SUPPORTING INFORMATION

Accelerated reduction of bromate in frozen solution

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Three Figures (Figure S1-S3)

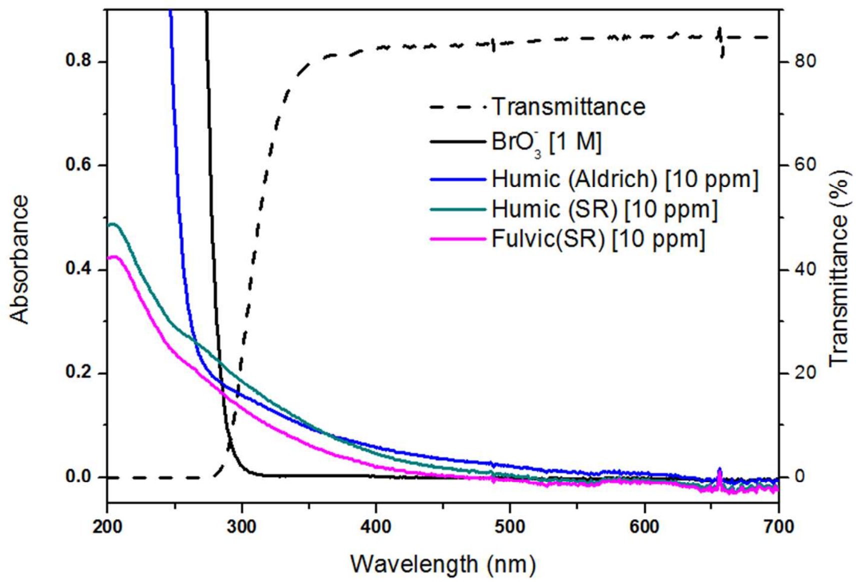

Figure S1. UV-visible absorption spectra of bromate and humic/fulvic acid solutions. Dashed black line is the transmittance of the pyrex filter employed for photo experiments.

