Supplementary Material

Adsorption of Tetracycline on Fe (Hydr)oxides: Effects of pH and Metal Cation (Cu^{2+}, Zn^{2+}, and Al^{3+}) Addition in Various Molar Ratios

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Preparation and characterizations of Fe (hydr)oxides

The suspensions of goethite and ferrihydrite were dialyzed until the electric conductivity was < 50 \( \mu \)S/cm\(^{-1} \). Final stock suspensions in 0.01M NaCl background were stored at 4 °C for a maximum of two weeks.

The X-ray powder diffraction analysis was conducted using the PANalytical X'Pert Pro MRD instrument with a step of 0.017° in a 2\( \Theta \) range from 15° to 90° with the Cu-K\( \alpha \) radiation (\( \lambda = 1.5406 \) nm, 40 kV, 40 mA). The point of zero charge was determined using the pH drift method [1]. The average particle sizes were measured by dynamic light scattering (Malvern/Nano-ZS, USA), and the specific surface areas were determined by N\(_2\)-BET method.

TC Adsorption on Fe (hydr)oxides

To avoid the possible photolysis of TC, the reaction vials were covered with Al foil and placed in a stainless steel chamber during the equilibration. Control experiments conducted at each tested pH in the absence of adsorbents showed that < 1% of TC was lost, implying the negligible photolysis of TC over the course of incubation. All experiments were performed in three replicates.
Figure S1. The molecular structure of tetracycline (TC) and dissociation constants (pKa) of the dominant acidic groups.

Phenolic diketone group, pKa$_2$ = 7.7
Tricarbonylamide group, pKa$_1$ = 3.3
Dimethylamino group, pKa$_3$ = 9.7
Figure S2. The UV/Vis absorption spectroscopy of TC and TC-metal complexes formed at the metal to TC molar ratio of 1 : 1 (each 0.0225 mM) for 24 h.
Figure S3. X-ray diffraction patterns of (a) 2-line ferrihydrite and (b) goethite
Figure S4. Effect of metals on the zeta potential of goethite.
Table S1. Characteristics of the Fe (hydr)oxides used in this study.

| Iron hydroxide         | pH_{PZC} | Particle size (nm) | Surface area (m² g⁻¹) |
|------------------------|----------|--------------------|-----------------------|
| 2-line Ferrihydrite    | 6.3      | 290.3              | 251.8                 |
| Geothite               | 6.5      | 466.5              | 25.0                  |
Table S2. Parameters of Freundlich isotherm model for TC adsorption on ferrihydrite and goethite.

|               | Ferrihydrite |         |         | Goethite |         |         |
|---------------|--------------|---------|---------|----------|---------|---------|
|               | K<sub>f</sub> | 1/n     | R<sup>2</sup> | K<sub>f</sub> | 1/n     | R<sup>2</sup> |
| TC only       |              |         |         |          |         |         |
| pH 3          | 1.202        | 0.222   | 0.991   | 0.141    | 0.400   | 0.980   |
| pH 4          | 2.079        | 0.318   | 0.962   | 0.300    | 0.833   | 0.993   |
| pH 5          | 2.140        | 0.232   | 0.990   | 0.387    | 0.700   | 0.940   |
| pH 6          | 2.763        | 0.288   | 0.983   | 0.759    | 0.855   | 0.991   |
| TC+Cu<sup>2+</sup> |              |         |         |          |         |         |
| pH 3          | 0.947        | 0.194   | 0.955   | 0.958    | 0.945   | 0.964   |
| pH 4          | 1.531        | 0.248   | 0.973   | 1.013    | 0.857   | 0.988   |
| pH 5          | 2.866        | 0.346   | 0.996   | 1.514    | 0.709   | 0.986   |
| pH 6          | 8.116        | 0.418   | 0.993   | 4.113    | 0.766   | 0.987   |
| TC+Zn<sup>2+</sup> |              |         |         |          |         |         |
| pH 3          | 1.111        | 0.227   | 0.973   | 0.208    | 0.688   | 0.868   |
| pH 4          | 1.876        | 0.313   | 0.975   | 0.328    | 0.787   | 0.968   |
| pH 5          | 2.261        | 0.306   | 0.977   | 0.457    | 0.661   | 0.972   |
| pH 6          | 2.839        | 0.282   | 0.957   | 0.999    | 0.820   | 0.986   |
| TC+Al<sup>3+</sup> |              |         |         |          |         |         |
| pH 3          | 1.288        | 0.199   | 0.996   | 2.241    | 1.167   | 0.958   |
| pH 4          | 2.198        | 0.257   | 0.999   | 1.665    | 1.003   | 0.963   |
| pH 5          | 2.400        | 0.265   | 0.957   | 0.751    | 0.704   | 0.956   |
| pH 6          | 1.886        | 0.203   | 0.980   | 1.119    | 0.716   | 0.961   |

Freundlich isotherm equation: q<sub>e</sub> = K<sub>f</sub>C<sub>e</sub>\(^{1/n}\); where q<sub>e</sub> is the amounts of TC adsorption onto Fe (hydr)oxides (mg g<sup>-1</sup>); C<sub>e</sub> = equilibrium concentrations of TC (mmol L<sup>-1</sup>); K<sub>f</sub> = Freundlich isotherm constants (mmol<sup>1-1/n</sup> L<sup>1/n</sup> g<sup>-1</sup>); n = adsorption intensity.
Table S3. Pseudo-second order parameters for TC adsorption on ferrihydrite and goethite at pH 3, 5, and 8.

|            | Ferrihydrite |               | Goethite |               |
|------------|--------------|---------------|----------|---------------|
|            | k            | q<sub>e</sub> | R<sup>2</sup> | k            | q<sub>e</sub> | R<sup>2</sup> |
| pH 3       | 0.691 g mmol<sup>-1</sup> h<sup>-1</sup> | 0.298 mmol g<sup>-1</sup> | 0.902     | 29.25 g mmol<sup>-1</sup> h<sup>-1</sup> | 0.007 mmol g<sup>-1</sup> | 0.900     |
| pH 5       | 2.351 g mmol<sup>-1</sup> h<sup>-1</sup> | 0.392 mmol g<sup>-1</sup> | 0.906     | 47.33 g mmol<sup>-1</sup> h<sup>-1</sup> | 0.032 mmol g<sup>-1</sup> | 0.999     |
| pH 8       | 1.340 g mmol<sup>-1</sup> h<sup>-1</sup> | 0.287 mmol g<sup>-1</sup> | 0.940     | 3.69 g mmol<sup>-1</sup> h<sup>-1</sup> | 0.015 mmol g<sup>-1</sup> | 0.841     |

Pseudo-second-order equation: \( \frac{dq}{dt} = k(q_e-q_t)^2 \), where \( k \) is the rate constant of adsorption; \( q_e \) is the amounts of TC adsorption onto Fe hydr(o)oxides at equilibrium; \( q_t \) is the amounts of TC adsorption onto Fe hydr(o)oxides at any time.
Reference:
[1] C. Sun, J.C. Berg, A review of the different techniques for solid surface acid–base characterization, Adv. Colloid Interface Sci. 105 (2003) 151-175.