

Supporting information

Alteration of Birnessite Reactivity in Dynamic Anoxic/Oxic Environments

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Table S1. Atomic concentrations by XPS survey scans for pristine birnessite and samples after reacted with OFL and different Mn(II) concentrations. 345 μM acid birnessite; 10 μM OFL; 10 mM NaCl; 0, 50, 200 μM Mn(II); 48 h reaction time; pH 8 (\pm 0.1).

	C (%)	O (%)	Mn (%)	K (%)	N (%)	Na (%)
Acid birnessite	27.3	44.9	20.9	6.9	BDL	BDL
N ₂ _0 μM Mn(II)	27.6	44.6	20.4	7.0	0.5	BDL
O ₂ _0 μM Mn(II)	24.3	43.3	17.5	6.1	BDL	8.7
N ₂ _50 μM Mn(II)	21.3	49.5	23.1	5.4	BDL	0.7
O ₂ _50 μM Mn(II)	24.6	44.6	24.6	6.2	BDL	BDL
N ₂ _200 μM Mn(II)	20.9	52.6	26.5	BDL	BDL	BDL
O ₂ _200 μM Mn(II)	21.2	50.5	28.3	BDL	BDL	BDL

BDL: below the detection limit (0.1%).

Table S2. Mn 2p_{3/2} XPS fitted parameters for pristine birnessite and samples after reacted with OFL and different Mn(II) concentrations. 345 μM acid birnessite; 10 μM OFL; 10 mM NaCl; 0, 50, 200 μM Mn(II); 48 h reaction time; pH 8 (\pm 0.1).

Sample	Acid	0 μM Mn(II)		50 μM Mn(II)		200 μM Mn(II)		
	birnessite	N ₂	O ₂	N ₂	O ₂	N ₂	O ₂	
AOS	3.87	3.70	3.65	3.63	3.60	3.40	3.33	
Mn(II)	Binding energy (eV)	640.1	640.3	640.4	640.7	640.9	641.1	641.4
	Area (%)	1.0	6.4	5.5	6.9	5.6	17.5	9.2
Mn(III)	Binding energy (eV)	642.4	642.3	642.3	642.4	642.4	642.1	642.3
	Area (%)	10.7	16.8	24.3	23.1	29.6	25.0	48.4
Mn(IV)	Binding energy (eV)	643.0	643.0	643.0	643.1	643.1	642.6	643.0
	Area (%)	88.3	76.8	70.2	70.0	64.8	57.5	42.4

Table S3. O 1s XPS fitted parameters for pristine birnessite and samples after reacted with OFL and different Mn(II) concentrations. 345 μM acid birnessite; 10 μM OFL; 10 mM NaCl; 0, 50, 200 μM Mn(II); 48h reaction time; pH 8 (\pm 0.1).

Sample		Acid birnessite	0 μM Mn(II) N ₂	0 μM Mn(II) O ₂	50 μM Mn(II) N ₂	50 μM Mn(II) O ₂	200 μM Mn(II) N ₂	200 μM Mn(II) O ₂
O _{latt}	Binding energy (eV)	530.2	530.1	530.0	530.1	530.1	529.8	530.0
	Area (%)	87.5	88.5	90.1	88.4	87.3	49.5	65.2
O _{ads}	Binding energy (eV)	531.7	531.5	531.5	531.5	531.6	531.0	531.1
	Area (%)	10.0	8.3	7.0	8.7	9.0	37.8	26.9
O _{surf}	Binding energy (eV)	532.7	532.6	532.7	532.6	532.6	531.9	532.2
	Area (%)	2.5	3.2	2.9	2.9	3.7	12.7	7.9

