

SUPPORTING INFORMATION

Chlorination of iodide-containing waters in the presence of CuO:

Formation of periodate

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Gunten).

13 figures and 2 kinetic models.

Figure S1 Calibration curve for the analyses of periodate (0-40 μM) by the DPD method

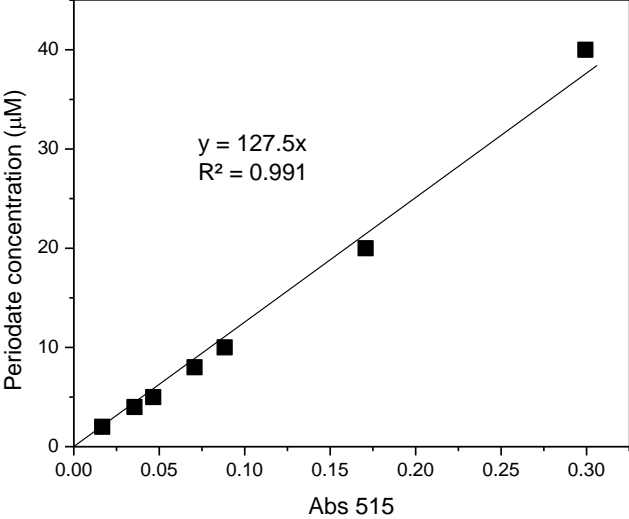


Figure S2 Plot of $1/[HOI]$ vs. time in the absence or presence of CuO. Experimental conditions:

$[HOI]_0 = 30 \mu\text{M}$, $[CuO] = 0.1 \text{ g/L}$, $T = 23 \text{ }^\circ\text{C}$

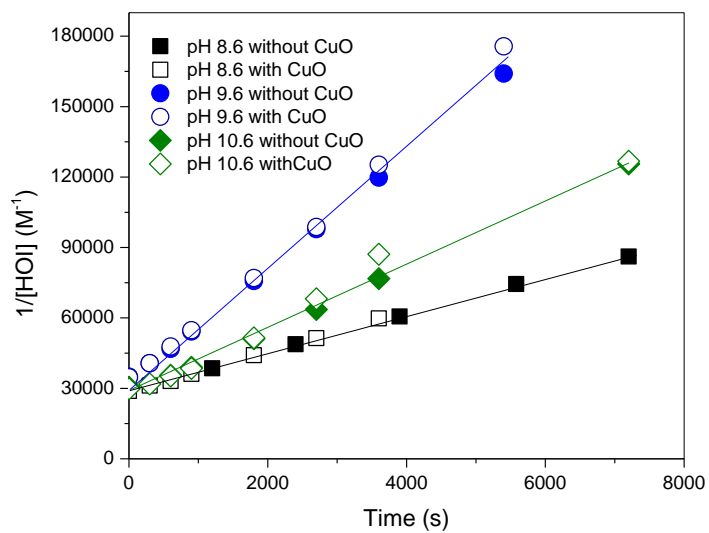


Figure S3 CuO-HOCl-I⁻ system: (a) Effect of CuO dose on pseudo-first-order kinetics of the oxidant decay; (b) Plot of iodate formation vs. oxidant exposure. Experimental conditions: [HOCl]₀ ≈ 11 μM, [I⁻]₀ = 1 μM, [CuO] = 0-0.5 g/L, pH= 8.6, T =22 °C.

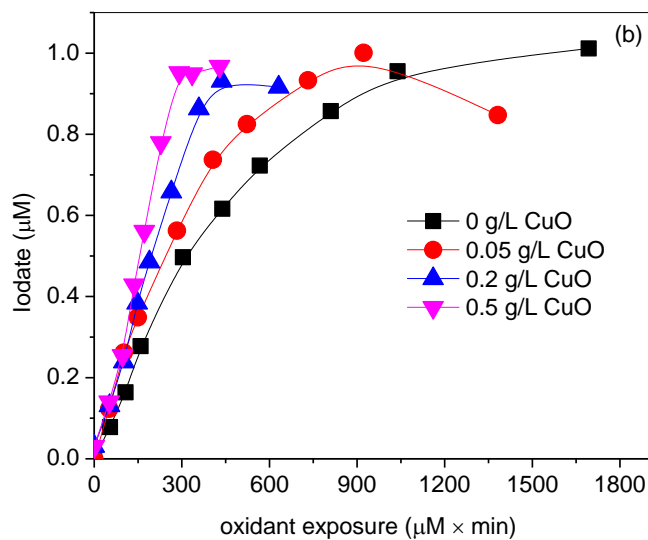
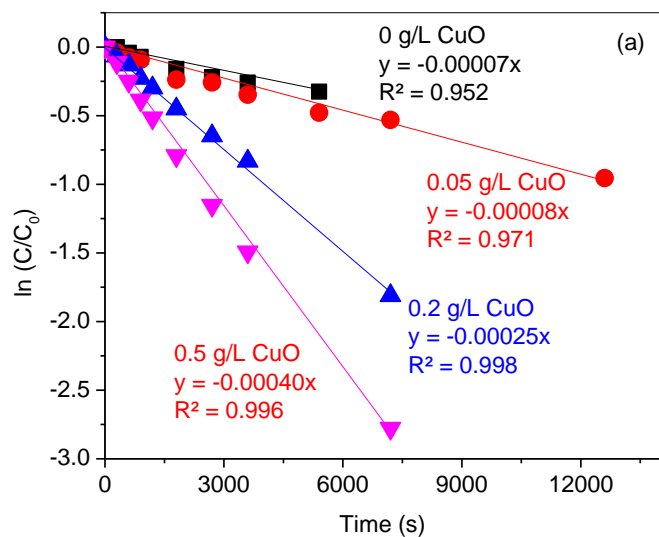


