Supplementary Information

Implementing a sustainable photochemical step to produce value-added products in flue gas desulfurization

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Supporting Figures and Tables

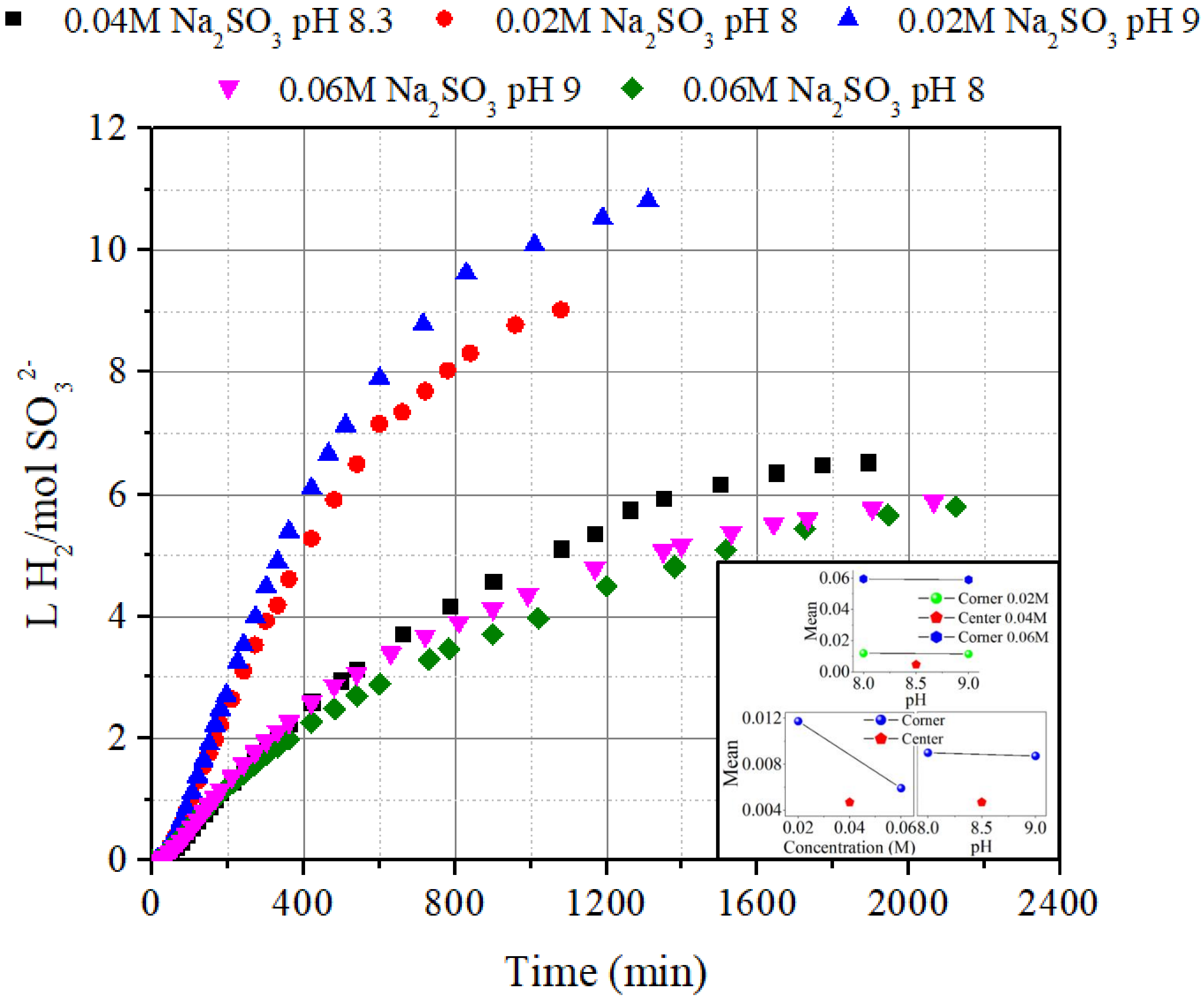

Figure S1. Hydrogen production from batch UV photooxidation of sodium sulfite solutions. Inset, *Top*: Interaction effects plots; and *Bottom*: Main effects plots of Na_2SO_3 concentration (M) and pH for the H_2 production.