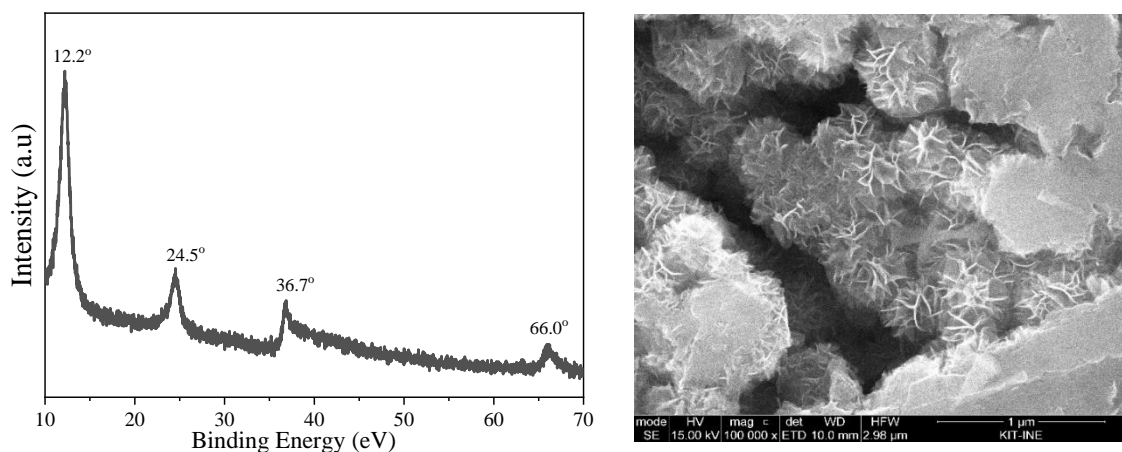


Figure S1. XRD and SEM images of the synthesized birnessite.

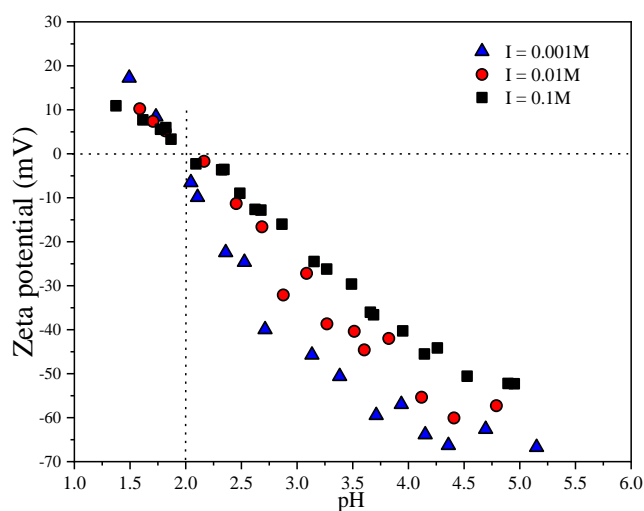


Figure S2. Zeta potential of acid birnessite samples. $\text{MnO}_2 = 0.2 \text{ g L}^{-1}$ (2.3 mM); $I = 0.1, 0.01, 0.001 \text{ M NaCl}$.

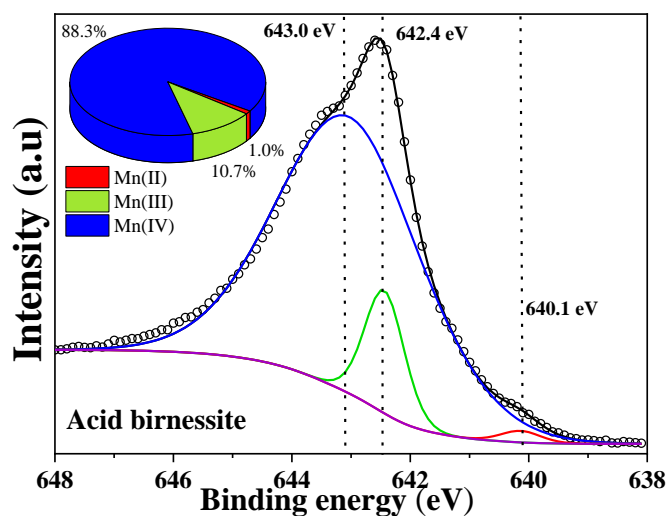


Figure S3. Fitting of Mn $2p_{3/2}$ XPS high resolution spectra of the synthesized acid birnessite.