Figure S4 Iodate in the presence of CuO at pH 8.6. Experimental conditions: $[\text{IO}_3^-]_0 = 5 \mu\text{M}$, pH= 8.6, $[\text{CuO}] = 0.1\text{-}0.2 \text{ g/L}$, (For one sample, the CuO was pretreated with $30 \mu\text{M}$ HOBr)

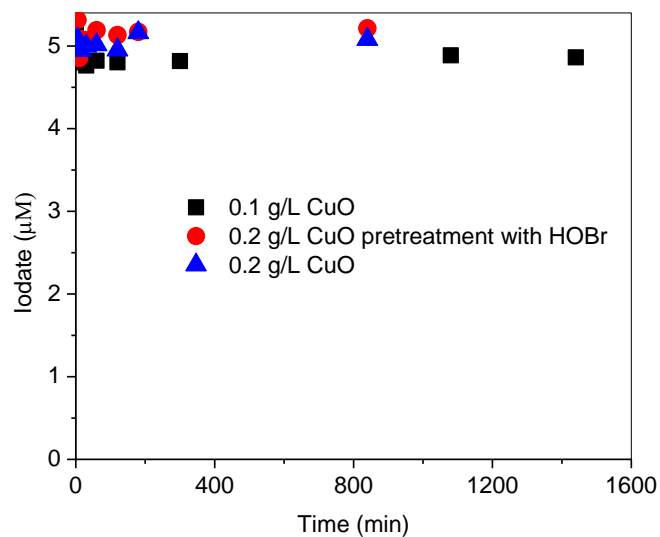


Figure S5 CuO-HOCl-I⁻ system: Effect of pH on pseudo-first-order kinetics of the oxidant decay.

Experimental conditions: [HOCl]₀ ≅ 11 μM, [I⁻]₀ = 1 μM, [CuO] = 0.2 g/L, pH= 6.6-9.6, T =22

°C.

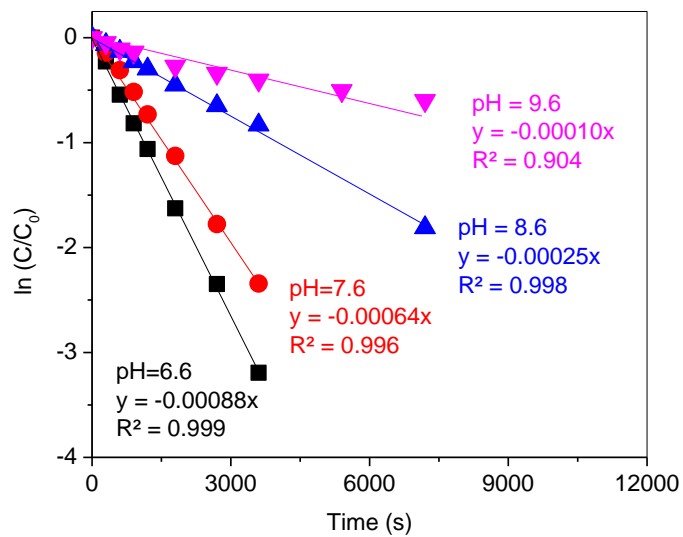
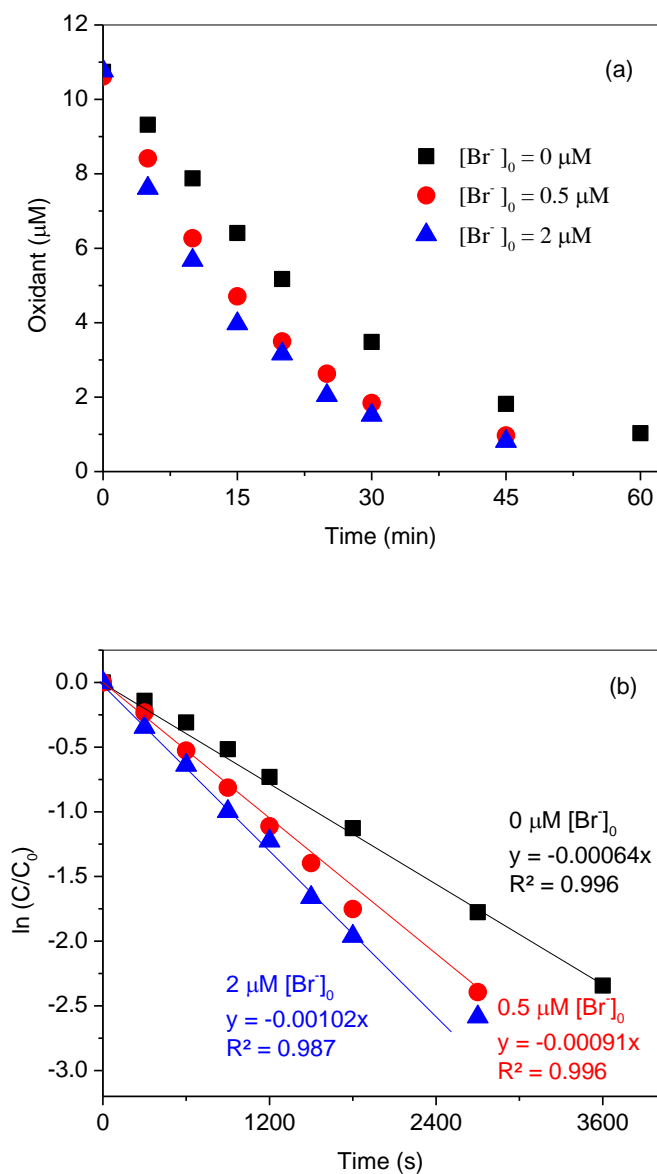