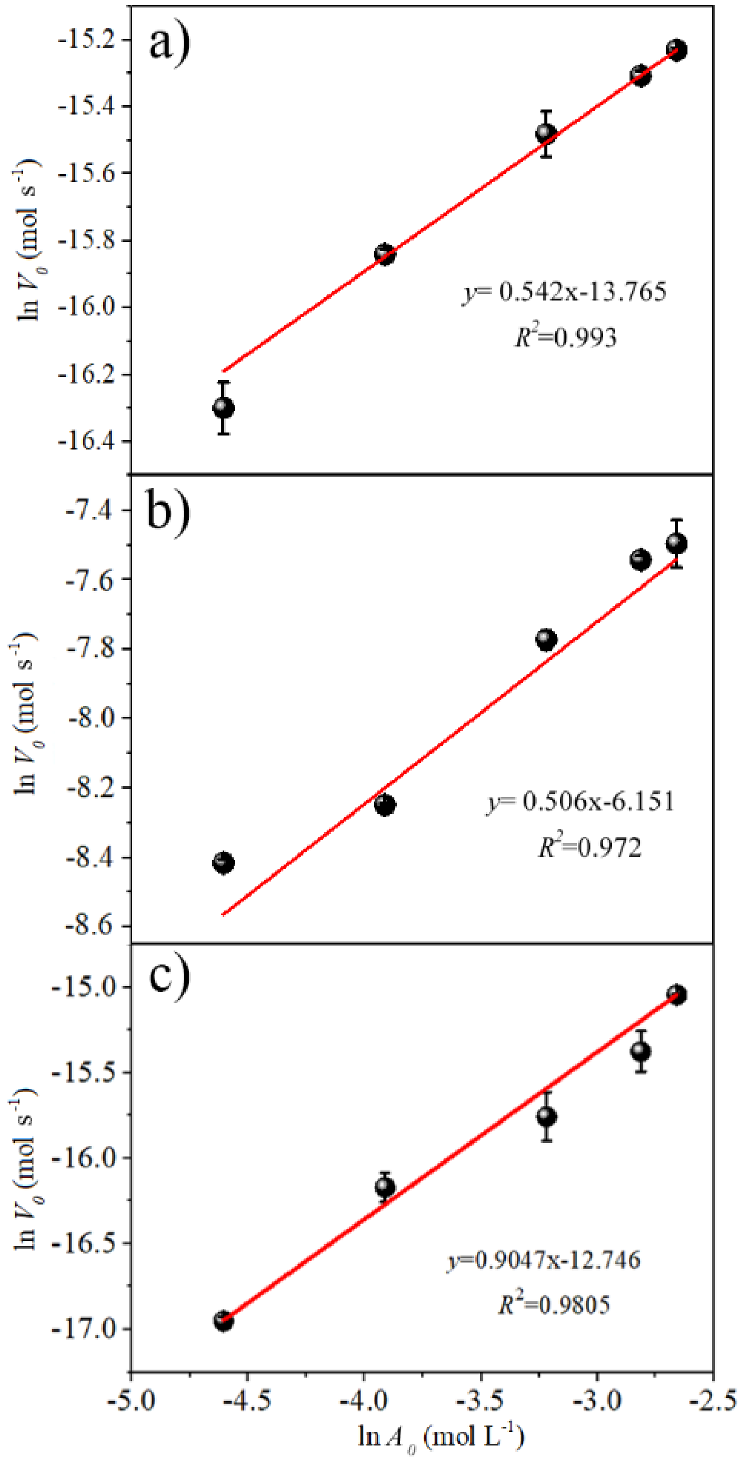

Figure S2. Reaction rate temperature dependence of batch UV photooxidation of sodium sulfite solutions at pH 9 and different initial concentrations. Van´t Hoff’s plots at a) 282.15 K; b) 303.15 K; c) 323.15 K.