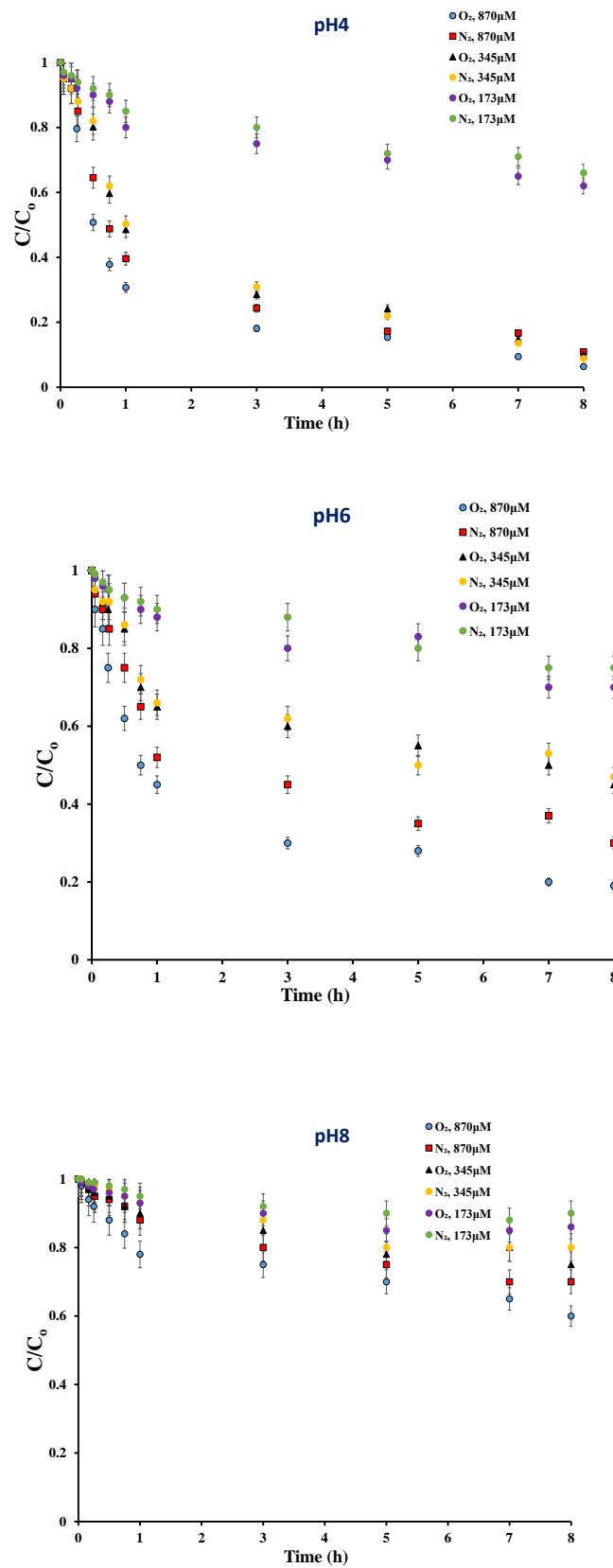


Figure S4. Removal kinetics of OFL at three pH values 4.0, 6.0, 8.0 (\pm 0.1), and three MnO₂ concentration: 173, 345, 870 μ M (or 15, 30, 75.6 mg/L); 10 μ M OFL; 10 mM NaCl; under anoxic (N₂) and oxic (O₂) conditions.

