Supporting information for

Practical Considerations for the Electrochemical Denitrification of Real Wastewater

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Text S1 Reagents and calculations

Reagents

$K_2Cr_2O_7$, H_2SO_4, KNO_3, $Na_3PO_4{\cdot}12H_2O$, Na_2CO_3, $CaCl_2$, Nessler reagent and N-(1-naphthyl)ethylenediamine dihydrochloride were purchased from Sinopharm Chemical Reagent Co., Ltd. Na_2SO_4 and NaCl were purchased from Shanghai Titan Scientific Co., Ltd. $K_2S_2O_8$ was purchased from Thermo Fisher Scientific (China) Co., Ltd.

Calculations of efficiency and energy consumption [1]

The NO_3^--N removal rate ($R(NO_3^-\text{-}N)$), NO_2^--N generation rate ($S(NO_2^-\text{-}N)$), NH_4^+-N generation rate ($S(NH_4^+\text{-}N)$) and TN removal efficiency (R(TN)) were calculated by the following equations,

$$R(NO_3^-\text{-}N) = [\ (C(NO_3^-\text{-}N)_0 - C(NO_3^-\text{-}N)_t) / C(NO_3^-\text{-}N)_0\ ] \times 100\% \quad (S1)$$

$$S(NO_2^-\text{-}N) = [\ C(NO_2^-\text{-}N)_t / C(NO_3^-\text{-}N)_0\ ] \times 100\% \quad (S2)$$

$$S(NH_4^+\text{-}N) = [\ C(NH_4^+\text{-}N)_t / C(NO_3^-\text{-}N)_0\ ] \times 100\% \quad (S3)$$

$$R(TN) = [(C(TN)_0 - C(TN)_t) / C(TN)_0\ ] \times 100\% \quad (S4)$$

$$dC(NO_3^-\text{-}N)_t/dt = -kC(NO_3^-\text{-}N)_t \quad (S5)$$

where $C(TN)_0$ and $C(NO_3^-\text{-}N)_0$ (mg/L) are the initial concentration of NO_3^--N, $C(NO_3^-\text{-}N)_t$, $C(NO_2^-\text{-}N)_t$ and $C(NH_4^+\text{-}N)_t$ (mg/L) are the concentrations of NO_3^--N, NO_2^--N and NH_4^+-N at time t, k (min^{-1}) is the pseudo-first-order reaction rate constant.

Electro energy utilization efficiency (φ) of the reaction products (NH_4^+-N, NO_2^--N and N_2) is determined by the expression,

$$\varphi = [(Q(NO_2^-\text{-}N)_t + Q(N_2\text{-}N)_t + Q(NH_4^+\text{-}N)_t)]/Q_t \times 100\% \quad (S6)$$

$$Q_t = JSt/1000 \quad (S7)$$

$$Q(NO_2^-\text{-}N)_t = 2 \times [C(NO_2^-\text{-}N)_t \times V/M_N] \times F \quad (S8)$$

$$Q(N_2\text{-}N)_t = 5 \times [(C(NO_3^-\text{-}N)_0 - C(NO_3^-\text{-}N)_t - C(NO_2^-\text{-}N)_t - C(NH_4^+\text{-}N)_t) \times V/M_N] \times F \quad (S9)$$

$$Q(NH_4^+\text{-}N)_t = 8 \times [C(NH_4^+\text{-}N)_t \times V/M_N] \times F \quad (S10)$$

Q_t (C) is the total electric quantity that provide at time t (s); J (mA/cm^2) is the current density; S (cm^2) is the area of cathode; $Q(NO_2^-\text{-}N)_t$, $Q(N_2\text{-}N)_t$ and $Q(NH_4^+\text{-}N)_t$ are the electric quantities that cost during NO_3^--N reduction to NO_2^--N, N_2-N and NH_4^+-N at time t; $C(NO_3^-\text{-}N)_0$ (mg/L) is the initial concentration of NO_3^--N; $C(NO_3^-\text{-}N)_t$, $C(NO_2^-\text{-}N)_t$ and $C(NH_4^+\text{-}N)_t$ (mg/L) are the concentrations of NO_3^--N, NO_2^--N and NH_4^+-N at time t; V is the volume of solution, M_N is the molar mass of N (14000 mg/mol) and F is the Faraday's constant (96487 C/mol)