Figure S6 CuO-HOCl-I-Br⁻ system: Effect of Br⁻ concentration on (a) oxidant decay, (b) pseudo-first-order kinetics of oxidant decay and (c) iodate formation. Experimental conditions: [HOCl]₀ ≅ 11 μM, [I]₀ = 1 μM, [Br⁻]₀ = 0-2 μM, [CuO] = 0.2 g/L, pH= 7.6, T =22 °C. It should be noted in Figure S5 c, symbols represent the experimental data; dashed lines are used to guide eyes; solid lines represent simulations from Model 1.



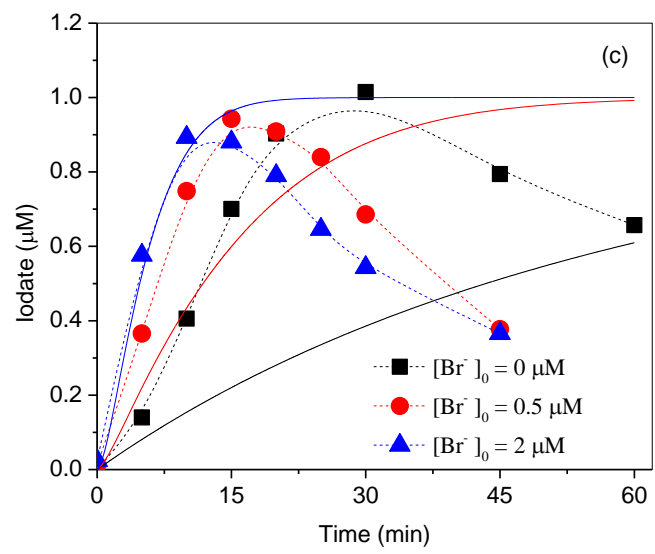


Figure S7 CuO-HOCl-IO₃⁻ system: Pseudo-first-order kinetics of the oxidant decay for varying pH values. Experimental conditions: [HOCl]₀ = 11 μM, [IO₃⁻]₀ = 1 μM, [CuO] = 0.2 g/L, pH= 6.6-9.6, T =22 °C.

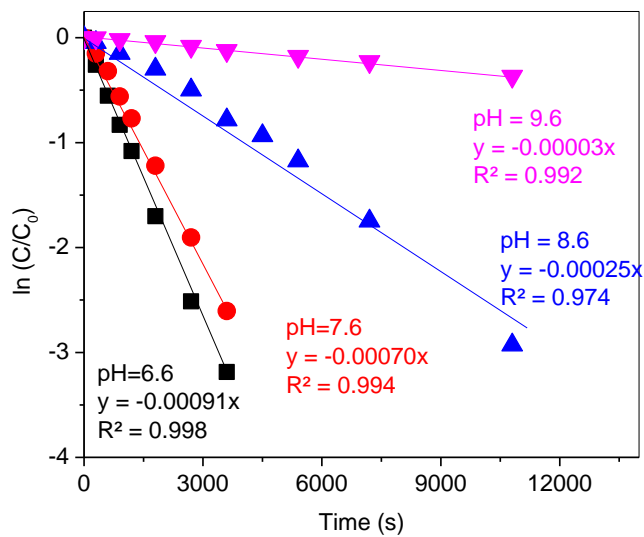


Figure S8 Calculated reduction potentials for various redox couples in the pH range 6.6 to 9.6.

