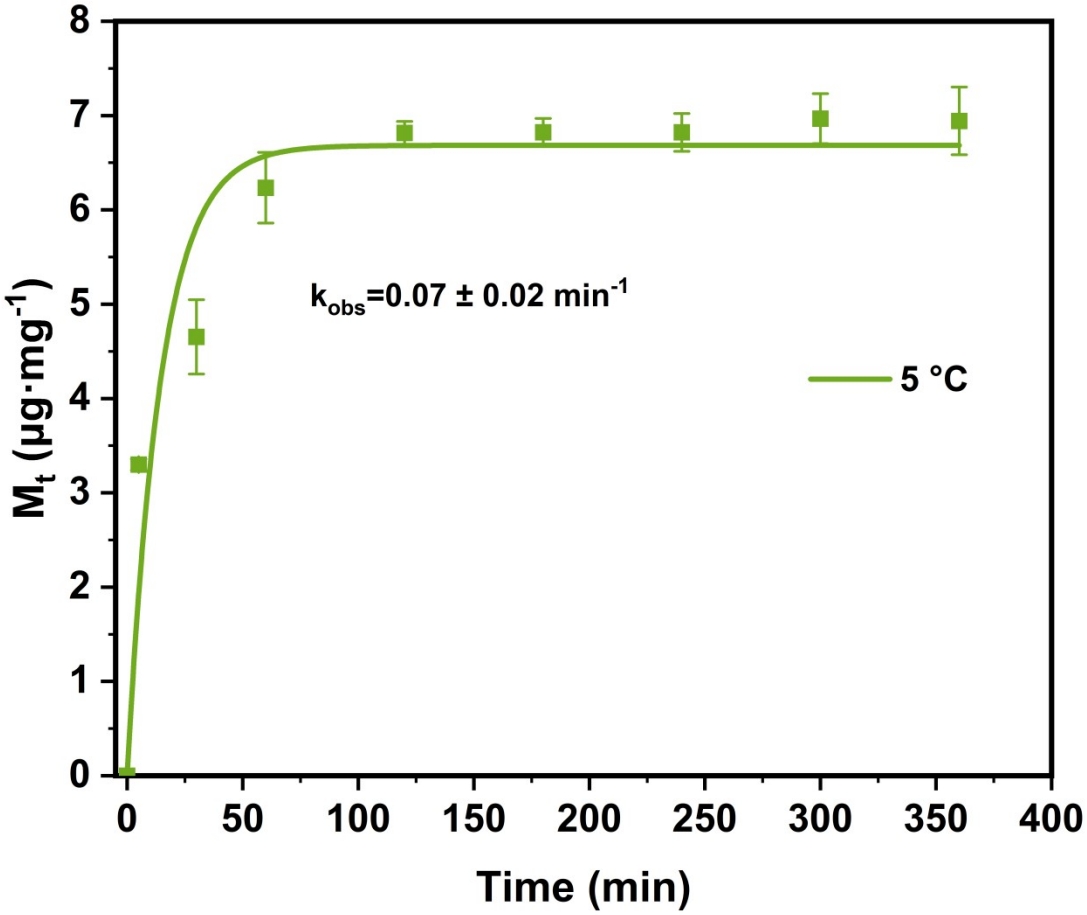

Fig. S2. Effects of δ-MnO_2 and 5.0 ℃ temperature on the oxidation amount of florfenicol (FF) with pseudo-first-order kinetic fitting. Experimental conditions: [δ-MnO_2] = 0.1 mg·mL^{-1}, [FF] = 800 μg·L^{-1}, and pH = 7.0.