Energy consumption (φ, kWh/kgTN) is determined by the expression,

$$\varphi = 1000 * IV_{ap}t/[(C(TN)_0 - C(TN)_t)Vr] \quad (S11)$$

I is the current density (A), Vap is applied voltage (V), t is electrolysis time (h), $C(TN)_0$ is the TN concentration (mg/L) and Vr is working cell volume (L).

Calculations of DFT

The DFT calculations were performed with the Vienna ab initio simulation package (VASP).[2] The Perdew−Burke−Ernzerhof functional (PBE) of generalized gradient approximation functional (GGA) was used for the electronic exchange and correlation effects. The adsorption models were simulated in a vacuum layer of 20 Å in the Z-direction. The reciprocal space was sampled by Monkhorst-Pack scheme with 3×3×1 grids. The absorbed models were free to move on all the directions during the calculation process. The energy tolerance of 10^{-5} was set for planes self-consistency

electronic relaxation. All atoms were relaxed fully until the Hellmann-Feynmann force acting on each atom was less than 0.03 eV/Å. To describe the vdw interaction, the dispersion corrections DFT-D2 was employed in this work.

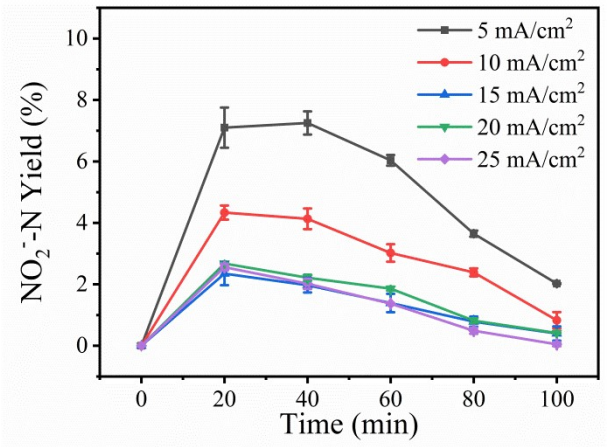

Fig. S1 Effect of the current density on the NO_2^--N.

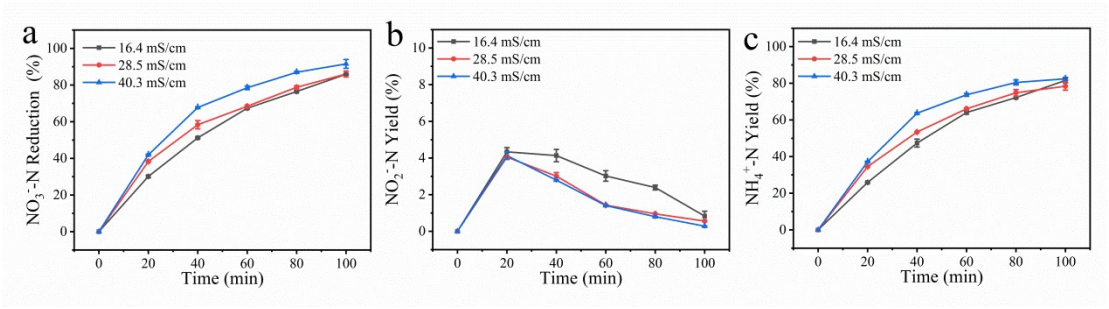

Fig. S2 Effects of the electrical conductivity on the (a) NO_3^--N reduction, (b) NO_2^--N and (c) NH_4^+-N yield.