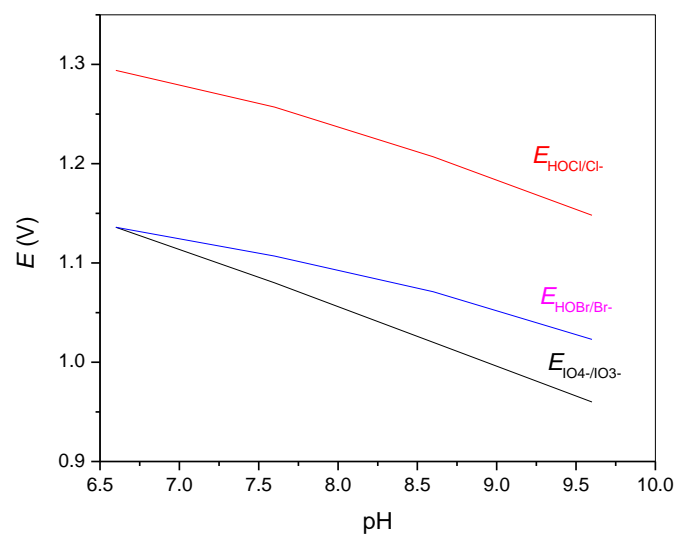


Figure S9 CuO-HOBr-IO₃⁻ system: Pseudo-first-order kinetics for oxidant decay for varying pH values. Experimental conditions: [HOBr]₀ = 10 μM, [IO₃⁻]₀ = 1 μM, [CuO] = 0.2 g/L, pH= 6.6-9.6, T =22 °C.

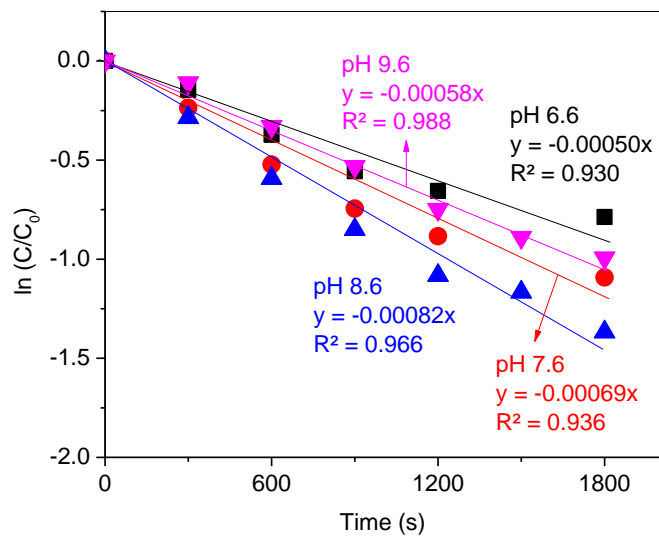


Figure S10 Periodate in the presence of CuO. Experimental conditions: pH= 8.6, [CuO] =0.1 g/L, [IO₄⁻]₀ = 22 or 40 μM, T = 22 °C.

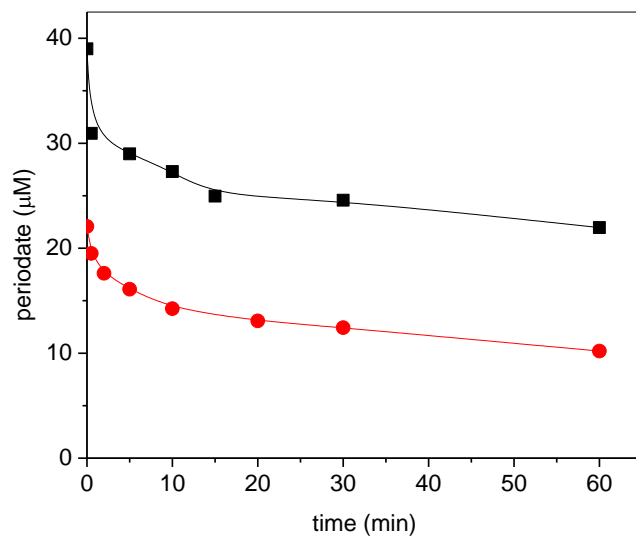
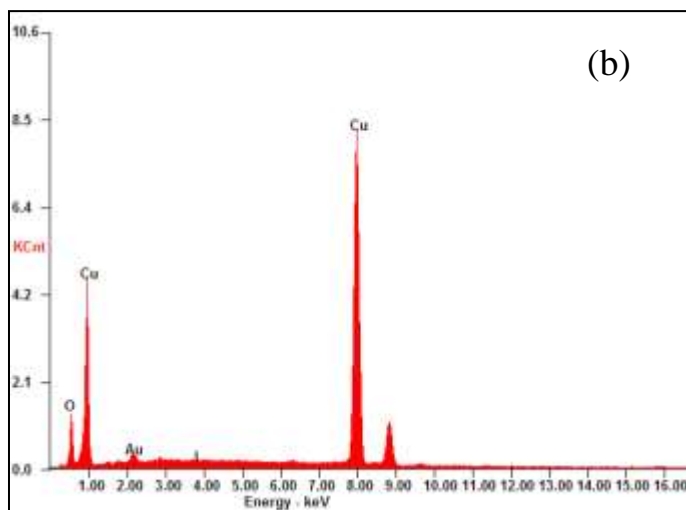
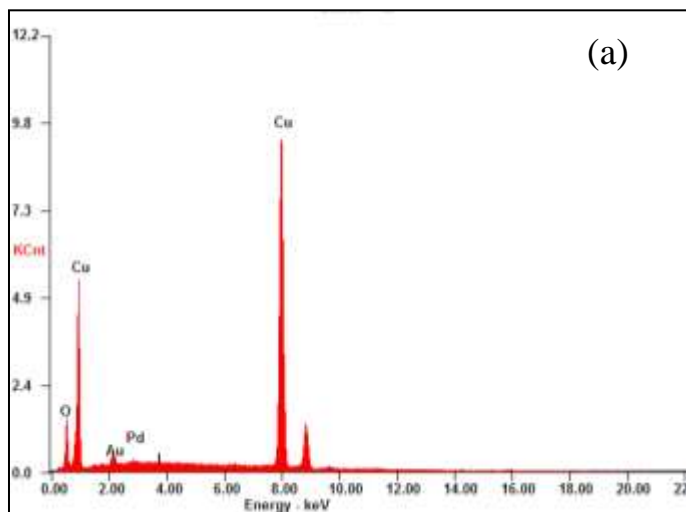


