Supporting Information

Cu(II) inhibited the transport of tetracycline in porous media: Role of complexation

Chang Xu[a, b], Bo Gong[a, b*], Shan Zhao[a, b], Xiao-Min Sun[c], Shu-Guang Wang[a, b, d, e], Chao Song[a, b*]

[a] *Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Qingdao, Shandong, 266237, China*

[b] *Shandong Key Laboratory of Environmental Processes and Health, School of Environmental Science and Engineering, Shandong University, Qingdao, Shandong, 266237, China*

[c] *Environment Research Institute, Shandong University, Qingdao 266237, China*

[d] *Sino-French Research Institute for Ecology and Environment (ISFREE), School of Environmental Science and Engineering, Shandong University, Qingdao, Shandong, 266237, China*

[e] *WeiHai Research Institute of Industrial Technology of Shandong University, Weihai, 264209, China*

* Corresponding author. Tel.: +86 532 58630936; Fax: +86 532 58630907.

E-mail address: songchao@sdu.edu.cn (Chao Song); bogong@sdu.edu.cn (Bo Gong)

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Fig. S1 The breakthrough curves of TC transport in saturated porous media in the presence of Cu(II) in seawater (A) and freshwater (B).

Fig. S2 The optimized structures of (A) TC, (B-D) TC-Cu complex A, B, and C with atomic number labels.

Fig. S3 The optimized adsorption structure of (A) Complex A ($CuHTC^{\pm}$), (B) Complex B ($CuHTC^{\pm}$) and (C) Complex C ($Cu_2TC^{\pm}$) on SiO_2 (001) surface with only weak intermolecular interactions.

Fig. S4 The PDOS of (A) TC-SiO_2, (B) Complex A-SiO_2, (C) Complex B-SiO_2, and (D) Complex C-SiO_2.

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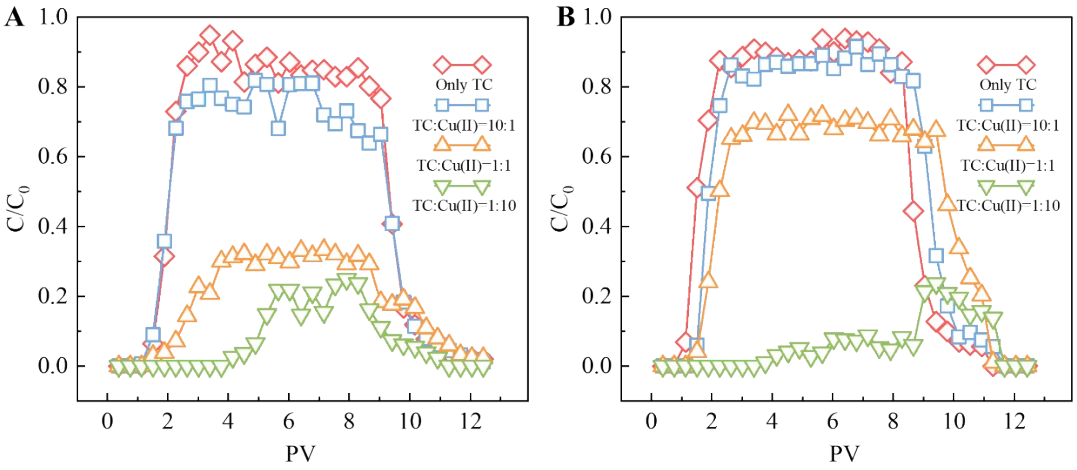
Table S5 The typical intermolecular bond distances and bond population between the TC/TC-Cu complex and SiO_2 (001) surface.