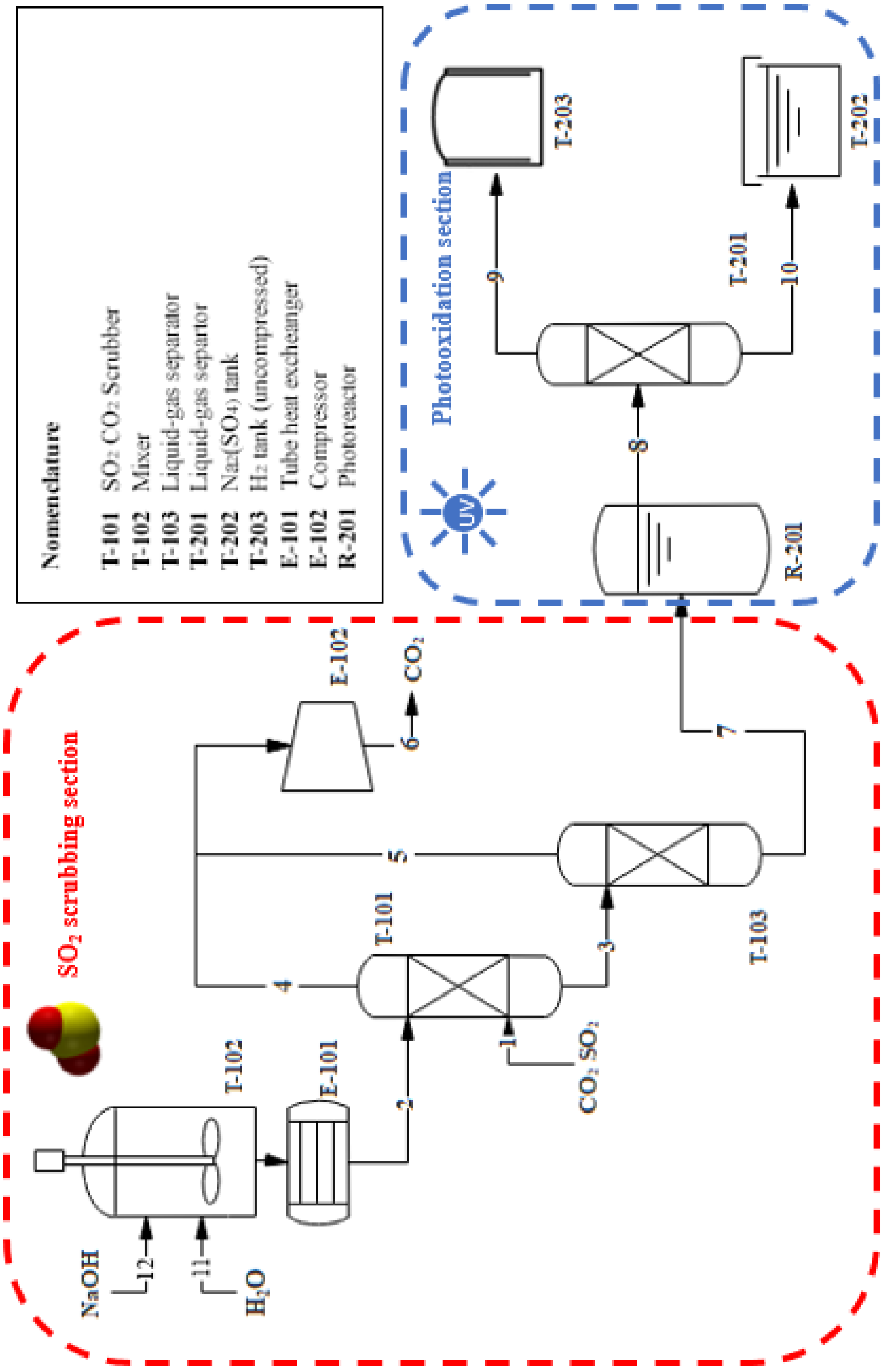

Figure S3. Simulation flowsheet of the NaOH-based SO_2/CO_2 capture process integrating an H_2 photooxidation production unit.