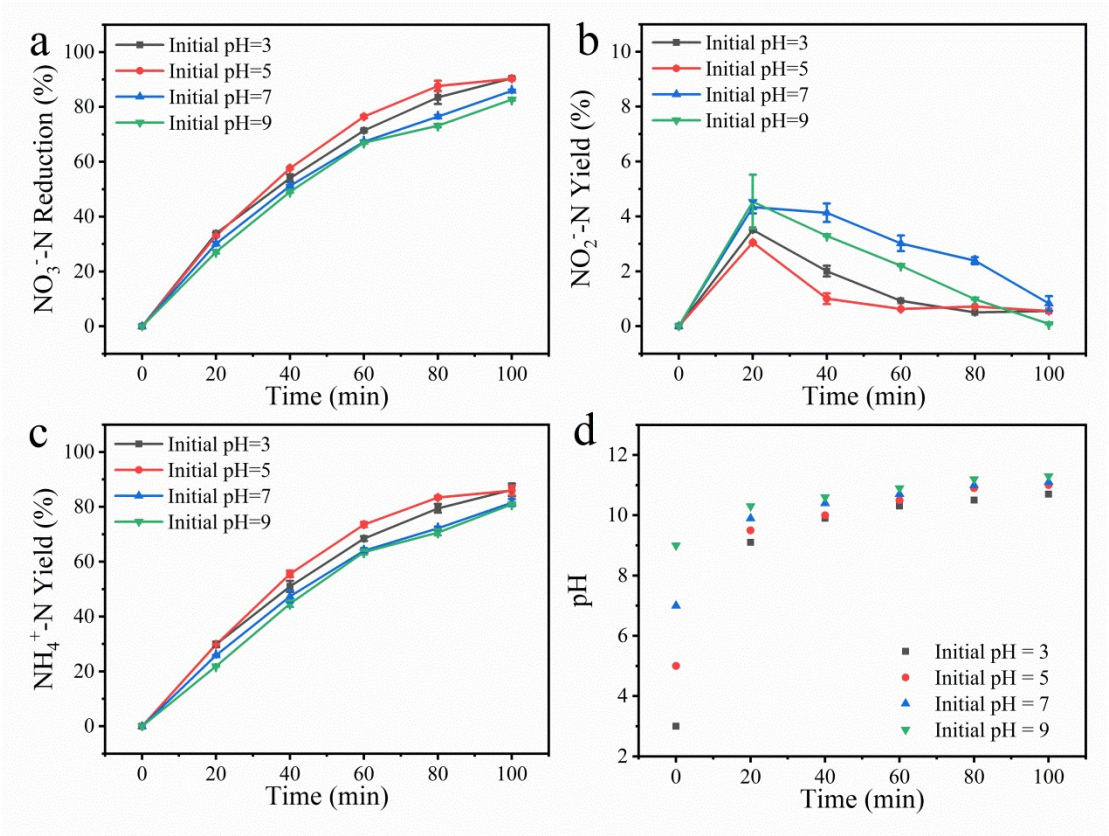

Fig. S3 Effects of initial pH on the (a) NO_3^--N reduction, (b) NO_2^--N and (c) NH_4^+-N yield, and (d) the change in pH throughout the experiments.

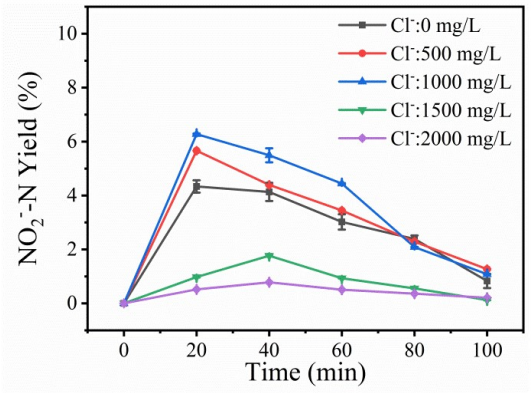

Fig. S4 Effect of Cl^- concentrations on the NO_2^--N.