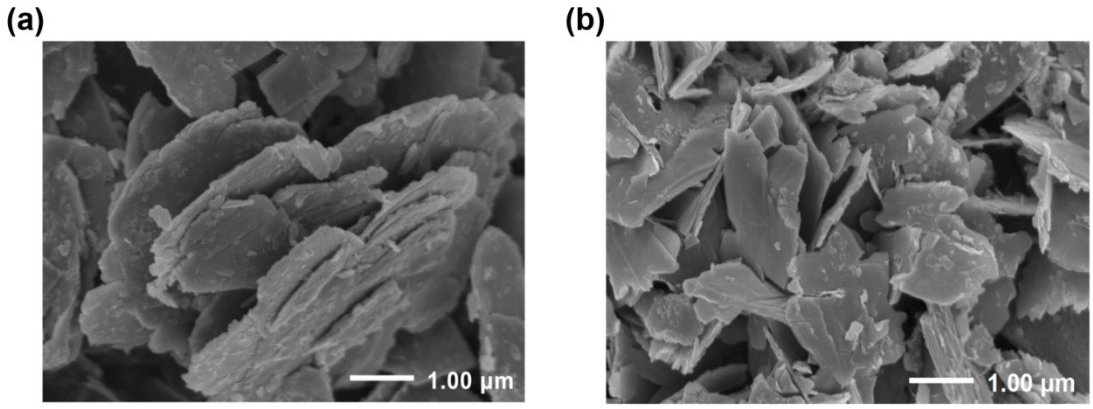

Fig. S3. Scanning electron microscopy (SEM) scans of δ-MnO_2 (a) before, and (b) after reaction.