Table S1. Operating conditions for NaOH-based SO_2/CO_2 capture process (FS2/UV).

Towers	**T-101**
Calculation model	RadFrac
Pressure (kPa)	100
Inlet flow rate (L/min)	
Gas	15.00
Liquid	0.15
Inlet temperature (K)	
Gas	333.15
Liquid	298.15
Diameter (m)	0.065
Length (m)	0.900
Packing type	Raschig rings

Pumps/compressors	**E-102**
Discharge pressure (kPa)	100

Reactors	**R-201**
Type	Plug-flow
Temperature (K)	298.15
Pressure (kPa)	100
Diameter (m)	0.250
Length (m)	0.450
Number of tubes	4

Vessels/Tanks	**T-102**	**T-103**	**T-201**
Temperature (K)	298.15	298.15	288.15
Pressure (kPa)	100	100	100

Table S2. Main inlet and outlet stream compounds for the FS2/UV process (mmol/min)

Compounds/ Streams	**Inlets**			**Outlets**		
	11	***12***	***1***	***6***	***9***	***10***
H_2O	8310.3	-	-	14.8	0.1	8376.6
OH^-	-	-	-	-	-	40.4
SO_4^{--}	-	-	-	-	-	2.7
CO_2	-	-	81.3	-	-	-
SO_2	-	-	2.7	-	-	-
H_2	-	-	-	-	2.7	-
Na^+	-	-	-	-	-	208.3
NaOH	-	208.3	-	-	-	-

Detailed Experimental Methods

Photooxidation of NH_4Cl aqueous solution in alkaline media

Preparation of NH_4Cl aqueous solution in alkaline media

The solution was prepared by adding 8.55 g of NH_4Cl (100.1% J.T.Baker®), diluted with deionized water (4.3 µS cm^{-1}) up to 2L, and adjusted the pH 8.3 with a phosphate buffer.

Gas monitoring

Gas evolution in the reactor headspace was measured by a gas chromatograph (Shimadzu Nexis GC-2030) equipped with a barrier discharge ionization detector (GC-BID). All photooxidation experiments reported here were carried out in the same reactor and conditions described within the manuscript. The reactor headspace was sampled at regular intervals (1h) for 9 hours, using an integrated gas autosampler valve connected to the gas chromatograph with an HP plot q column (Agilent®). The reactor was filled with 2 L of the abovementioned solution, thus obtaining 0.9 L of headspace. In the case of the gas mixture of reference containing N_2, O_2, and H_2, this was introduced directly into the injector utilizing a chromatography syringe (0.2 mL) loaded from a gas canister containing the mixture.

Raman spectroscopic measurements

Measurements were carried out in a Raman spectrometer (ProRaman-L Enwave Optronics) equipped with a 785 nm excitation laser. All photooxidation experiments reported here were carried out in the same reactor and conditions described within the manuscript. The aqueous phase within the photoreactor was sampled, taking aliquots of 1 mL at irregular intervals for 30 hours. These aliquots were directly analyzed in the spectrometer averaging 30 acquisitions of 6 s.