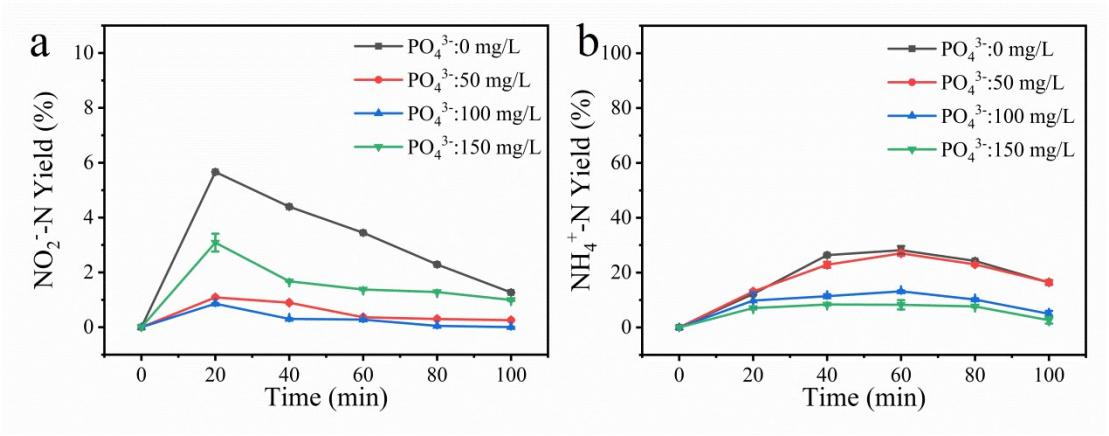

Fig. S5 Effects of the PO_4^{3-} concentration on the (a) NO_2^--N and (b) NH_4^+-N yield.

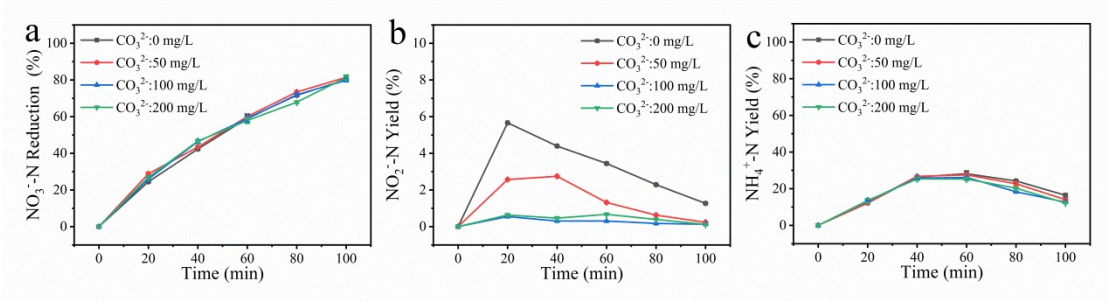

Fig. S6 Effects of the CO_3^{2-} concentration on the (a) NO_3^--N reduction, (b) NO_2^--N yield and (c) NH_4^+-N yield.

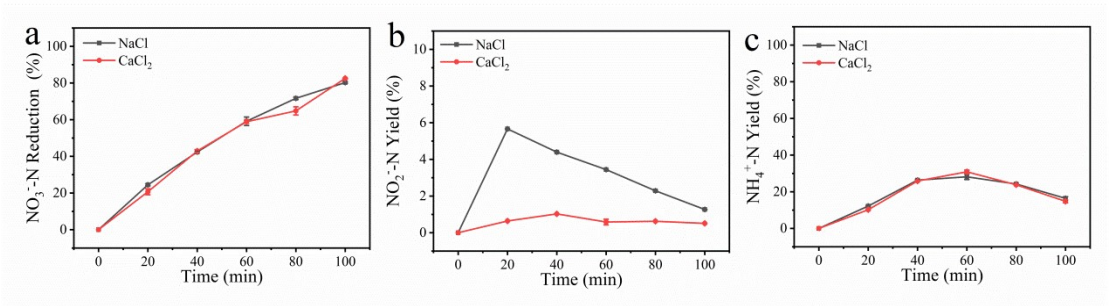

Fig. S7 Effects of Ca^{2+} on the (a) NO_3^--N reduction, (b) NO_2^--N yield and (c) NH_4^+-N yield.