Figure S11 SEM-EDS spectra for reacted CuO particles: (a) CuO blank; (b) CuO-IO₃⁻; (c) CuO-HOCl-IO₃⁻ and (d) CuO-IO₄⁻. Experimental conditions: [CuO] = 1.0 g/L, [HOCl]₀ = 8.6 mM, [IO₄⁻]₀ = 1 mM, [IO₃⁻]₀ = 10 mM, pH= 8.6, T =22 °C, reaction time = 4 h.



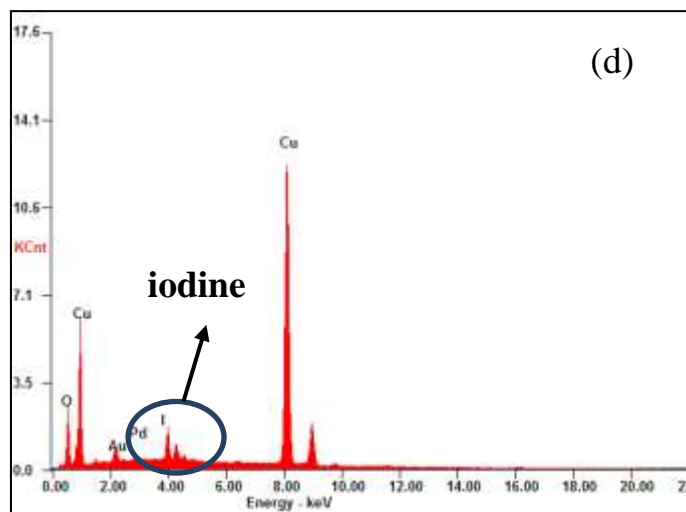
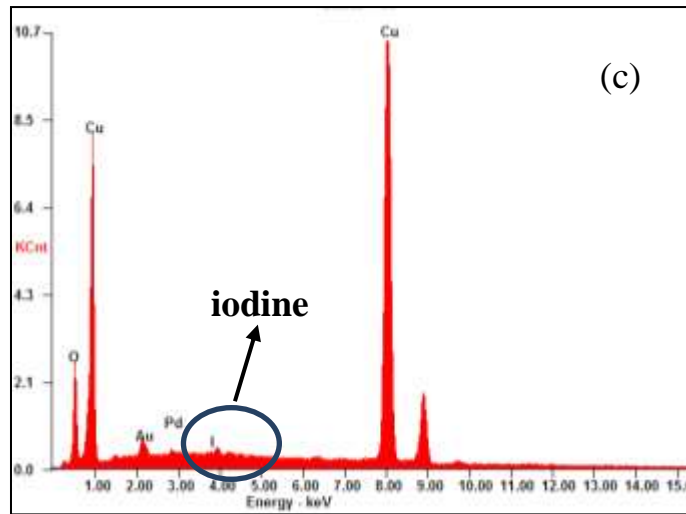


Figure S12 XPS spectra for reacted CuO particles: (a) CuO blank; (b) CuO-IO₃⁻; (c) CuO-HOCl-IO₃⁻ and (d) CuO-IO₄⁻. The iodine signals are marked in blue. Experimental conditions: [CuO] = 1.0 g/L, [HOCl]₀ = 8.6 mM, [IO₄⁻]₀ = 1 mM, [IO₃⁻]₀ = 10 mM, pH= 8.6, T =22 °C, reaction time = 4 h.