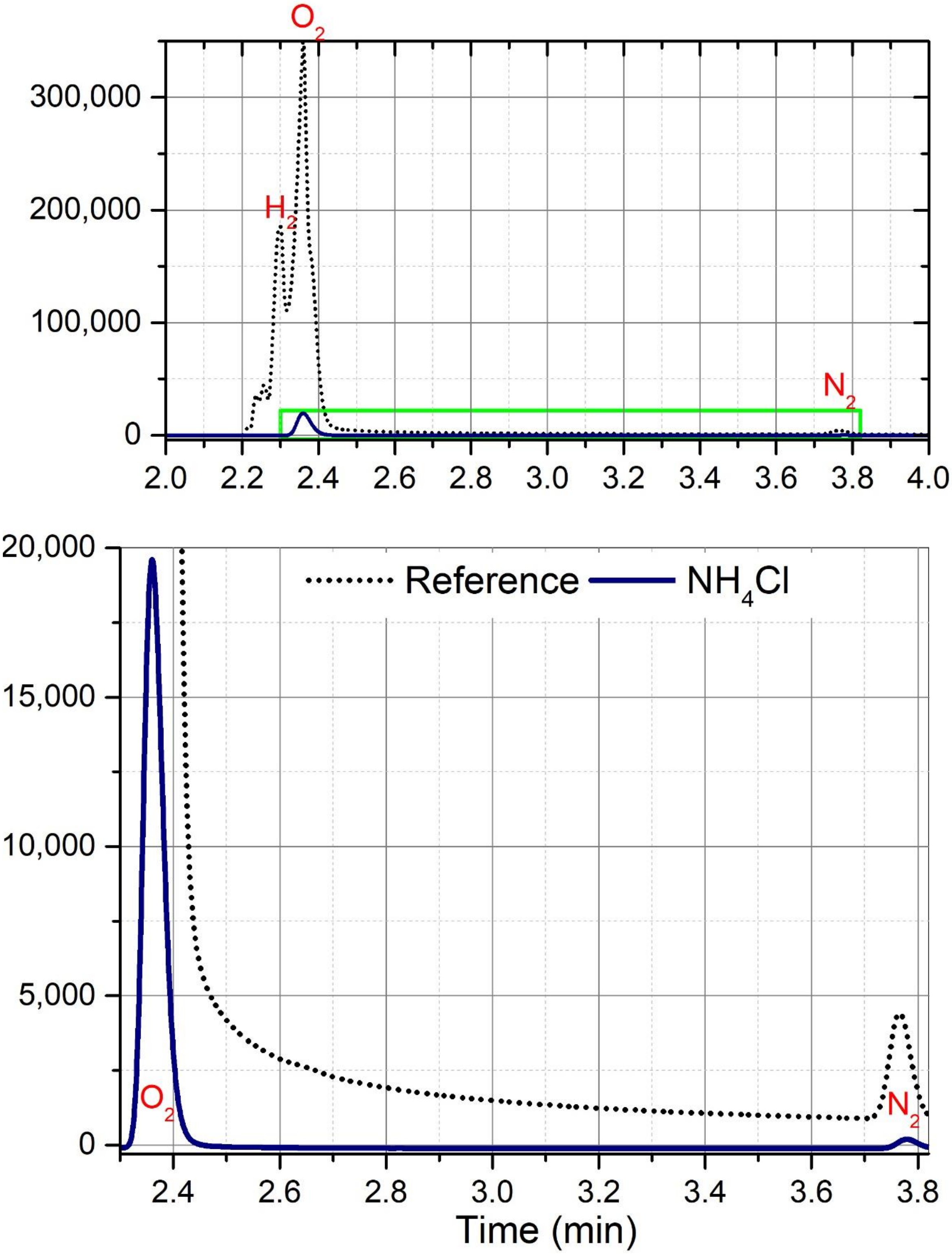

Figure S4. Gas chromatograms of the headspace above an NH_4Cl solution ([0.08M]; initial pH = 8.3) irradiated with a UV light source (254 nm) for 9 hours, compared with a gas mixture of reference containing N_2, O_2, and H_2.