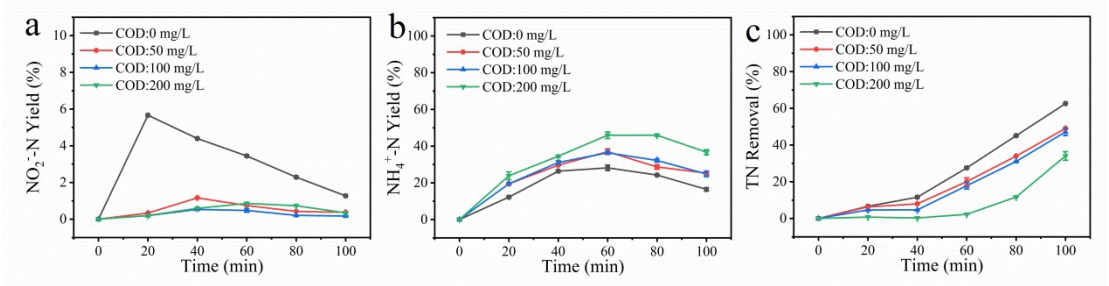

Fig. S8 Effects of COD on the (a) NO_2^--N yield, (b) NH_4^+-N yield and (c) TN removal.

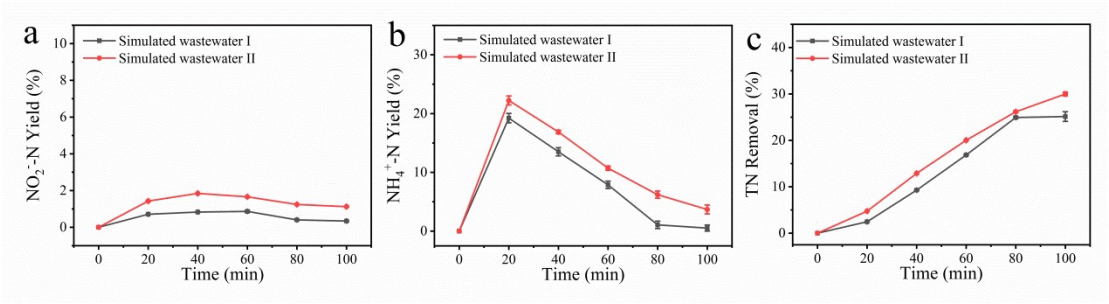

Fig. S9 (a) NO_2^--N yield, (b) NH_4^+-N yield and (c) TN removal of simulated wastewater I and simulated wastewater II

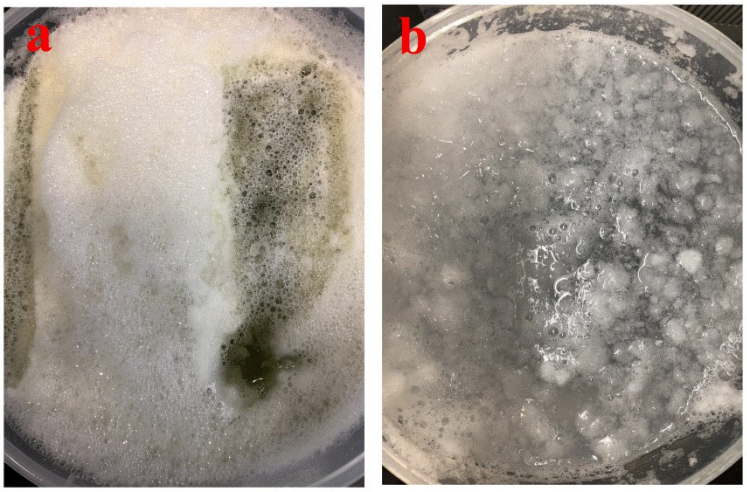

Fig. S10 Water sample (a) during and (b) after reaction.

