

Supplementary material

Photochlorination of aniline in Fe³⁺-containing saline water under simulated solar light irradiation

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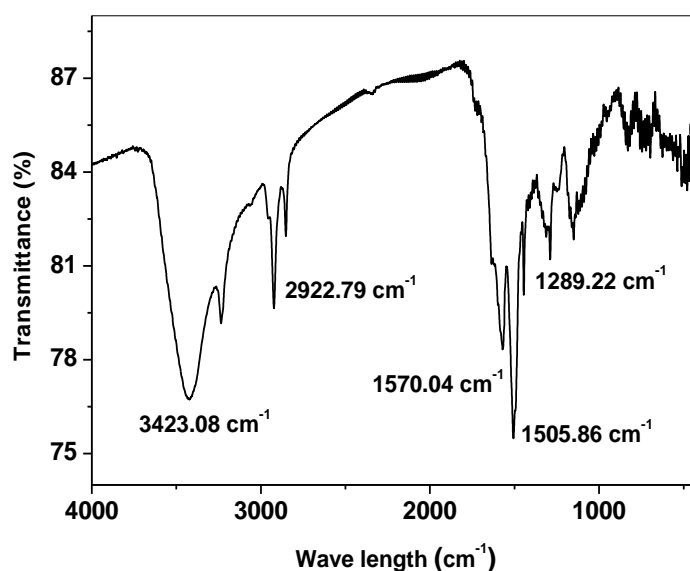


Fig. S1. FTIR spectrum of dark water-insoluble substance formed in the presence of 1.0-mM aniline, 0.5 mM FeCl₃ and 0.2 M NaCl, at pH 2.45 adjusted by HClO₄.

The FTIR spectrum of the dark substance, which is water-insoluble, formed in the irradiated experiment, was given in Fig. S1. The signals observed show good agreements with previous reports on polyaniline.^[1-3] The broad band at 3423.08 cm⁻¹ is due to the single-bridge polymeric association or to N-H stretching vibrations; 2922.79 cm⁻¹ is due to =C-H of aromatic ring stretching. The bands at 1570.40 and 1505.86 cm⁻¹ are respectively attributed to quinonoid and benzenoid ring stretching vibrations. The peak of 1289.22 cm⁻¹ is assigned to C-N stretching of secondary aromatic amine.

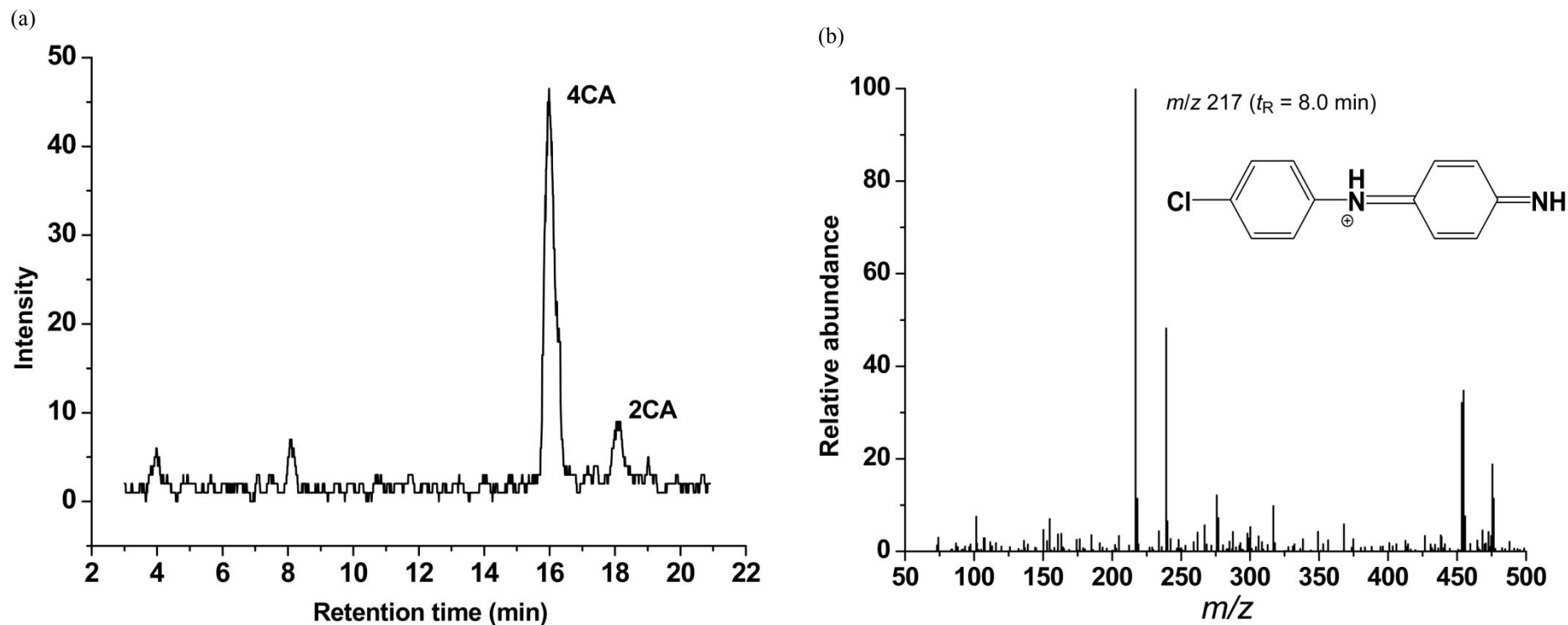


Fig. S2. (a) Selected ion monitoring of chlorinated aniline, 4CA and 2CA. (b, c) Proposed structures and mass spectra of the phototransformation products of 4CA. They are obtained from HPLC-MS detection of the solution after the solid phase extraction, in the presence of 1-mM aniline, 0.5 mM FeCl₃ and 0.2 M NaCl, at pH 2.45 after 4-h irradiation.

