Study of Catalytic ozonation for Tetracycline hydrochloride

Degradation in water by silicate ore supported Co₃O₄

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| Name | Tetracycline hydrochloride (TCH) | | | | |
|---------------------------|----------------------------------|---|--|--|--|
| Formula | $C_{22}H_{24}N_2O_8{\cdot}HCl$ | OH O OH O O OH / NH ₂ | | | |
| FW (g mol ⁻¹) | 480.9 | 9 10 11 11a 12 12a 1 | | | |
| $\lambda_{max}(nm)$ | 365 | B C B A • HCl | | | |
| Structure | | 7 H_3C OH $N(CH_3)_2$ OH | | | |

Table S1 Physicochemical property of tetracycline hydrochloride

Table S2 Content of Co element in CoSO and concentration of leached cobalt ions

| Impregnation concentration | Content of Co element in | Concentration of leached cobalt |
|----------------------------|--------------------------|-------------------------------------|
| | CoSO | ions |
| 0.3 mol L ⁻¹ | 6.3% | $0.009 \text{ mg } \mathrm{L}^{-1}$ |
| 0.5 mol L ⁻¹ | 11.2% | $0.014 \text{ mg } \mathrm{L}^{-1}$ |
| 1.0 mol L ⁻¹ | 24.3% | $0.025 \text{ mg } \mathrm{L}^{-1}$ |
| 1.5 mol L ⁻¹ | 30.5% | $0.030 \text{ mg } \mathrm{L}^{-1}$ |

Table S3 First-order rate constants for TCH and TOC removal among different processes.

| Desser | ТСН | | TOC | |
|---------------------|------------------------|----------------|------------------------|----------------|
| Plocess — | k (min ⁻¹) | R ² | k (min ⁻¹) | R ² |
| CoSO/O ₃ | 0.110 ± 0.006 | 0.993 | 0.014 ± 0.001 | 0.992 |
| SO/O ₂ | 0.012 ± 0.001 | 0.986 | 0.002 ± 0.0001 | 0.997 |
| O ₃ | 0.024 ± 0.001 | 0.996 | 0.004 ± 0.0003 | 0.986 |
| CoSO/O ₂ | 0.012 ± 0.001 | 0.989 | 0.002 ± 0.0002 | 0.997 |
| SO/O ₃ | 0.048 ± 0.002 | 0.998 | 0.007 ± 0.0004 | 0.971 |

The uncertainty of rate constants corresponds to 95% confidence level. The total degree of freedom was 9.



Fig. S1. Schematic of experimental apparatus for ozonation. (1, dry air; 2, gas flowmeter; 3, ozone generator; 4, microporous titanium diffuser; 5, ozonation reactor; 6, sampling point; 7, magnetic stirrer; 8, KI trap; 9, constant temperature water bath; 10, cryostat).



Fig. S2 Ozone concentration in ultra-pure water under experimental conditions



Fig. S3. Effect of impregnation concentration on ozonation of TCH with CoSO.

pH = 7.0; initial TCH = 30 mg L^{-1} ; T = 20 °C; gaseous ozone = 1.0 mg L^{-1} ; catalyst = 1.0 g L^{-1} .



Fig. S4 Effect of calcination temperature on ozonation of TCH with CoSO. pH = 7.0; initial TCH = 30 mg L^{-1} ; T = 20 °C; gaseous ozone = 1.0 mg L^{-1} ; catalyst = 1.0 g L^{-1} .



Fig S5. Effect of calcination time on ozonation of TCH with CoSO. pH = 7.0; initial TCH = 30 mg L^{-1} ; T = 20 °C; gaseous ozone = 1.0 mg L^{-1} ; catalyst = 1.0 g L^{-1} .



Fig. S6 SEM images of the samples SO (a) and CoSO (b).



Fig. S7 EDS spectrum of (a) SO, (b) CoSO, and (c)-(f) elemental mapping of the CoSO catalyst .



Fig. S8. Zeta potential of CoSO.



Fig. S9 Influence of TBA on catalytic ozonation of TCH. Initial pH = 7.0; initial TCH = 30 mg L^{-1} ; T = 20 °C; gaseous ozone = 1.0 mg L^{-1} ; catalyst = 1.0 g L^{-1} .



Fig. S10. Degradation efficiency of TCH in the presence of hydrogen peroxide. Initial pH = 7.0; initial TCH = 30 mg L⁻¹; T = 20 °C; gaseous ozone = 1.0 mg L⁻¹; catalyst = 1.0 g L⁻¹. $H_2O_2 = 10$ µmol L⁻¹