Supplementary Materials

Text S1 Calculation of ammonia removal contribution

This study classified the removal of ammonia from H-CWs into three pathways. The first pathway is nitrification-denitrification promoted by hematite substrate as confirmed by inhibition culture experiments; the second pathway is Feammox process verified by isotope culture. The third is other pathways such as plant uptake, ammonia evaporation, and so on. Ammonia removal from G-CWs can be considered to be through the third pathway. As described in Text 3.2, $^{30}N_2$ can only be produced via Feammox pathway by adding inhibitors. In contrast, $^{30}N_2$ produced without adding inhibitors was a joint contribution of Feammox and nitrification-denitrification. Therefore, the contribution of Feammox and nitrification-denitrification to ammonia removal can be calculated by the following equations (Eqs. (S1) and (S2)).

$$\text{Feammox contribution rate} = \frac{(H_{ar} - G_{ar}) \times \frac{^{30}N_2(Y)}{^{30}N_2(N)}}{H_{ar}}, \quad \text{(S1)}$$

$$\text{Nitrification-denitrification contribution rate} = \frac{(H_{ar} - G_{ar}) \times (1 - \frac{^{30}N_2(Y)}{^{30}N_2(N)})}{H_{ar}}, \quad \text{(S2)}$$

where

H_{ar} is the H-CW ammonia removal,

G_{ar} is the G-CW ammonia removal,

$^{30}N_2(Y)$ is the $^{30}N_2$ produced with the addition of inhibitors,

$^{30}N_2(N)$ is the $^{30}N_2$ produced without the addition of inhibitors.

Text S2 Quantification of the operational lifespan of hematite in CWs

As per the XPS findings pertaining to the hematite packing, it has been determined that approximately 13.54% of Fe(III) undergoes reduction to Fe(II). Within our investigation, the reduction of hematite is predominantly influenced by three key factors: hydraulic retention time

(HRT), operational duration, and the rate of ammonia removal. Equation (S3) facilitates the transformation of operating periods at varying HRTs into equivalent durations at HRT = 3 days. Furthermore, Eq. S4 facilitates the computation of the operational lifespan of the hematite filler at an HRT of 3 days. The calculation of the operational lifespan of the hematite regrettably fails to account for the intricate dynamics of microbial adaptation and the inherent semiconducting attributes of hematite. Consequently, it is reasonable to surmise that the actual operational lifespan exceeds the calculated outcomes.

$$E_d = \frac{N_i \times R_7 \times \frac{60 + I_d}{7} + N_i \times R_5 \times \frac{60}{5} + N_i \times R_2 \times \frac{60}{2}}{N_i \times R_3 \times \frac{1}{3}} + 60 \quad , \qquad \text{(S3)}$$

$$\text{Operational lifespan} = \frac{\frac{100\%}{13.54\%} \times E_d}{365} \quad , \qquad \text{(S4)}$$

where

E_d is the transformation of operating periods into equivalent durations at HRT = 3 days,

N_i is the NH_4^+-N concentration of 35 mg/L in the influent,

I_d is the incubation days (conservatively estimated at 200 days),

R_7, R_5, R_3, R_2 are the removal rates of NH_4^+-N at HRT of 7 days, 5 days, 3 days, and 2 days.