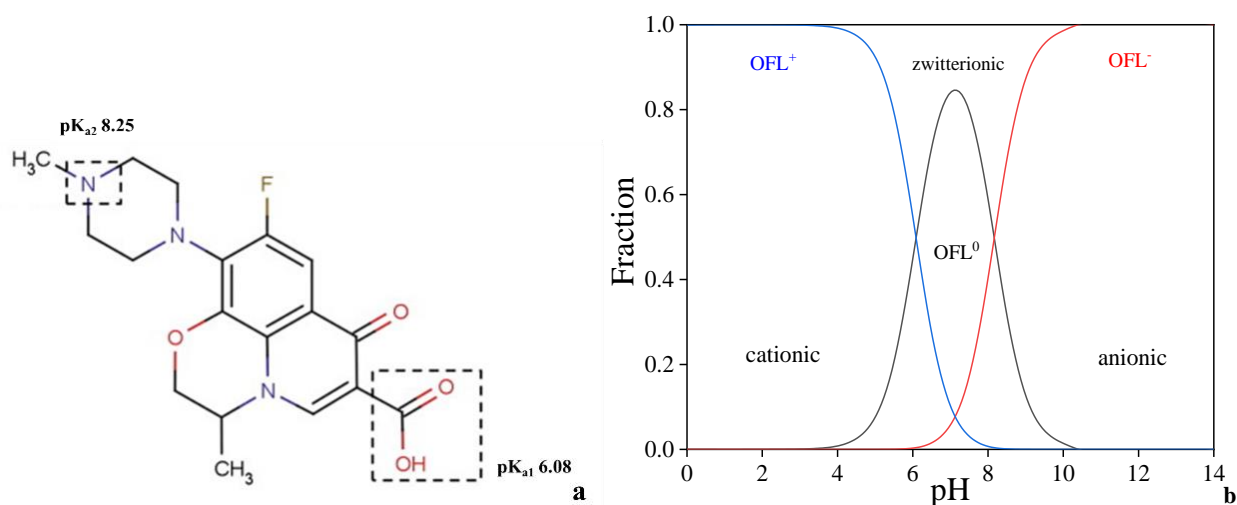


Figure S5. (a) Chemical speciation of OFL vs pH. (b) pK_{as} of OFL ($pK_{a,1} = 6.08$ and $pK_{a,2} = 8.25$) at infinite dilution were obtained from conditional pK_a values and the Davies equation. 10 mM NaCl.