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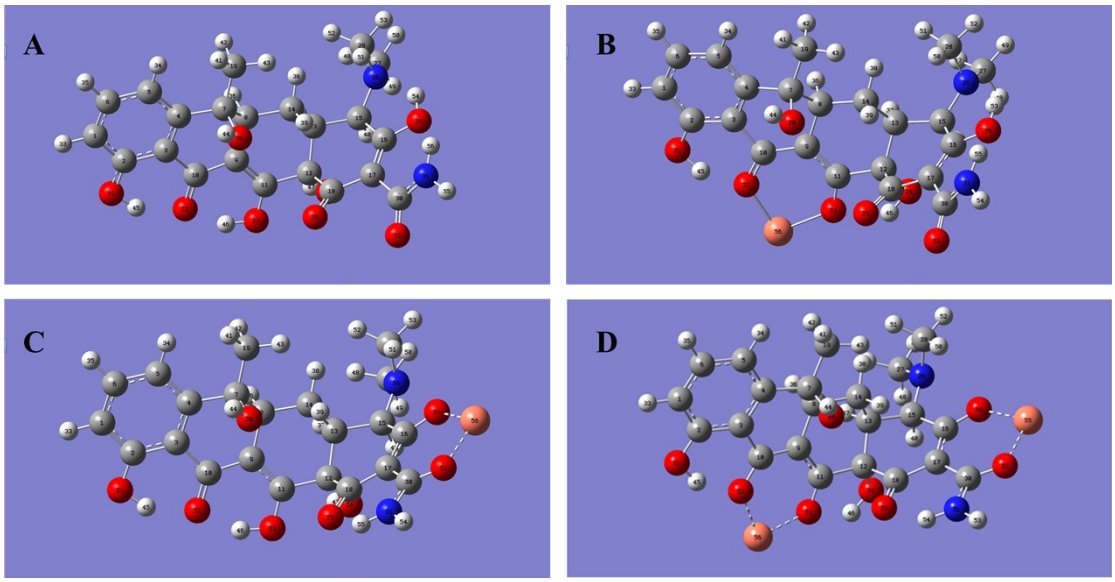

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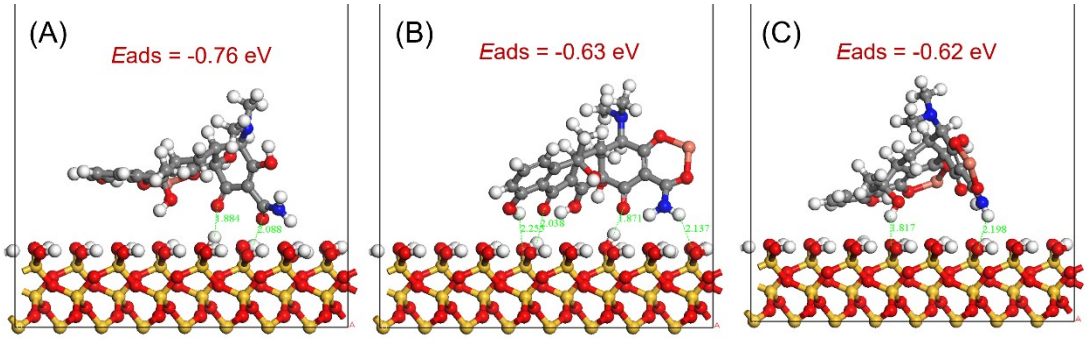

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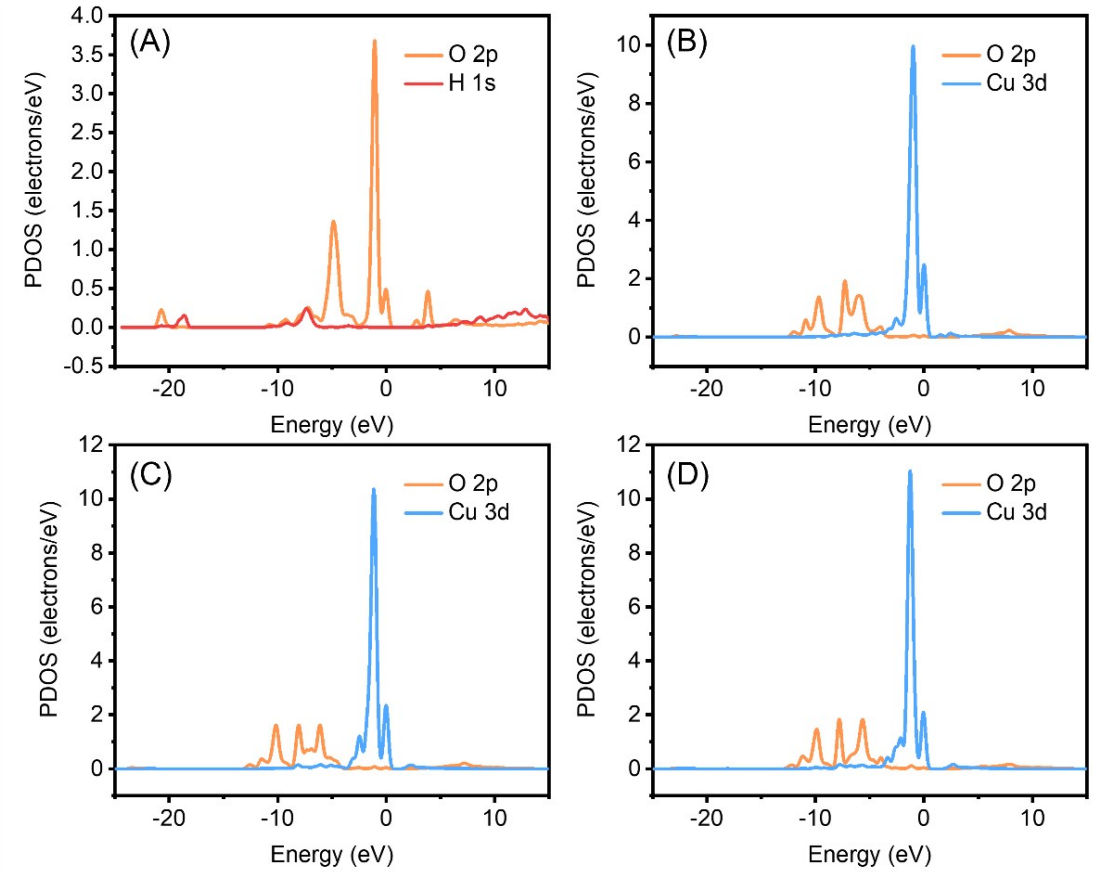