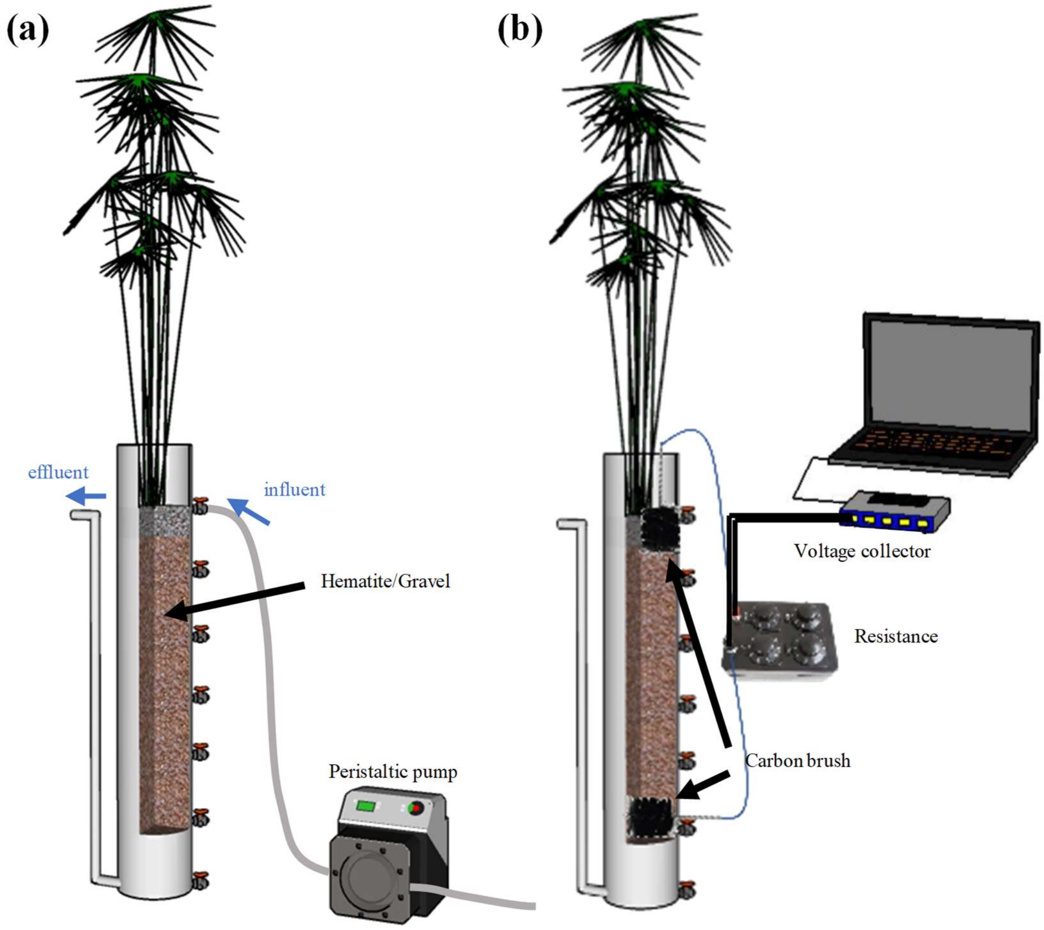

Fig. S1 Constructed wetland unit configuration (a) and hematite constructed wetland microbial fuel cell unit configuration (b).

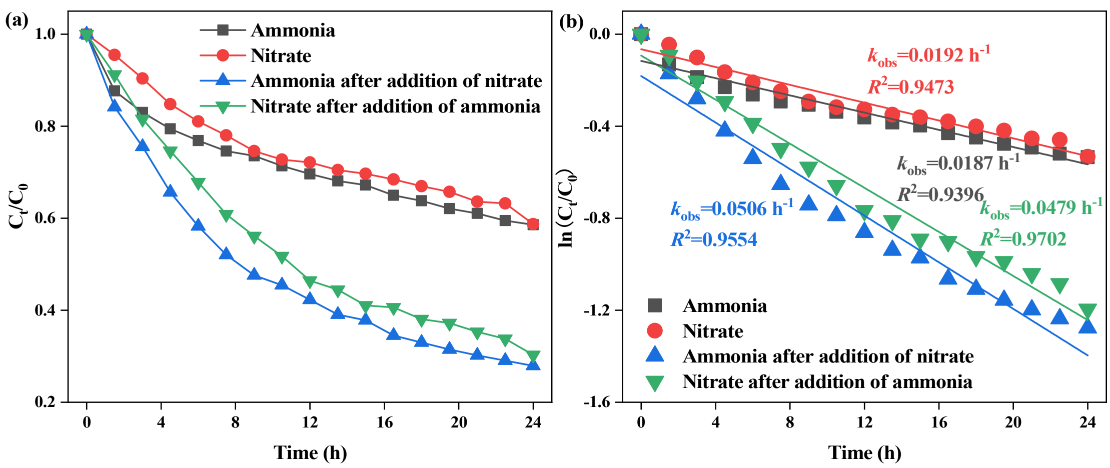

Fig. S2 Ammonia and nitrate removal performance (a) and kinetics (b) of H-CWs. C_0 and C_t represent the pollutant concentrations at time 0 and t, respectively.