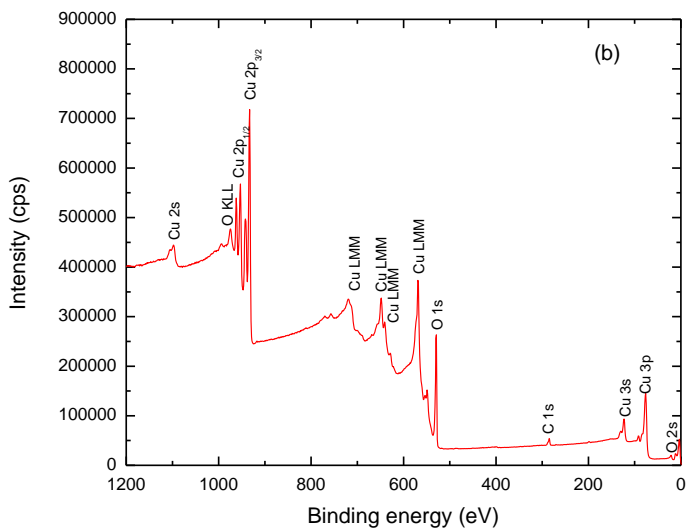
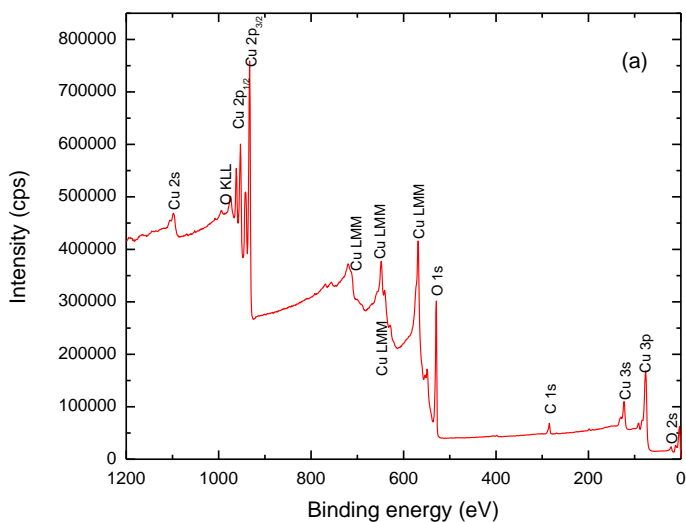
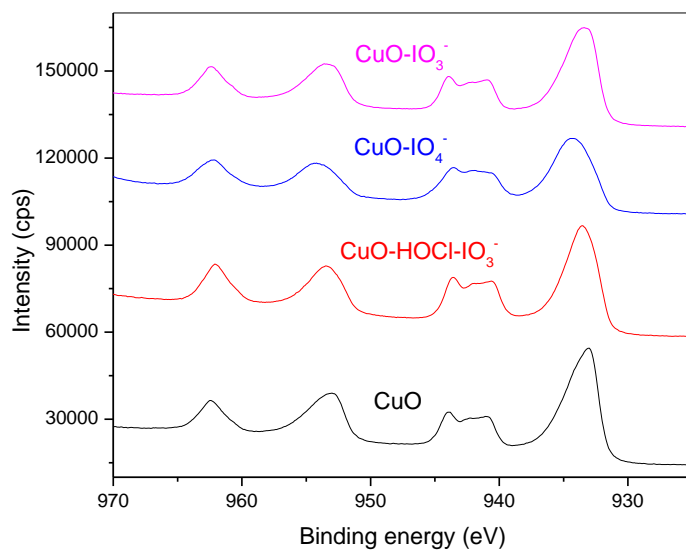


Figure S13 Copper 2p XPS spectra for various reacted CuO particles.



Model 1: Kinetic modeling of iodate formation during chlorination of iodide-containing waters in the presence of bromide

No.	Reactions	Rate constants ($M^{-1} s^{-1}$)	pK_a	References
1	$HOCl \rightleftharpoons OCl^- + H^+$		7.6	1
2	$H^+ + OCl^- \rightleftharpoons HOCl$			
3	$HOBr \rightleftharpoons OBr^- + H^+$		8.8	2
4	$OBr^- + H^+ \rightleftharpoons HOBr$			
5	$HOI \rightleftharpoons OI^- + H^+$		10.4	3
6	$H^+ + OI^- \rightleftharpoons HOI$			
7	$HOCl + I^- \rightleftharpoons HOI + Cl^-$	4.30E+08		4
8	$HOCl + Br^- \rightleftharpoons HOBr + Cl^-$	1.55E+03		5
9	$OCl^- + Br^- \rightleftharpoons OBr^- + Cl^-$	9.00E-04		5
10	$HOBr + I^- \rightleftharpoons HOI + Br^-$	5.00E+09		6
11	$OBr^- + I^- \rightleftharpoons OI^- + Br^-$	6.80E+05		6
12	$HOCl + HOI \rightleftharpoons IO_2^- + Cl^- + 2H^+$	8.20E+00		7
13	$OCl^- + HOI \rightleftharpoons IO_2^- + Cl^- + H^+$	5.20E+01		7
14	$HOBr + OI^- \rightleftharpoons IO_2^- + Br^- + H^+$	1.90E+06		8
15	$OBr^- + OI^- \rightleftharpoons IO_2^- + Br^-$	1.80E+03		8
16	$HOCl + IO_2^- \rightleftharpoons IO_3^- + Cl^- + H^+$	1.00E+06		this study
17	$OCl^- + IO_2^- \rightleftharpoons IO_3^- + Cl^-$	1.00E+06		this study
18	$HOBr + IO_2^- \rightleftharpoons IO_3^- + Br^- + H^+$	1.00E+08		this study
19	$OBr^- + IO_2^- \rightleftharpoons IO_3^- + Br^-$	1.00E+08		this study

