

Supporting Information

An Integrated Electrochemical System for Synergistic Cathodic Nitrate Reduction and Anodic Sulfite Oxidation

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S1. Analytical methods for NO₃⁻RR

S1.1 Testing methods for the ions

The ionic testing methods for NO₃⁻RR are same with the reported work.

S1.2 Calculation methods for relevant parameters

The removal efficiency of NO₃⁻-N ($R(\text{NO}_3^--\text{N})$), selectivity of NO₂⁻-N ($S(\text{NO}_2^--\text{N})$), selectivity of NH₄⁺-N ($S(\text{NH}_4^+-\text{N})$), can be calculated using **Eqs. S1-S3**.

$$R(\text{NO}_3^--\text{N}) = \frac{C_0(\text{NO}_3^--\text{N}) - C_t(\text{NO}_3^--\text{N})}{C_0(\text{NO}_3^--\text{N})} \times 100\% \quad (\text{S1})$$

$$S(\text{NO}_2^--\text{N}) = \frac{C_t(\text{NO}_2^--\text{N}) - C_0(\text{NO}_2^--\text{N})}{C_0(\text{NO}_3^--\text{N}) - C_t(\text{NO}_3^--\text{N})} \times 100\% \quad (\text{S2})$$

$$S(\text{NH}_4^+-\text{N}) = \frac{C_t(\text{NH}_4^+-\text{N}) - C_0(\text{NH}_4^+-\text{N})}{C_0(\text{NO}_3^--\text{N}) - C_t(\text{NO}_3^--\text{N})} \times 100\% \quad (\text{S3})$$

where $C_0(\text{NO}_3^--\text{N})$, $C_0(\text{NO}_2^--\text{N})$ and $C_0(\text{NH}_4^+-\text{N})$ are the initial concentrations of NO₃⁻-N, NO₂⁻-N, and NH₄⁺-N, respectively, $C_t(\text{NO}_3^--\text{N})$, $C_t(\text{NO}_2^--\text{N})$ and $C_t(\text{NH}_4^+-\text{N})$ are the concentrations of NO₃⁻-N, NO₂⁻-N, and NH₄⁺-N at time t , respectively,

Furthermore, the kinetics was fitted by pseudo-first order model (**Eq. 4**):

$$-\ln \left[\frac{C_t}{C_0} \right] = k_r t + A \quad (\text{S4})$$

where k_r and A are fitting constants.

S2. Analytical methods for SOR

S2.1 Testing methods for the SO₃²⁻

The SO₃²⁻ concentration was detected using the iodometric method (HG/T 2784-2012), which involved the following procedure:

(1) 5 mL of iodine standard solution was taken in an iodine flask and the volume

was marked as V_1 . Then, 1 mL of the test solution containing SO_3^{2-} was added and mixed well;

(2) $\text{Na}_2\text{S}_2\text{O}_3$ solution was used to titrate the solution until it turned pale yellow, and then 2 mL of starch solution was added;

(3) The titration was continued with $\text{Na}_2\text{S}_2\text{O}_3$ solution until the blue color just faded away, and the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution consumed was recorded as V_2 ;

(4) A blank experiment was performed without the addition of the test solution containing sulfite ions, and the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution consumed was recorded as V_0 .

S2.2 Calculation methods for relevant parameters

The concentration of SO_3^{2-} ($C(\text{SO}_3^{2-})$) and the oxidation rate ($O(\text{SO}_3^{2-})$) were calculated using **Eqs. S5-S6**.

$$C(\text{SO}_3^{2-}\text{-S}) = \frac{16 \times (V_0 - V_2) \times C_{\text{Na}_2\text{S}_2\text{O}_3}}{V_1} \quad (\text{S5})$$

$$O(\text{SO}_3^{2-}\text{-S}) = \frac{C_0(\text{SO}_3^{2-}\text{-S}) - C_t(\text{SO}_3^{2-}\text{-S})}{C_0(\text{SO}_3^{2-}\text{-S})} \quad (\text{S6})$$

where $C_0(\text{SO}_3^{2-})$ and $C_t(\text{SO}_3^{2-})$ are the concentrations of $\text{SO}_3^{2-}\text{-S}$ at time 0 and t , respectively, $C_{\text{Na}_2\text{S}_2\text{O}_3}$ represents the concentration of added $\text{Na}_2\text{S}_2\text{O}_3$ solution. The kinetics was also fitted by pseudo-first order model (k_o and B are fitting constants).

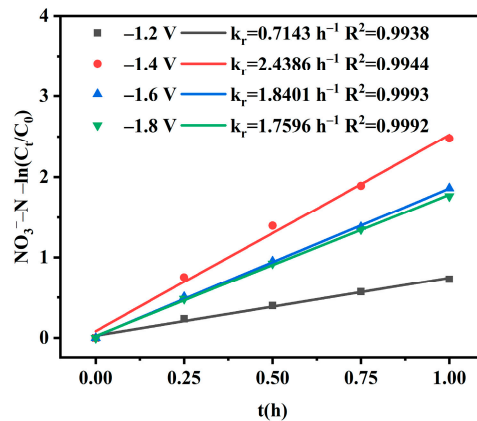


Figure S1. Fitting results of pseudo-first-order kinetic model for single electrochemical reduction of nitrate at different potentials.