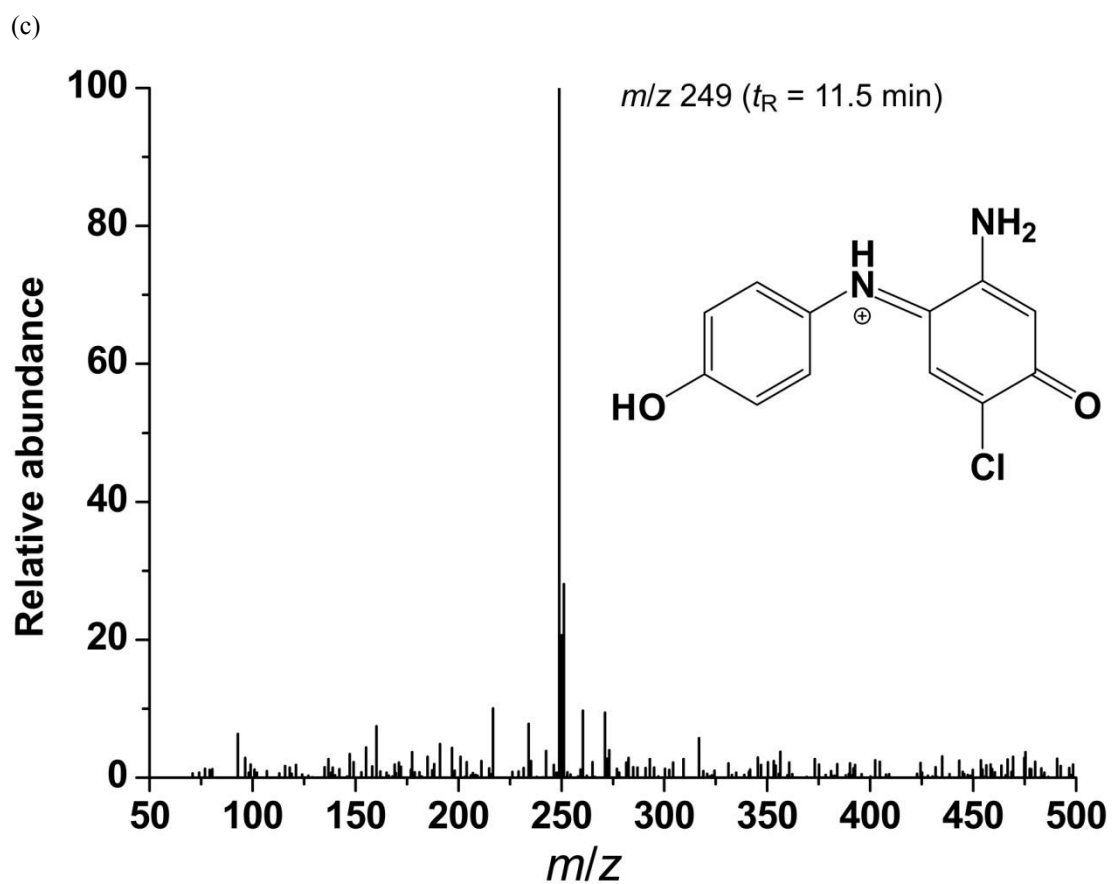


Fig. S2. (Cont.)

Calculation methods of Fe species distribution

The calculation method of the fractions of Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, FeCl^{2+} and FeCl_2^+ in Fig.4a is as follows.

The corresponding stability constants^[4] are as follows (a = activity):

$$K_{\text{FeCl}} = a(\text{FeCl}^{2+})a(\text{Fe}^{3+})^{-1} a(\text{Cl}^-)^{-1} = 30.2 \quad (1)$$

$$K_{\text{FeOH}} = a(\text{FeOH}^{2+}) a(\text{Fe}^{3+})^{-1} a(\text{OH}^-)^{-1} = 3.47 \times 10^{11} \quad (2)$$

$$K_{\text{FeCl}_2} = a(\text{FeCl}_2^+) a(\text{FeCl}^{2+})^{-1} a(\text{Cl}^-)^{-1} = 4.47 \quad (3)$$

$$K_{\text{FeCl}_3} = a(\text{FeCl}_3) a(\text{FeCl}_2^+)^{-1} a(\text{Cl}^-)^{-1} = 0.10 \quad (4)$$

According to the Law of mass conservation, we could get the equation:

$$a(\text{Total}) = a(\text{Fe}^{3+}) + a(\text{FeCl}^{2+}) + a(\text{FeCl}_2^+) + a(\text{FeCl}_3) + a(\text{FeOH}^{2+}) \quad (5)$$

From the five formulas above, it can be deduced:

$$a(\text{Total}) = a(\text{Fe}^{3+}) \times \{1 + K_{\text{FeCl}} \times [\text{Cl}^-] + K_{\text{FeCl}} \times K_{\text{FeCl}_2} \times [\text{Cl}^-]^2 + K_{\text{FeCl}} \times K_{\text{FeCl}_2} \times K_{\text{FeCl}_3} \times [\text{Cl}^-]^3 + K_{\text{FeOH}} \times [\text{OH}^-]\} \quad (6)$$

As a result, the proportion of each iron complex is obtained from the equations above. (In the aqueous solutions, the concentrations of the ligands ($[\text{Cl}^-]$ and $[\text{OH}^-]$) interfere with the distribution of ion complexes, while the total amount of FeCl_3 added does not.)

References

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