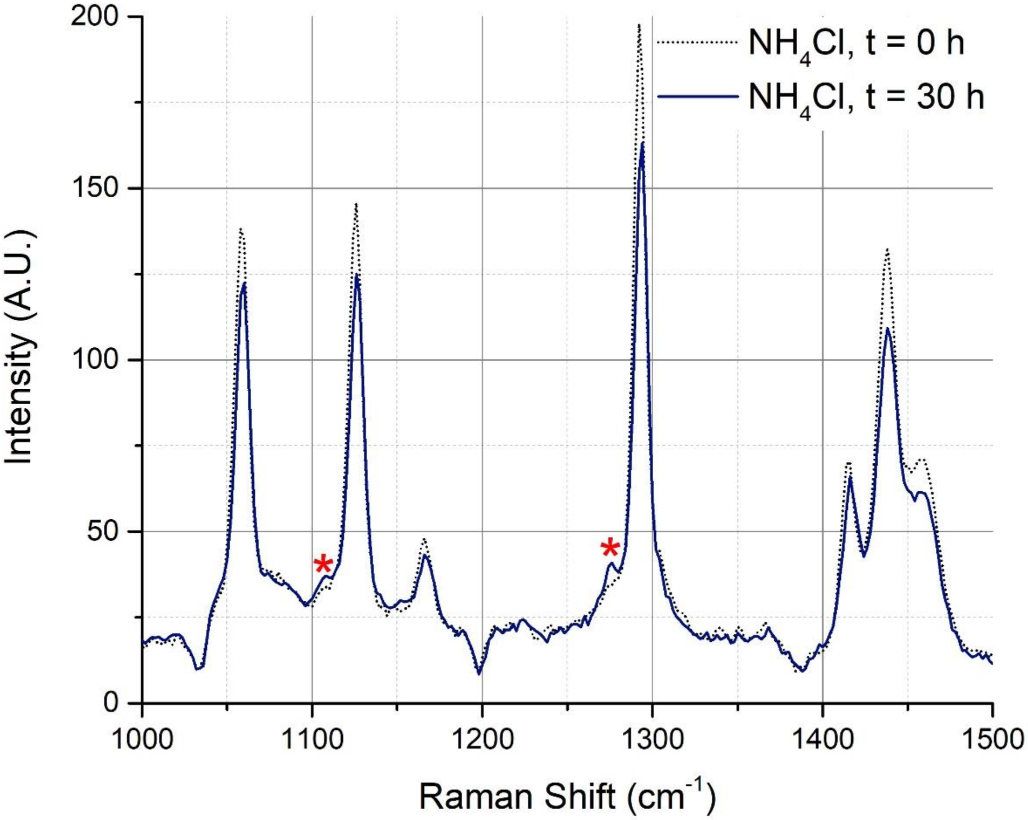

Figure S5. Raman spectra obtained at 785 nm from a NH_4Cl solution ([0.08M]; initial pH = 8.3) before UV irradiation (t = 0 h; black short-dotted line) and after 30 hours of irradiation (t = 30 h; blue line) with a UV light source (254 nm). Red stars denote the appearance of new Raman bands after 30 h, while initial Raman bands weakened because of ammonium photodepletion.

Photooxidation of sulfite aqueous solution in batch and with recirculation

Photooxidation of $(NH_4)_2SO_3$ aqueous solution

Solutions were prepared by adding 10.1 g of $(NH_4)_2SO_3$ (92% Alfa Aesar®), which were diluted with deionized water (4.3 μS cm^{-1}) up to 2 L, and pH was adjusted to 8.3 with a phosphate-based buffer. Each solution was introduced to the photoreactor, and then this was operated in batch mode or a recirculation (8 L h^{-1}) mode for one hour (Figure S6). Initial reaction rates (mL H_2 min^{-1}) were assessed by water displacement within a column during the first 60 minutes, monitoring hydrogen evolution every 15 minutes. These experiments were at least replicated three times for each operating mode.

Photooxidation of Na_2SO_3 aqueous solution

Solutions were prepared by adding 5.14 g of Na_2SO_3 (98% Alfa Aesar®), diluted with deionized water (4.3 μS cm^{-1}) up to 2 L, and adjusted pH 8.0 with a phosphate buffer. Each solution was introduced to the photoreactor, and then this was operated in batch mode or a recirculation (8 L h^{-1}) mode for one hour (Figure S6). Initial reaction rates (mL H_2 min^{-1}) were assessed by water displacement within a column during the first 60 minutes, monitoring hydrogen evolution every 15 minutes. These experiments were at least replicated three times for each operating mode.