Model 2: Kinetic modeling of CuO-activated HOBr oxidation of iodate

1. Reactions for the CuO-activated HOBr oxidation of iodate with optimized rate constants

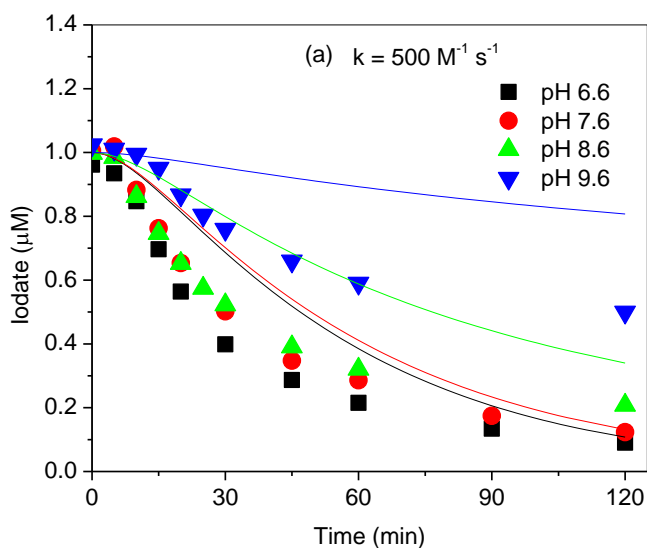
No.	Reactions	Proposed rate constants	Note
1	$\text{HOBr} \rightleftharpoons \text{OBr}^-$	$1 \times 10^9 \text{ s}^{-1}$	HOBr dissociation
2	$\text{OBr}^- \rightleftharpoons \text{HOBr}$	Adjusted by the pH, e.g., pH=7.6, this value is $1.58 \times 10^{10} \text{ s}^{-1}$	HOBr dissociation
3	$\text{CuO} + \text{OBr}^- \rightleftharpoons \text{CuOOBr}$	$1 \times 10^{-4} \text{ s}^{-1}$	Pre-equilibrium of complex formation
4	$\text{CuOOBr} \rightleftharpoons \text{CuO} + \text{OBr}^-$	$1 \times 10^{-3} \text{ s}^{-1}$	Pre-equilibrium of complex formation
5	$\text{CuO} + \text{HOBr} \rightleftharpoons \text{CuOHOBBr}$	$1 \times 10^{-4} \text{ s}^{-1}$	Pre-equilibrium of complex formation
6	$\text{CuOHOBBr} \rightleftharpoons \text{CuO} + \text{HOBr}$	$1 \times 10^{-3} \text{ s}^{-1}$	Pre-equilibrium of complex formation
7	$\text{CuOOBr} + \text{HOBr} \rightleftharpoons \text{CuOBrO}_2 + \text{Br}^-$	$500 \text{ M}^{-1} \text{ s}^{-1}$	BrO_2^- formation
8	$\text{CuOOBr} + \text{OBr}^- \rightleftharpoons \text{O}_2 + \text{CuO} + 2\text{Br}^-$	$100 \text{ M}^{-1} \text{ s}^{-1}$	O_2 formation
9	$\text{CuOHOBBr} + \text{HOBr} \rightleftharpoons \text{CuOBrO}_2 + \text{Br}^-$	$2 \text{ M}^{-1} \text{ s}^{-1}$	BrO_2^- formation
10	$\text{CuOHOBBr} + \text{OBr}^- \rightleftharpoons \text{O}_2 + \text{CuO} + 2\text{Br}^-$	$1 \text{ M}^{-1} \text{ s}^{-1}$	O_2 formation
11	$\text{CuOHOBBr} + \text{IO}_3^- \rightleftharpoons \text{IO}_4^- + \text{CuO} + \text{Br}^-$	$2000 \text{ M}^{-1} \text{ s}^{-1}$	IO_4^- formation
12	$\text{CuOBrO}_2 + \text{HOBr} \rightleftharpoons \text{CuO} + \text{BrO}_3^- + \text{Br}^-$	$10000 \text{ M}^{-1} \text{ s}^{-1}$	BrO_3^- formation