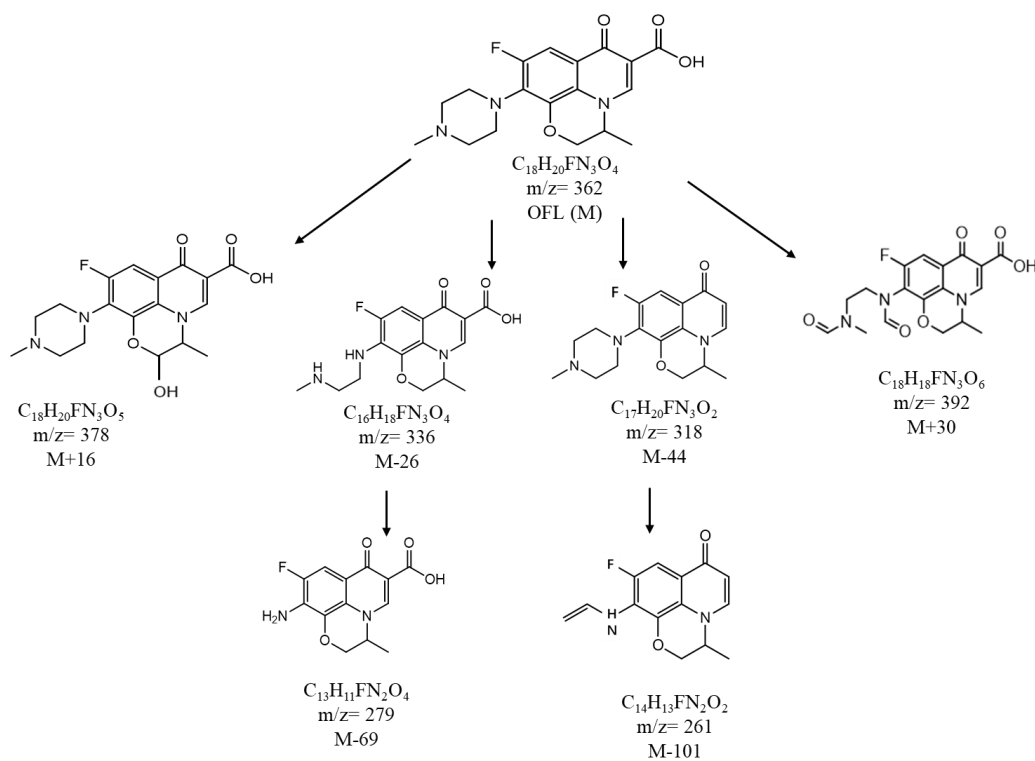


Figure S6. Proposed oxidation pathway of OFL as analyzed by LC/MS. Product of $m/z = 279$ was classified as the M-69 because of its structural similarity to the M-69 product of CIP (Zhang and Huang, 2005).

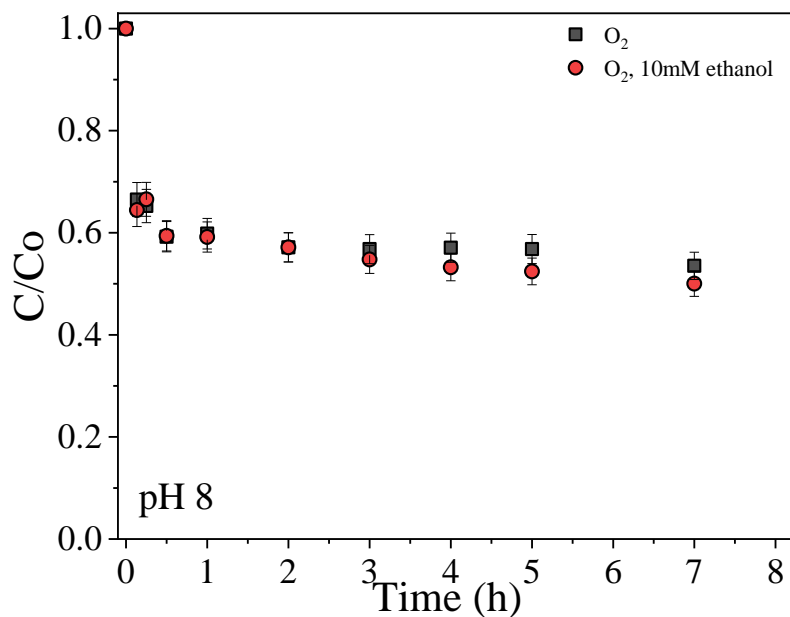


Figure S7. Removal kinetics of OFL in the presence of oxygen and ethanol at pH 8 (± 0.1). 345 μM acid birnessite; 10 μM OFL; 10 mM NaCl; 10 mM ethanol.