Fig. S4 The PDOS of (A) TC-SiO_2, (B) Complex A-SiO_2, (C) Complex B-SiO_2, and (D) Complex C-SiO_2.

Table S1 Common ions and water quality parameters in seawater and freshwater.

Test item	Unit	Seawater	Freshwater
Ca^{2+}	mg/L	438	80.1
Mg^{2+}	mg/L	804	19.1
NO_3^-	mg/L	4.89	<0.004
SO_4^{2-}	mg/L	1.88×10^3	81.6
Cl^-	mg/L	1.58×10^4	104
Na^+	mg/L	7.88×10^3	42.6
pH	-	7.86	8.51
TOC	mg/L	7.83	10.16
Conductivity	mS/cm	32.4	0.67

Table S2 The total DFT energies of TC species with different charges or spin multiplicities before complexation process.

Structure	Charge	Number of unpair electron	Spin multiplicity	Energy (Hartree)
$HTC^{\pm}$ (A)	0	1	2	-1560.711
HTC^{-} (A)	-1	0	1	-1560.886
$HTC^{\pm}$ (B)	0	1	2	-1560.707
HTC^{-} (B)	-1	0	1	-1560.892
$TC^{\pm}$ (C)	0	0	1	-1560.022
$TC^{\pm}$ (C)	0	2	3	-1560.060
TC^{-1} (C)	-1	1	2	-1560.245
TC^{-2} (C)	-2	0	1	-1560.412
TC^{-2} (C)	-2	0	3	-1560.059

Blue indicates the lowest energy of TC species under this condition.

Table S3 The total DFT energies of TC-Cu species with different charges or spin multiplicities after complexation process.

Structure	Charge	Numbers of unpair electron	spin multiplicity	Energy (Hartree)
Complex A ($CuHTC^{+}$)	1	1	2	-3200.633
Complex A ($CuHTC^{\pm}$)	0	0	1	-3200.833
Complex B ($CuHTC^{+}$)	1	1	2	-3200.651
Complex B ($CuHTC^{\pm}$)	0	0	1	-3200.840
Complex C (Cu_2TC^{2+})	2	0	1	-4839.888
Complex C (Cu_2TC^{2+})	2	2	3	-4839.924
Complex C (Cu_2TC^{+})	1	1	2	-4840.130
Complex C ($Cu_2TC^{\pm}$)	0	0	1	-4840.313

Blue indicates the lowest energy of the complex under this condition.

Table S4 The Cu-O bond distances and Mayer bond orders in TC-Cu complexes.

Structure	Cu-O distance (Å)	Mayer bond order
Complex A ($CuHTC^{\pm}$)	1.950	0.377
	1.943	0.398
Complex B ($CuHTC^{\pm}$)	1.952	0.389
	1.945	0.408
Complex C ($Cu_2TC^{\pm}$)	1.948	0.380
	1.942	0.400
	1.948	0.396
	1.942	0.413

Table S5 The typical intermolecular bond distances and bond population between the TC/TC-Cu complex and SiO_2 (001) surface.

Structure	Hydrogen bond		Cu-O	
	distance (Å)	population	distance (Å)	population
TC-SiO_2	1.569	0.13	/	/
	2.476	0.00	/	/
	2.488	0.01	/	/
Complex A-SiO_2	1.648	0.11	2.008	0.09
	1.917	0.05		
	2.117	0.02		
	2.464	0.01		
Complex B-SiO_2	/	/	1.943	0.10
Complex C-SiO_2	2.477	0.01	1.892	0.14