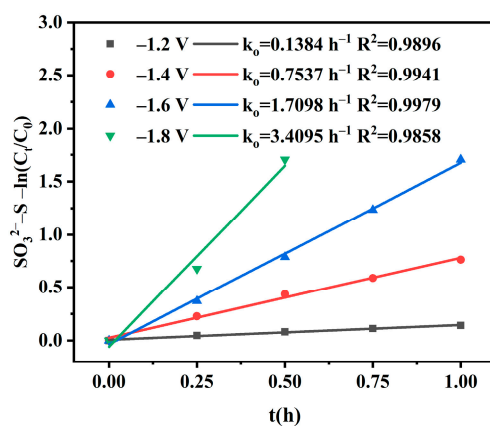


Figure S2. Fitting results of pseudo-first-order kinetic model for single electrochemical oxidation of sulfite at different potentials.

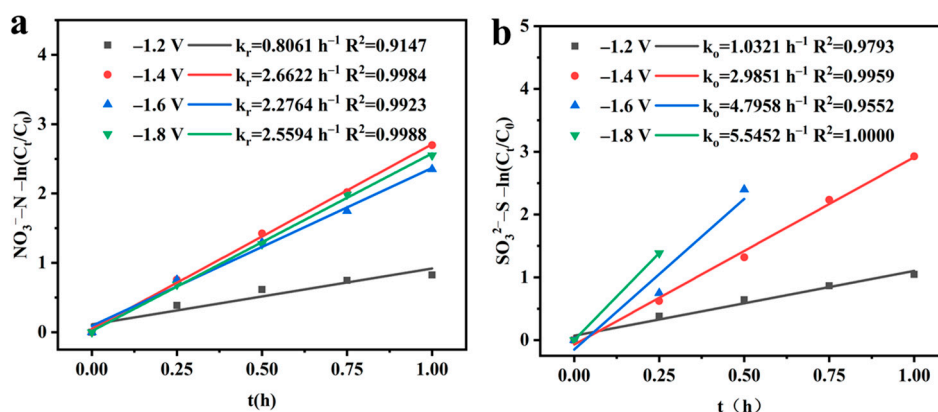


Figure S3. Fitting results of pseudo-first-order kinetic model for integrated electrochemical system at different potentials; (a) nitrate reduction reaction; (b) sulfite oxidation reaction.

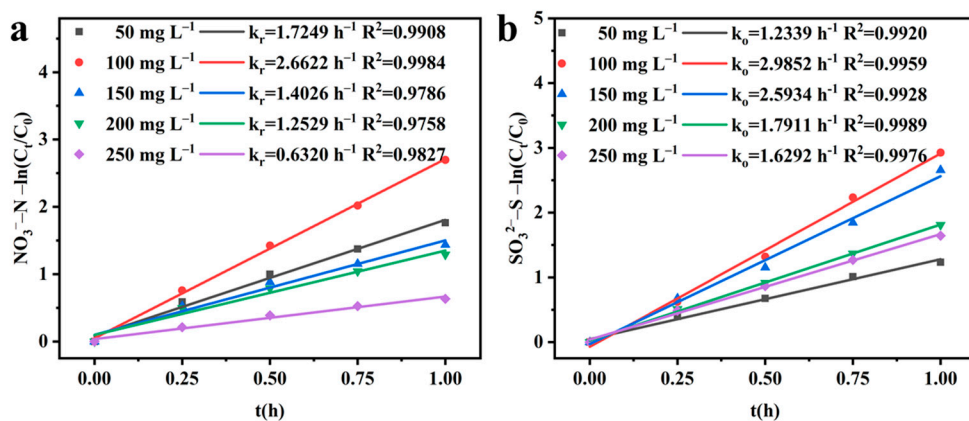


Figure S4. Fitting results of pseudo-first-order kinetic model for integrated electrochemical system at different initial $\text{NO}_3^- - \text{N}$ concentrations; (a) nitrate reduction reaction; (b) sulfite oxidation reaction.

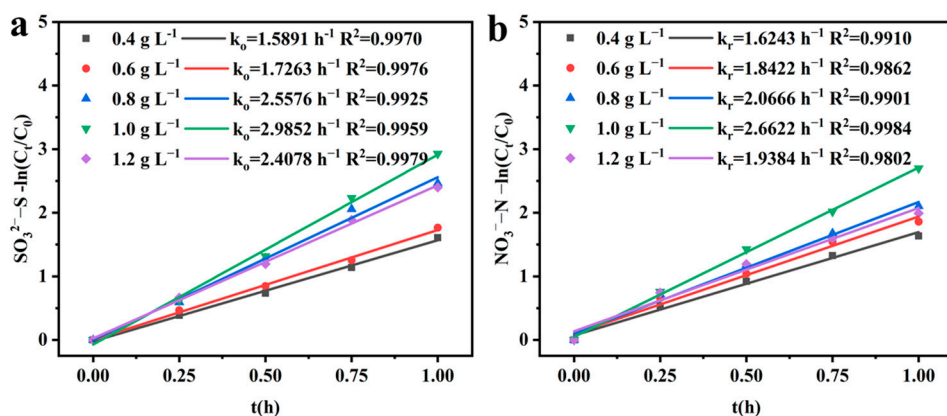


Figure S5. Fitting results of pseudo-first-order kinetic model for integrated electrochemical system at different initial $\text{SO}_3^{2-} - \text{S}$ concentrations; (a) sulfite oxidation reaction; (b) nitrate reduction reaction.