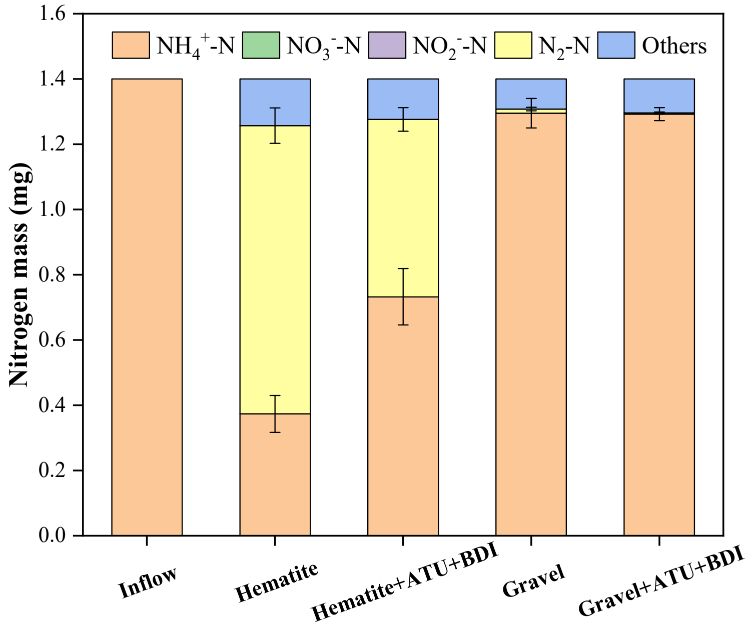

Fig. S3 N mass for hematite substrates and gravel substrates in inhibitor incubations. Others include nitrogen adsorbed by the substrate as well as nitrous oxide and other organic nitrogen formed by microbial metabolism. (ATU: allylthiourea, A nitrification process inhibitor; BDI: procyanidins, a biological denitrification inhibitor).

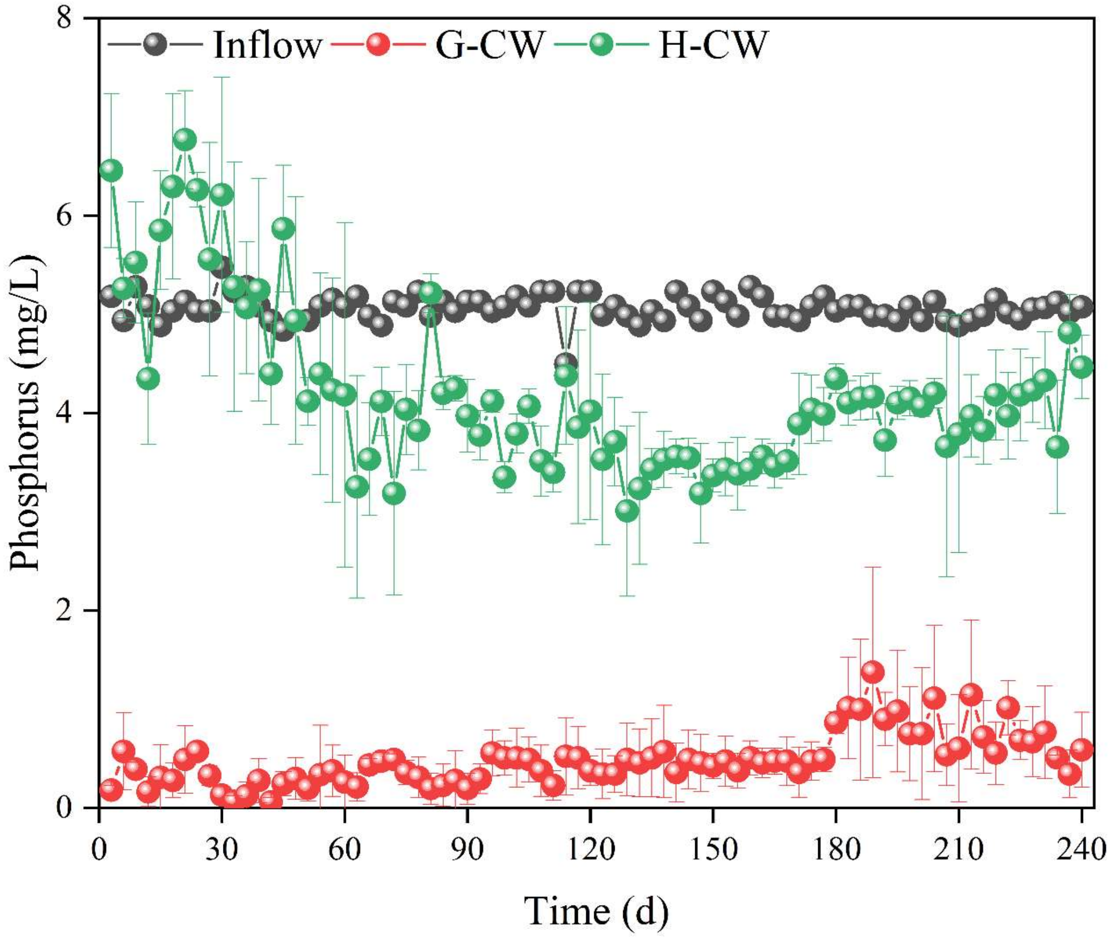

Fig. S4 Concentrations of Phosphorus in the influent and effluents of CWs over the experimental period.