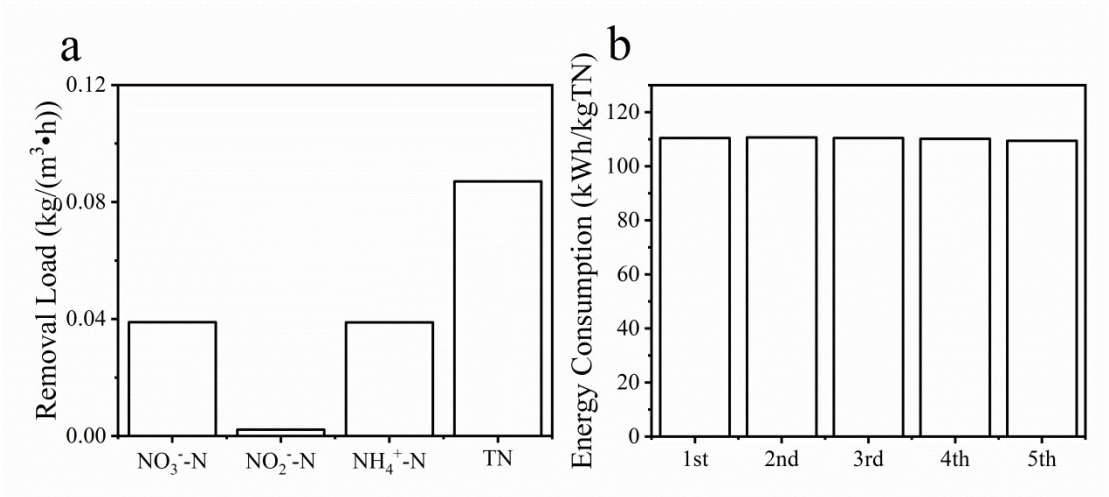

Fig. S11 (a) The removal load of NO_3^--N, NO_2^--N, NH_4^+-N and TN, and (b) the energy consumption in different cycle.

Table. S1. COD of solutions before and after reaction and removal load

Items	COD of solutions		
Before reaction (mg/L)	50	100	200
After reaction (mg/L)	42.9	87.3	185.6
COD removal load (kg/(m^3·h))	4.3×10^{-3}	7.6×10^{-3}	8.6×10^{-3}

Table. S2. Operating cost for real water treatment*

Items	Quantitative estimation	Total cost/$
Ti/IrO_2–RuO_2 anode	39.225 $ × 2 ÷ 1000	0.079
brass cathode	0.925 $ × 2 ÷ 1000	0.002
DC power supply	0.024 kW × 6 h × (1 T ÷ 1.2 g/mL ÷ 2.5 L) × 0.093 $/ (kW·h)	4.464
mechanic stirrer	0.008 kW × 6 h × (1 T ÷ 1.2 g/mL ÷ 2.5 L) × 0.093 $/(kW·h)	1.488

*The density of real wastewater is 1.2 mg/mL. The cell voltage between electrodes was 6.0 V when the current density was 10 mA/cm^2.

TN Removal amount = 564.5 mg/L − 42.3 mg/L = 522.2 mg/L = 522.2 g/T

Total cost of 1 T wastewater =(0.079 $ + 0.002 $ + 4.464 $ +1.488 $) ÷ 522.2 g= 0.012 $/$g_{TN}$

Notes and references

1. L. Su, K. Li, H. Zhang, M. Fan, D. Ying, T. Sun, Y. Wang and J. Jia, Electrochemical nitrate reduction by using a novel Co3O4/Ti cathode, *Water Res*, 2017, **120**, 1-11.
2. G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Physical Review B*, 1996, **54**, 11169-11186.