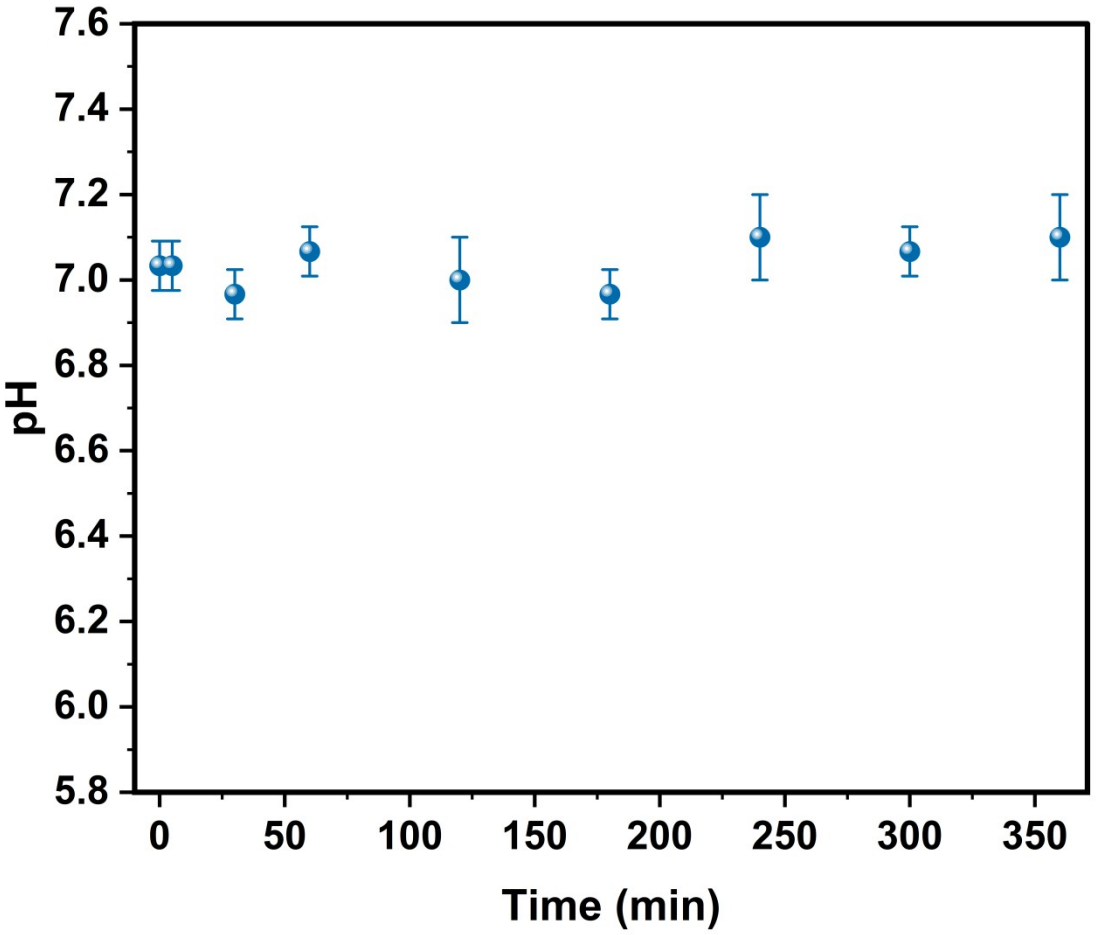

Fig. S4. pH variation in the δ-MnO_2-FF reaction system at 5.0 °C. Experimental conditions: [δ-MnO_2] = 0.1 mg·mL^{-1}, [FF] = 800 μg·L^{-1}, and pH = 7.0.