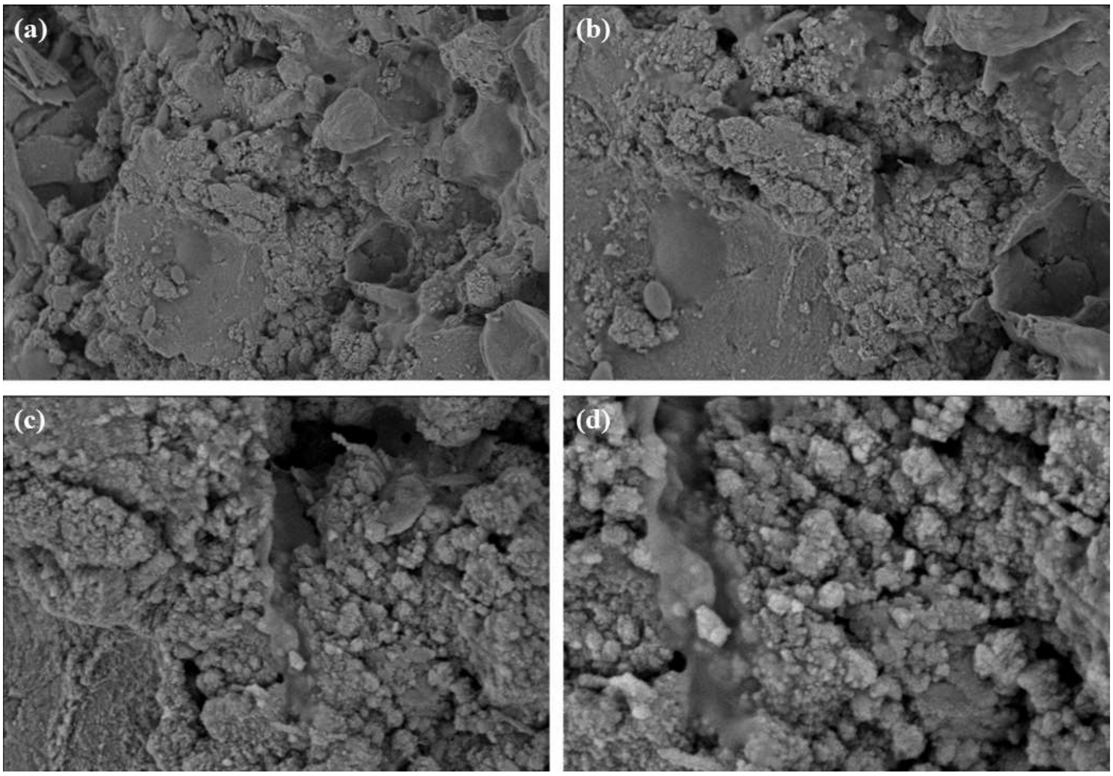

Fig. S5 The surface morphology from SEM images of initial gravel at (a) 10K × ; (b) 20K × ; (c) 50K × ; and (d) 100K × .