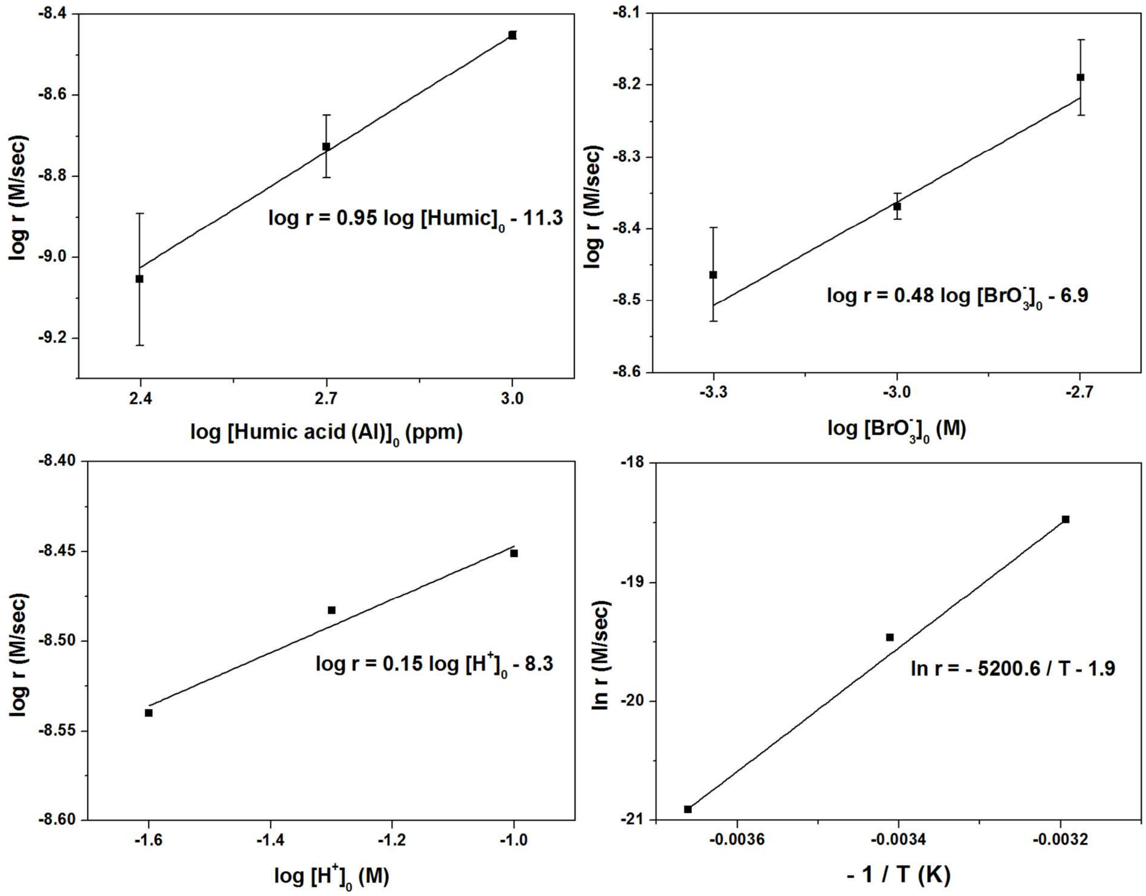

Figure S2. The rate law determination of bromate reduction by humic acid in aqueous solutions. The slope of the plot of (log r) *vs* log [conc] determines the order for each reactant. The order for [humic acid], [BrO_3^-] and [H^+] is determined to be 1, 0.5 and 0.15, respectively. In a similar way, the slope of (ln r) *vs* (-1/T) determines E_a/R value from Arrhenius equation, $k = Ae^{-Ea/(RT)}$. Therefore, the following rate law is derived:

$$-\frac{d[BrO_3^-]}{dt}(mol \cdot L^{-1} \cdot s^{-1}) = r = Ae^{-5200.6/T}\,[Humic\ acid(Al)]^1[BrO_3^-]^{0.5}[H^+]^{0.15} \quad \textbf{(eq S1)}$$

$$A = 8.52(\pm 1.39) \times 10^{-3}\ [mol^{0.35} \cdot L^{-0.35} \cdot ppm^{-1} \cdot s^{-1}]$$

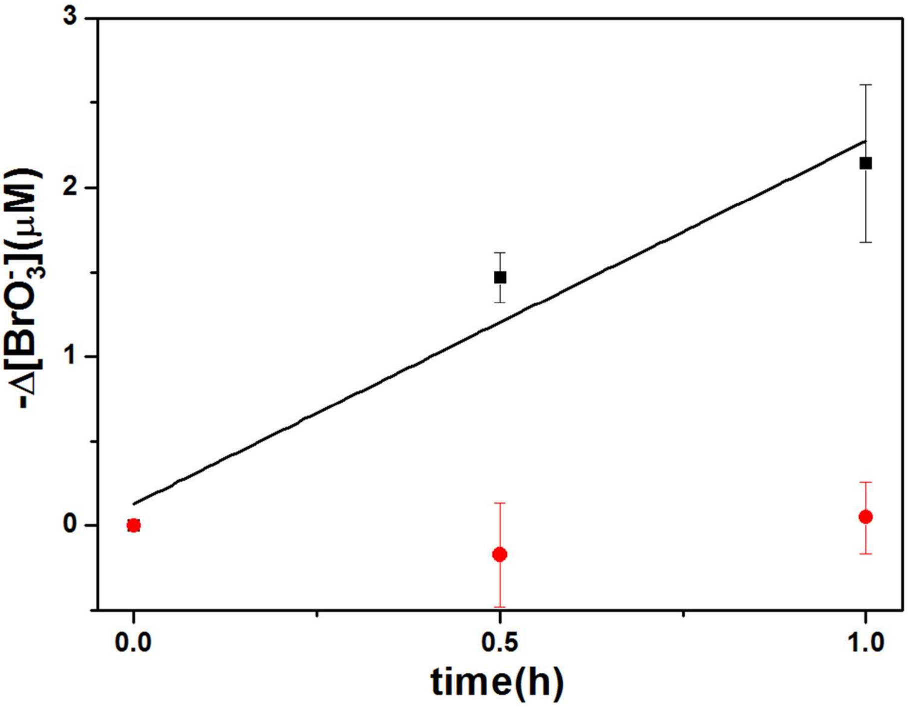

Figure S3. Initial rate determination of bromate reduction by humic acid in ice. 0.5 wt% glycerol was added to control the liquid content in the frozen solution. According to a previous study,[43] a frozen solution of 0.5 wt% glycerol at 251.2 K should contain the liquid fraction of 0.01 (*i.e.,* solutes concentrated by 100 times). Therefore, it was assumed that the concentrations of humic, bromate and proton are enhanced 100 times in the liquid phase in ice. The control experiment without humic acid induced a negligible bromate reduction (red circle), which indicates that the presence of glycerol does not affect the bromate reduction process in ice. Experimental condition: $[BrO_3^-]_0$ = 100 μM, $[\text{humic acid(Al)}]_0$ = 10 ppm, pH_i = 3.0, $[\text{glycerol}]_0$ = 0.5 wt%, T = 251.2 K

According to **eq S1**, the bromate reduction rate in the glycerol-water ice (based on the assumption that the solute concentrations are enhanced by 100 times in the grain boundary liquid fraction) is calculated to be 6.2×10^{-10} mol·L^{-1}·s^{-1}, which is very close to the experimental value of 6.0×10^{-10} mol·L^{-1}·s^{-1} (shown in **Figure S3**).