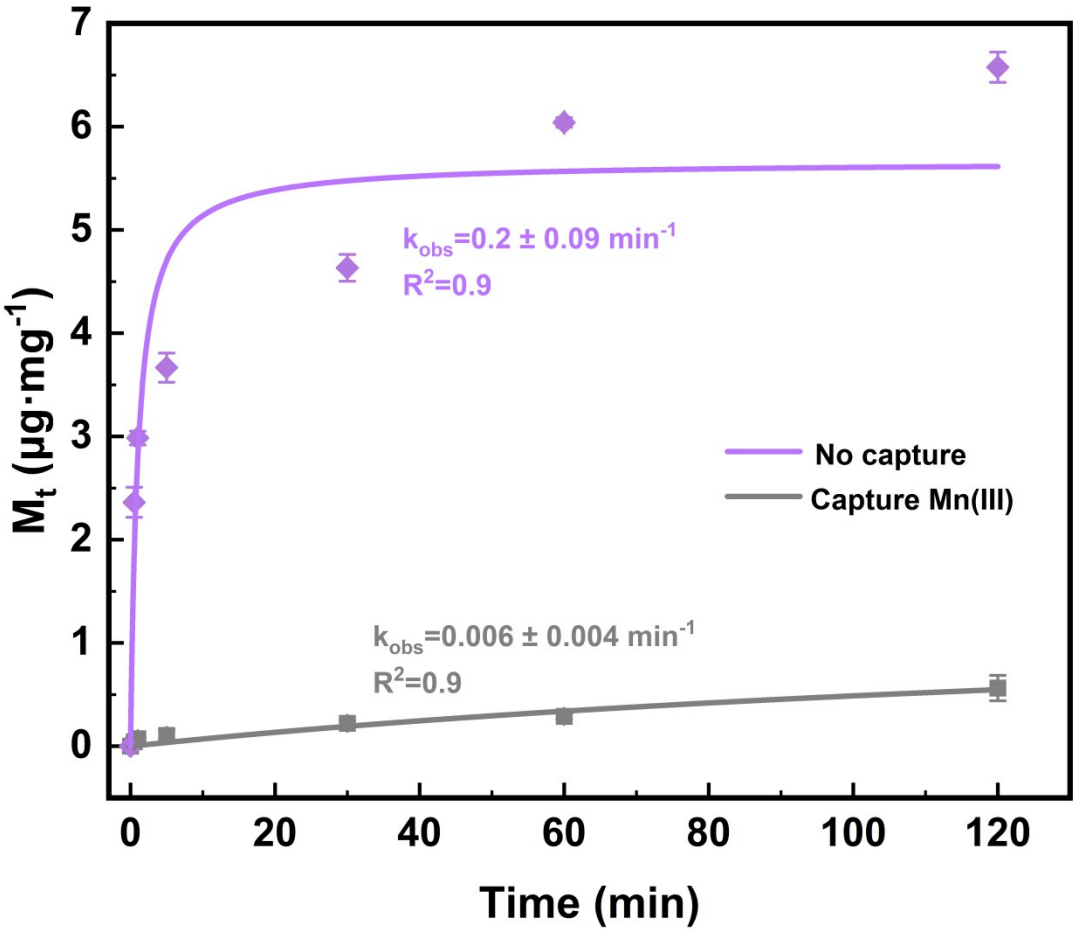

Fig. S5. Effect of Na-PP on masking Mn(III) and the equilibrium oxidation amount of florfenicol (FF). Experimental conditions: [δ-MnO_2] = 0.1 mg·mL^{-1}, [FF] = 800 μg·L^{-1}, [Na-PP] = 50 mmol·L^{-1}, and pH = 7.0.

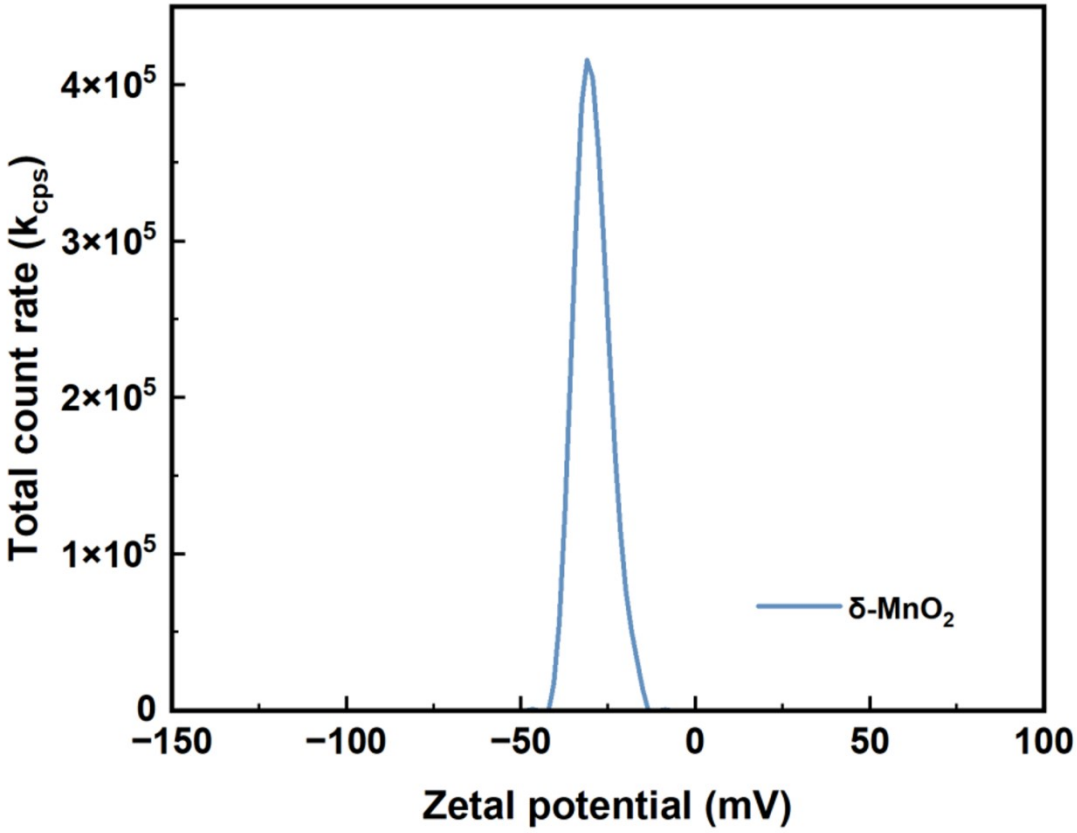

Fig. S6. Zeta potential of δ-MnO_2 at pH = 7. Experimental conditions: [δ-MnO_2] = 0.1 mg·mL^{-1}.

Table S1 Natural population analysis charge distribution and Fukui index of florfenicol.