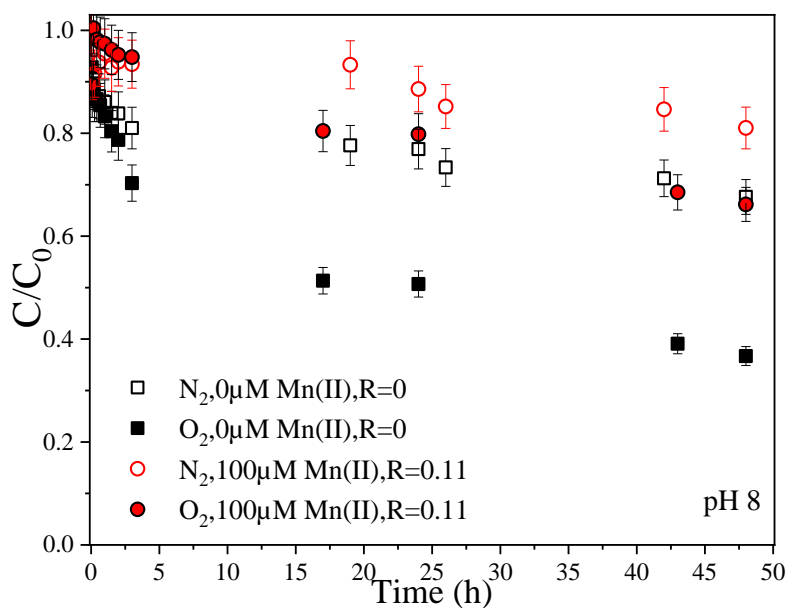


Figure S8. Removal kinetics of pipemidic acid (PIP) under oxidic and anoxic conditions at pH 8 (± 0.1). 20 μM PIP; 870 μM acid birnessite; 10 mM NaCl; 0,100 μM Mn(II); 48 h. The R represents the Mn(II)/MnO₂ molar ratio.

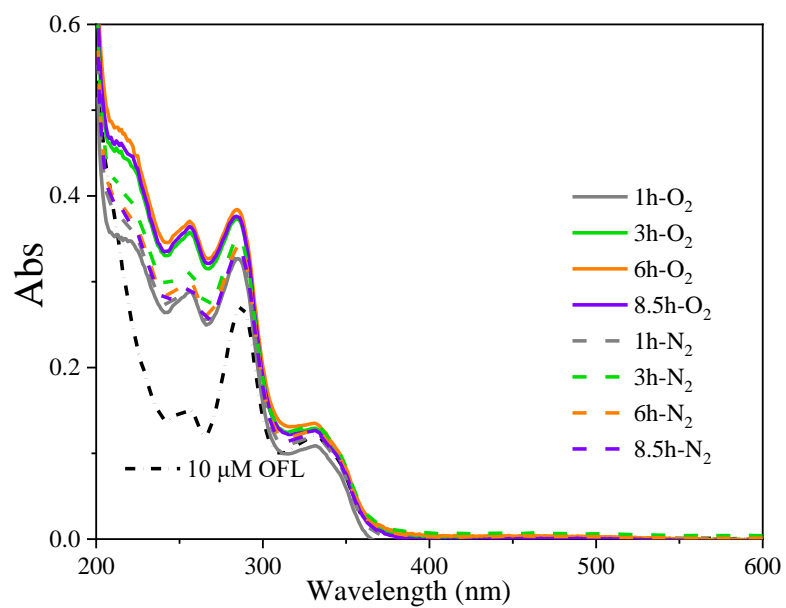


Figure S9. UV-Vis spectra during reaction under anoxic and oxic conditions at pH 8 (\pm 0.1). 345 μ M acid birnessite; 10 μ M OFL; 10 mM NaCl; 200 μ M Mn(II); 1 mM sodium pyrophosphate.

