Study of Catalytic ozonation for Tetracycline hydrochloride Degradation in water by silicate ore supported Co$_3$O$_4$

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Table S1 Physicochemical property of tetracycline hydrochloride

| Name | Tetracycline hydrochloride (TCH) |
|------|---------------------------------|
| Formula | C_{22}H_{24}N_{2}O_{8}·HCl |
| FW (g mol$^{-1}$) | 480.9 |
| $\lambda_{\text{max}}$ (nm) | 365 |

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

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

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

| Process       | TCH                        | TOC                        |
|---------------|----------------------------|----------------------------|
|               | $k$ (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$_2$O$_2$ = 10 μmol L$^{-1}$