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0
1(C)	-0.0367	-0.0652	-0.011	0.0257	0.0285	0.0271
2(C)	-0.032	-0.0662	-0.009	0.023	0.0342	0.0286
3(C)	-0.0361	-0.0798	-0.0021	0.0339	0.0437	0.0388
4(C)	-0.0285	-0.0669	-0.0087	0.0198	0.0384	0.0291
5(C)	-0.0236	-0.0517	0.0042	0.0278	0.0281	0.0279
6(C)	-0.0022	-0.0457	0.0255	0.0277	0.0435	0.0356
7(H)	0.0459	0.0298	0.0638	0.018	0.0161	0.017
8(H)	0.0562	0.0372	0.0719	0.0157	0.019	0.0174
9(H)	0.0566	0.0359	0.0723	0.0157	0.0207	0.0182
10(H)	0.0487	0.032	0.0655	0.0168	0.0167	0.0167
11(S)	0.556	0.5342	0.5968	0.0408	0.0218	0.0313
12(O)	-0.3618	-0.3932	-0.2532	0.1085	0.0314	0.07
13(O)	-0.3611	-0.3935	-0.2683	0.0928	0.0324	0.0626
14(C)	-0.064	-0.082	-0.0263	0.0377	0.018	0.0278
15(H)	0.0514	0.0448	0.0708	0.0194	0.0066	0.013
16(H)	0.0506	0.0445	0.0682	0.0176	0.0061	0.0119
17(H)	0.0577	0.038	0.0794	0.0217	0.0197	0.0207
18(C)	0.0598	0.0504	0.07	0.0102	0.0094	0.0098
19(H)	0.0317	0.019	0.0492	0.0174	0.0127	0.0151
20(O)	-0.2106	-0.2253	-0.195	0.0156	0.0146	0.0151
21(H)	0.1777	0.1634	0.1926	0.0149	0.0144	0.0146
22(C)	0.0334	0.0297	0.0478	0.0144	0.0037	0.0091
23(H)	0.033	0.0324	0.0442	0.0112	0.0006	0.0059
24(C)	0.062	0.0558	0.0795	0.0174	0.0062	0.0118
25(H)	0.0299	0.0235	0.0476	0.0178	0.0064	0.0121

Continued Table S1 Natural population analysis charge distribution and Fukui index of florfenicol.

Atom	q(N)	q(N+1)	q(N-1)	f^-	f^+	f^0
26(H)	0.0403	0.0292	0.0531	0.0128	0.0111	0.012
27(N)	-0.0941	-0.1129	-0.0214	0.0728	0.0187	0.0457
28(H)	0.1286	0.1124	0.1491	0.0205	0.0162	0.0184
29(F)	-0.1549	-0.1636	-0.1243	0.0306	0.0087	0.0197
30(C)	0.1466	0.1068	0.1714	0.0248	0.0398	0.0323
31(O)	-0.2571	-0.326	-0.1709	0.0862	0.0689	0.0775
32(C)	0.0633	0.0111	0.0579	-0.0054	0.0522	0.0234
33(H)	0.048	0.0252	0.0509	0.0029	0.0228	0.0128
34(Cl)	-0.0495	-0.1477	-0.0059	0.0435	0.0982	0.0709
35(Cl)	-0.0662	-0.2367	-0.0366	0.0296	0.1704	0.1

Table S2

Toxicity Category

Logarithmic-transformed toxicity range	Class
$\lg k \leq 0$	Very toxic
$0 < \lg k \leq 1$	Toxic
$1 < \lg k \leq 2$	Harmful
$\lg k > 2$	No harmful

1. O. Reséndiz Hernández, L. A. Cruz Santiago, J. Vega Moreno, E. J. Del Angel Gómez, A. L. Martínez Salazar, A. A. Lemus Santana and B. Portales Martínez, Int. J. Hydrogen Energy, 2024, 108, 141-158, DOI: 10.1016/j.ijhydene.2024.04.095.
2. M. W. Sutherland and B. A. Learmonth, Free Radical Res., 1997, 27, 283-289, DOI: 10.3109/10715769709065766.