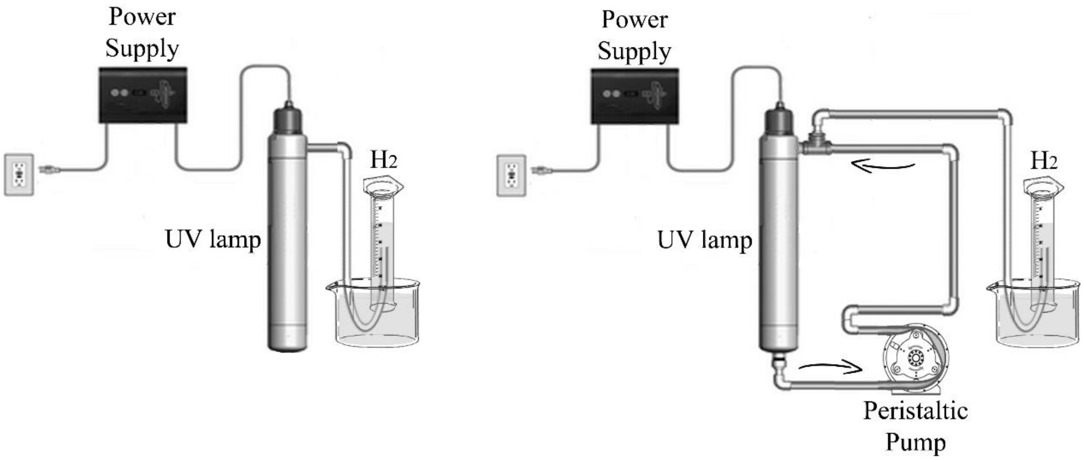

Figure S6. Schematic illustration of operation modes for the photooxidation experiments: *Left*: batch, and *Right*: recirculation

Statistical analysis

The batch and recirculation mode results were statistically compared using the Tukey method with 95% confidence. Figure S7 shows the results obtained for both systems. These interval plots demonstrated that in the case of $(NH_4)_2SO_3$ there is no significant difference in the initial rates obtained in batch and recirculation mode. Therefore kinetic parameters are robust enough to model the chemical behavior. However, that was not the case with Na_2SO_3, where there is a significant difference in the initial rates, showing that kinetic parameters are suitable only to model the photoreactor in batch mode.

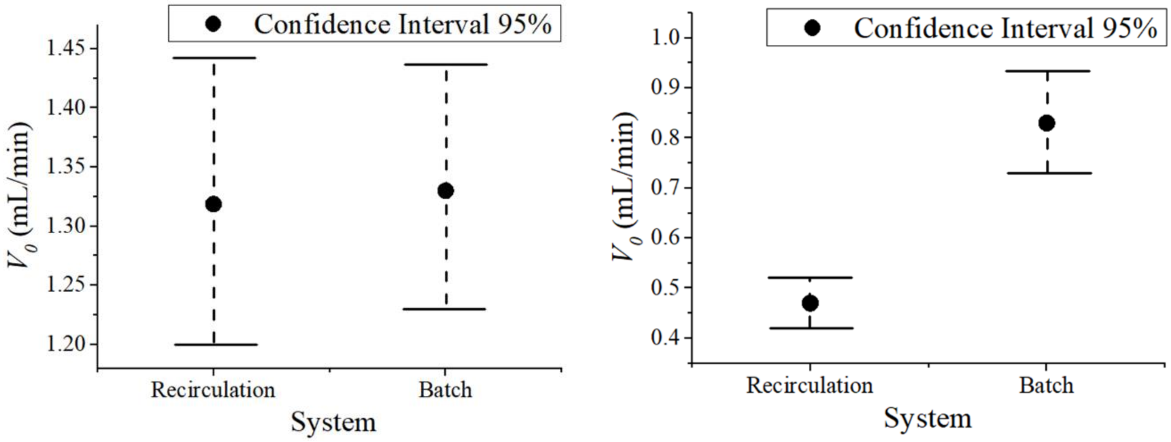

Figure S7. Interval plots of the photooxidation of sulfite aqueous solutions: *Left*: $(NH_4)_2SO_3$, and *Right*: Na_2SO_3.