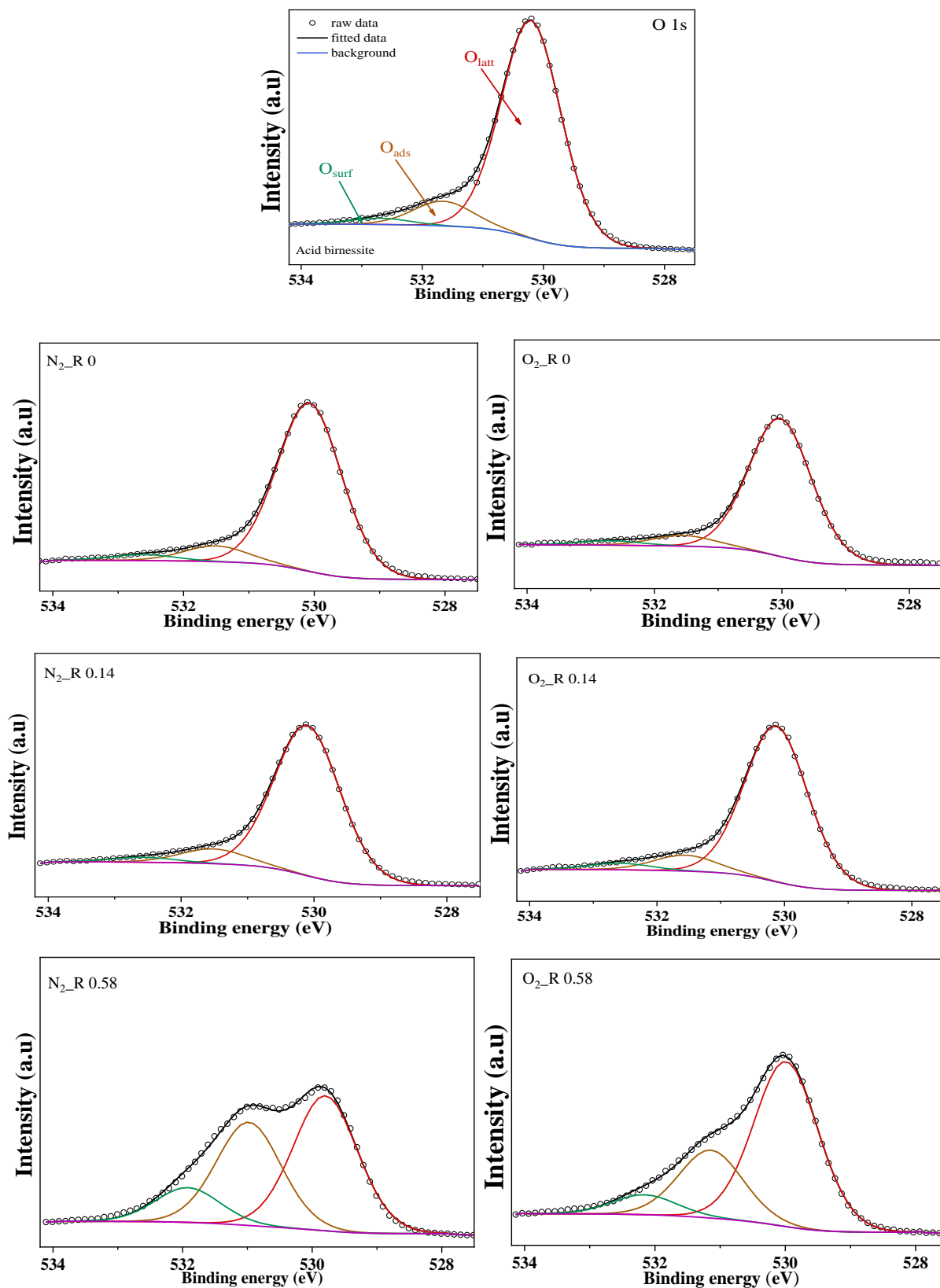


Figure S10. Fitting of O 1s XPS high resolution spectra of pristine MnO₂ and samples treated with Mn(II) and OFL under oxidic and anoxic condition. The R represents the Mn(II)/MnO₂ molar ratio. 345 μM acid birnessite; 10 μM OFL; 10 mM NaCl; 0, 50, 200 μM Mn(II); 48 h reaction time; pH 8 (±0.1).