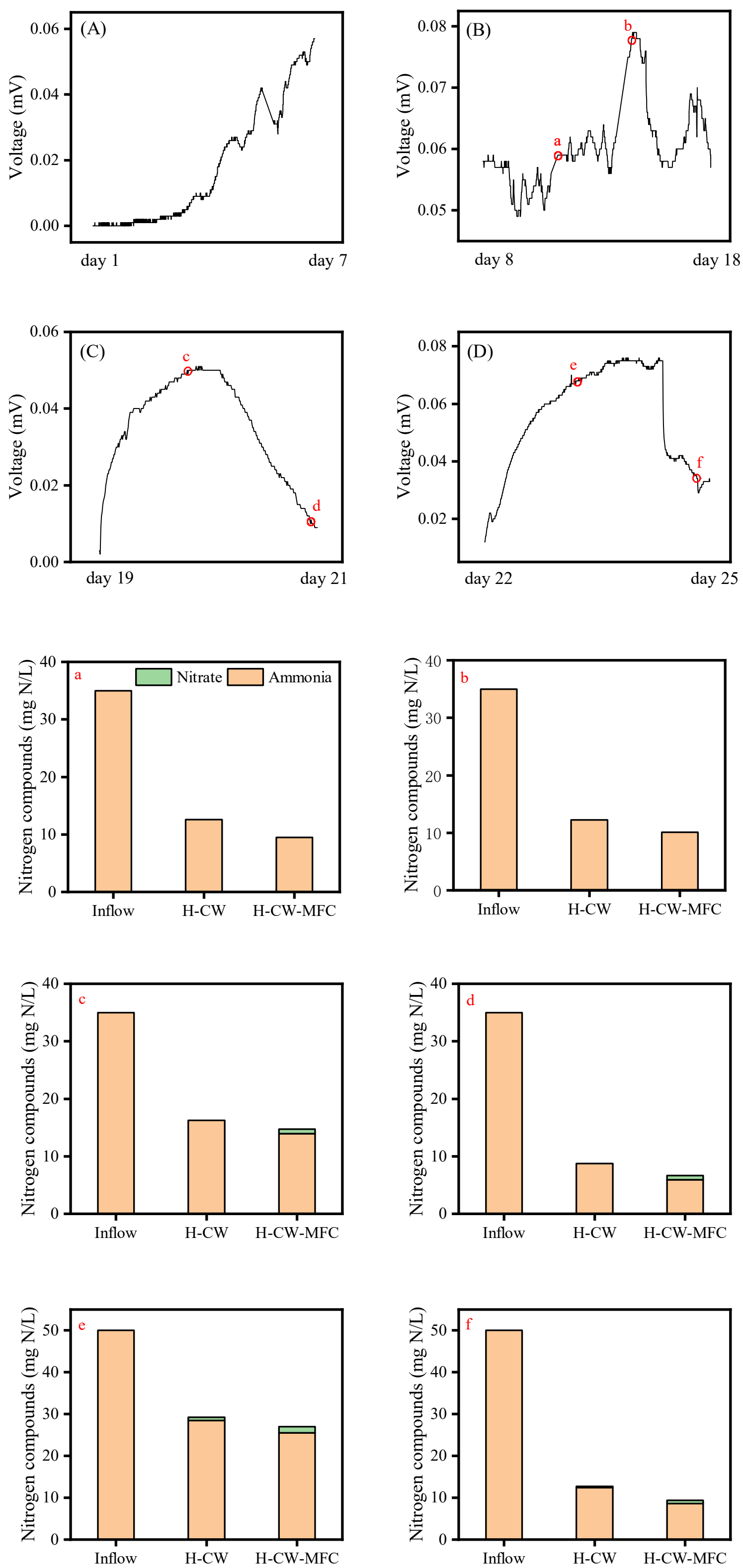

Fig. S6 After H-CW was converted to H-CW-MFC, the voltage rose during the incubation phase (A) and remained above 50 mV during the relative stability phase (B). Voltage variation for the batch experiment with 35 mg/L of influent ammonia (C) and for the batch experiment with 50 mg/L of influent ammonia (D). The red circles represent the corresponding voltages at the time of sampling. a, b, c, d, e, f represents the water quality during sampling.

Table S1 Composition of the trace element solution.

Trace element chemicals	Addition (g/L)
$ZnSO_4·7H_2O$	0.4
$MnCl_2·4H_2O$	0.5
$CoCl_2·6H_2O$	0.6
$CuCl_2·6H_2O$	0.05
H_3BO_4	1.0
$NiCl_2·6H_2O$	0.04
$Na_2MO_4·2H_2O$	0.06

Notes: This is a recipe for the 1000 times-concentrated trace element solution.

Table S2 The introduction concentration of nitrogen compounds at 0 and 24 h and other substances in the influent of the two batch experiments.

Substances	Batch 1		Batch 2	
	0	24	0	24
NH_4^+-N (mg/L)	35	—	—	35
NO_3^--N (mg/L)	—	21	21	—
Other composition in the influent (mg/L)	$NaHCO_3$ (100), KH_2PO_4 (5), $CaCl_2·2H_2O$ (100), $MgCl_2·6H_2O$ (60), EDTA-Na (20), $ZnSO_4·7H_2O$ (0.4), $MnCl_2·4H_2O$ (0.5), $CoCl_2·6H_2O$ (0.6), $CuCl_2·6H_2O$ (0.05), H_3BO_4 (1.0), $NiCl_2·6H_2O$ (0.04), $Na_2MO_4·2H_2O$ (0.06)			

Table S3 Mean pH, dissolved oxygen (DO) and redox potential (ORP) of CWs effluent.

Samples	pH	DO (mg/L)	ORP
HCW1	6.598	0.009	−82.2
HCW2	6.618	0.012	−96.3
HCW3	6.570	0.009	−71.1
GCW1	7.038	0.012	−348.0
GCW2	7.020	0.013	−341.5
GCW3	7.040	0.009	−327.5