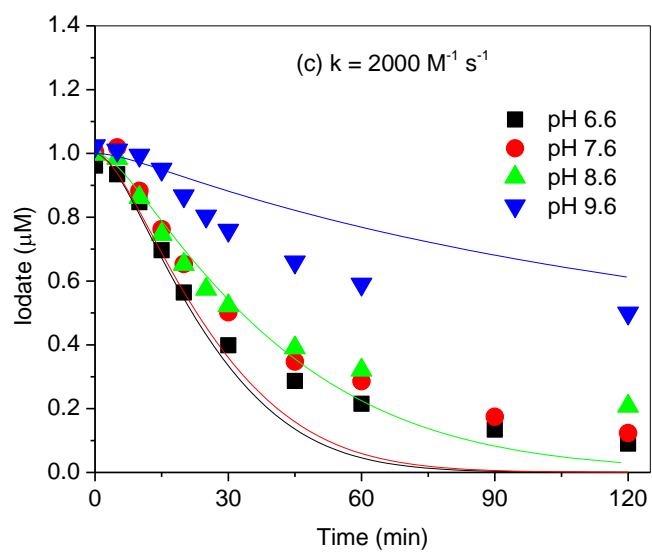
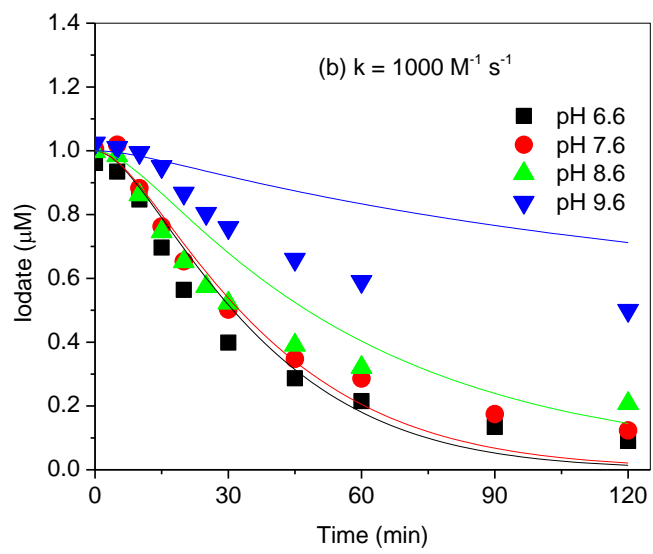
According to our previous model for CuO-enhanced disproportionation of HOBr, the reaction was initiated by a pre-equilibrium step by a complex formation between HOBr/OBr⁻ and CuO.⁹ This initial phase is considered to be the rate-limiting step of the overall catalytic reaction. The steady-state concentration of the CuOOBr/CuOHOBBr species consists of 10% of the initial HOBr/OBr⁻, respectively. Due to the enhanced reactivity of HOBr/OBr⁻ in the presence of CuO, CuOOBr/CuOHOBBr species can react with HOBr/OBr⁻ to produce bromite, and further to bromate in the absence of other coexisting substances. In the presence of iodate, the reaction

between CuO-HOBr and IO_3^- will be important due to a higher rate constant. Based on the proposed model, the approximate extent and kinetics of iodate oxidation could be estimated (Figure S12). Model calculations were performed using the software Kintecus.¹⁰

2. Rate constant sensitivity analyses

In this model, CuO is present in large excess (i.e., the variation of the CuO species distribution with pH was not taken into account). The rate constants for reactions 1-10 and reaction 12 were adopted from our previous study.⁹ For the key step for iodate oxidation (reaction 11), the rate constants were varied from 500 to 5000 $\text{M}^{-1} \text{s}^{-1}$. It can be seen from Figure S14 that an increase of the rate constant for reaction 11 significantly enhances iodate oxidation. It is observed that the model simulation with a rate constant of 2000 $\text{M}^{-1} \text{s}^{-1}$ has the best agreement with the experimental results among these proposed values (Figure S14 c).





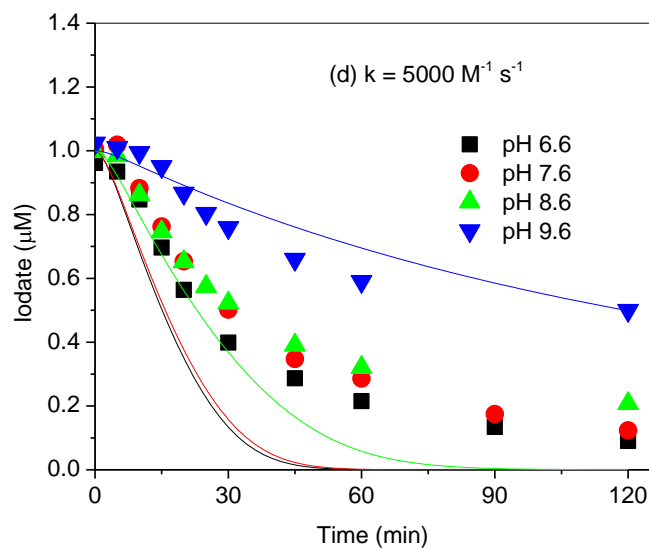


Figure S14. The influence of a rate constant variation of reaction 11 on the oxidation of iodate. Model conditions: $[\text{HOBr}]_0 = 10 \mu\text{M}$, $[\text{IO}_3^-]_0 = 1 \mu\text{M}$, $[\text{CuO}]_0 = 1 \text{ M}$. (lines: model simulations; symbols: experimental data)

3. Limitation of this conceptual model

Even though the oxidation of iodate was successfully reproduced for different pH conditions, the HOBr decay was overestimated, whereas the bromate formation was underestimated. This can be expected because the obtained rate constants represent estimates and can indicate the order of magnitude. Within these limitations, our model can reproduce the experimental system satisfactorily.

References

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