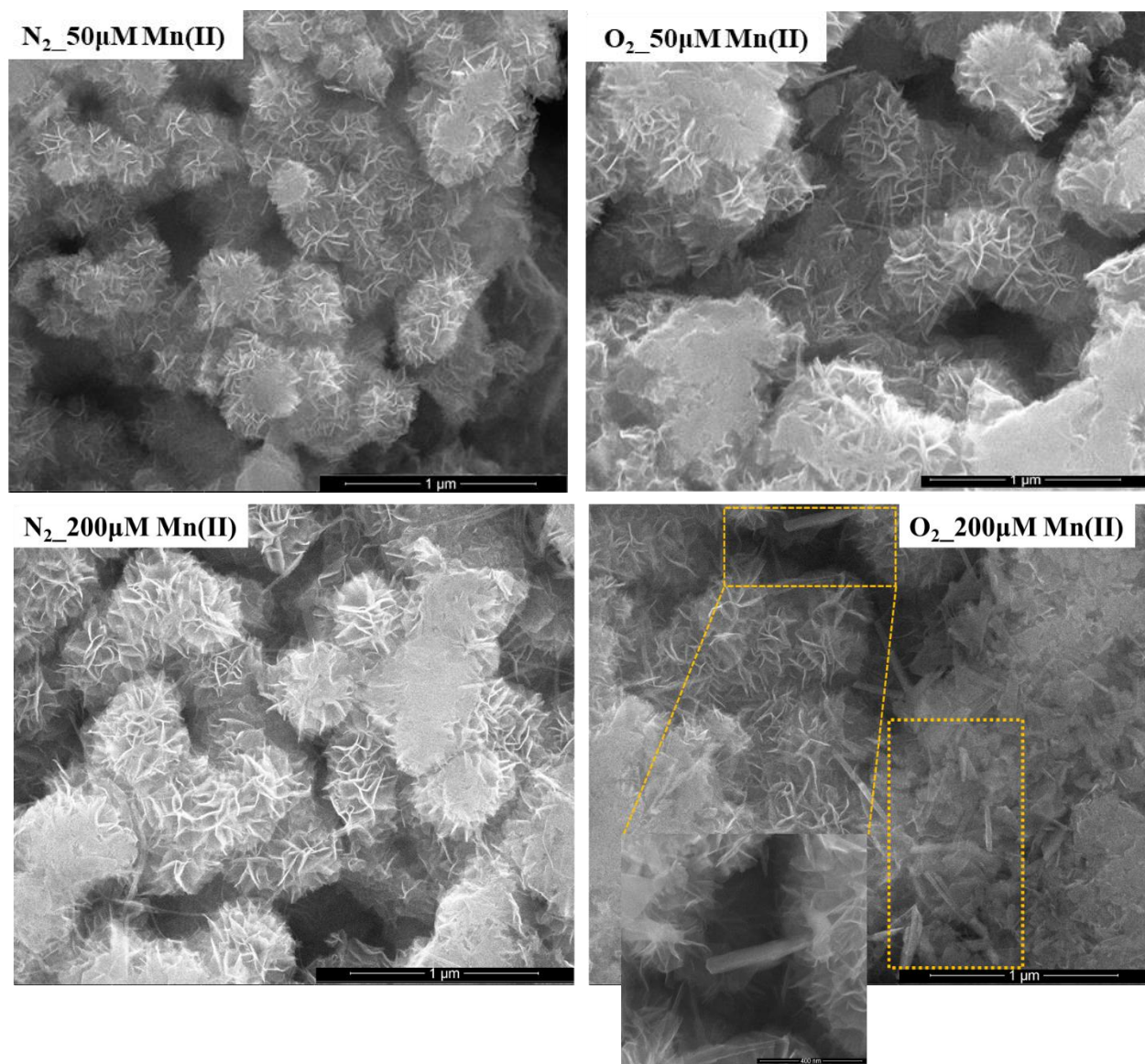


Figure S11. SEM images for samples after reaction with OFL and different Mn(II) concentrations. 345 µM acid birnessite; 10 µM OFL; 10 mM NaCl; 50, 200 µM Mn(II); 48 h reaction time; pH 8 (± 0.1).

References

Zhang, H., Huang, C., 2005. Oxidative Transformation of Fluoroquinolone Antibacterial Agents and Structurally Related Amines by Manganese Oxide. *Environ. Sci. Technol.* 39, 4474-4483.