Supporting materials

S1. Detailed description of the photocatalytic reactor

The photocatalytic reactor used in this study is an annular plug-flow reactor composed of two concentric borosilicate glass tubes. The inner tube supports the photocatalytic medium on its outer surface, while the gaseous effluent flows axially through the annular gap formed between the two tubes. The outer surface of the inner tube was coated with the photocatalytic medium. This support, 250 µm thick, is composed of cellulose fibers coated with 18 g/m² of TiO_2 (Ahlstrom model 1048 – PC 500 Millennium, specific surface area of 350 m²/g, anatase phase, 20 g/m² of SiO_2, and 2 g/m² of zeolites, Ahlstrom, Finland). The photocatalytic surface developed over the active length L_r covered 0.286 m², with a total TiO_2 mass of 5.1 g. Ten sampling ports were distributed along the reactor length to monitor concentration profiles of various species.

The gas flow in the annular photoreactor operates under laminar conditions for all experiments reported in this study. The Reynolds number, calculated using the hydraulic diameter of the annular gap as characteristic length, is approximately 60. Under these conditions, the flow is steady and fully developed.

To assess axial dispersion of NCl_3 inside the reactor, the Peclet number (P) and the axial Peclet number were calculated for the tested flow rate, using its standard expression for tubular flow reactors (错误!未找到引用源。)) (Villermaux, 1993):

$$P = \frac{U_m L_r}{D_m} \quad , \quad \text{(S1)}$$

$$P_a = \frac{U_m d_h}{D^*}$$

where U_m is the mean flow velocity (m/s) Here, D_m is the molecular diffusion coefficient of NCl_3 (9.6×10^{-6} m²/s) (Gérardin et al., 2013). D^* is the axial dispersion coefficient (m²/s), given by the Taylor equation (错误!未找到引用源。)):

$$D^* = D_m + \frac{{U_m}^2 d_h^2}{192 D_m} \quad , \quad \text{(S2)}$$

The axial dispersion coefficient D^* captures the combined effect of molecular diffusion and flow-induced dispersion. Axial dispersion is considered negligible for annular photoreactor with $P \approx 100$ (Villermaux, 1993), which was verified under our conditions.

The velocity distribution is described by 错误!未找到引用源。) with Eqs. (S4) and (S5) (Gérardin et al., 2013):

$$u(r) = \frac{2U_m}{1 + \alpha^2 - \beta}\left[1 - \left(\frac{r}{r_e}\right)^2 + \beta ln\left(\frac{r}{r_e}\right)\right] \quad , \quad \text{(S3)}$$

with

$$\alpha = \frac{r_i}{r_e} \quad , \qquad \text{(S4)}$$

$$\beta = \frac{1-\alpha^2}{2\ln\left(\frac{1}{\alpha}\right)} \quad , \qquad \text{(S5)}$$

S2. Experimental protocol

NCl_3 was generated in a continuous stirred-tank reactor (CSTR), supplied with hypochlorite (12 mol/m³ from a NaClO solution, Merck, 6% of active chlorine, USA) and ammonium sulfate (4×10^{-1} mol/m³, from ammonium sulfate crystals, Sigma-Aldrich, >99.0%, USA) solutions, maintaining a Cl/N ratio of 15. The pH was adjusted to 4 using phosphoric acid (Fluka, 85%, USA) to stabilize trichloramine and favor its formation. About 95% of the NCl_3 formed was stripped to the gas phase using a dry air flow through a column. By-products were removed using a sulfamic acid (Sigma-Aldrich, 98%, USA) trap, so that only trichloramine was carried forward. The resulting air, enriched in NCl_3, was then mixed with humidified air to reach a relative humidity between 50% and 85%.

Gas sampling was carried out at reactor inlet, outlet, and several intermediate positions. Following the method described by Héry et al. (Héry et al., 1995), a two-step system was used: a silica gel cartridge (18-35 mesh, Macherey-Nagel, Germany) coated with sulfamic acid (Sigma-Aldrich, 98%, USA), and a quartz filter (37mm, Merck Millipore, USA) soaked in sodium carbonate (Sigma-Aldrich, 99.99%, USA) and diarsenic trioxide (100 mesh power, 99.99%, Thermo Scientific, USA). Trichloramine was reduced to chlorides ions, which were then quantified by ion chromatography with suppressed conductivity detection. The setup thus allowed separate detection of NCl_3 and other oxidizing chlorine species like hypochlorous acid, dichlorine, monochloramine, and dichloramine.

References

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