Trade-off between electrochemical and microbial nutrient eliminations in iron anode-assisted constructed wetlands: The specificity of voltage level

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Abstract: Currently, the *in-situ* application of iron anode-assisted constructed wetlands (IACWs) in micro-polluted secondary effluent is an ideal solution for ensuring zero-valent iron reactivity, compensating for cold-impaired microbial denitrogenation, and effectively removing nitrogen and phosphorus. Meanwhile, the emergence of solar cells brings the dawn for large-scale application of IACWs without energy consumption concern. To the best of our knowledge, most of the hitherto-reported studies focused on the effects of distinct voltage levels (VLs) on nutrient removal efficiencies in IACWs, and failed to holistically elucidate the pivotal role of VL on nutrient eliminations from the aspects of electrocatalytic behaviors and microbiological mechanisms (community succession, interspecies interactions, and metabolism features), which further impedes establishing performance-pathway-community connections. More importantly, little information is available on the dynamical variations of electrochemical and microbial nutrient removals at various VLs, especially taking water temperature (WT) variations into account. Herein, five solar-driven IACWs at 0, 1, 5, 10, and 15 V were established to treat secondary effluent for 109 days across moderate to low WTs. Results showed that total nitrogen (TN) (4.87 ~ 54.42%) and total phosphorus (TP) (20.66 ~ 97.35%) removals both ascended as VL raised, which primarily occurred in the cathodic regions and anodic upstream, respectively. More sustainable nitrogen elimination was achieved at lower VLs (≤ 5 V). Electrochemical contribution quantification revealed that electrochemical denitrogenation strengthened as VL improved (144.3 ~ 965.7 mg m^{-2} d^{-1}), whereas severe anodic hardening and cathodic clogging in later operation impaired the dominant electrochemical denitrification at higher VLs (≥ 10 V). In contrast, microbial denitrogenation followed hump-shaped variational pattern with rising VL (peaked at 5 V). Microbial community and function analyses further clarified that despite VL elevation induced denitrifying microbiota evolution and up-regulated functional gene abundance, microbial denitrification function was significantly constrained at higher VLs. Particularly, the highest network complexity (at 1 V) and modularity (at 5 V) bred IACWs to better withstand low WT and high iron concentration. Overall, 5 V balanced electrochemical and microbial denitrogenation to obtain persistently effective TN removal. Nonetheless, 15 V would be more suitable to deal with sudden surges in influent nutrient load. Additionally, intensified electro-coagulation dephosphorization was verified to remove most TP via adsorption and co-precipitation. This work provided a preferred VL regulation strategy to facilitate *in-situ* sustainable nutrient purification of low-polluted wastewater in IACWs, and has practical significance for CW administrators seeking to comprehend the outcomes of VL modulation and maintain well-tuned solar-driven IACWs for nutrient eliminations.

Keywords: Voltage level; Nutrient removals; Iron anode; Constructed wetlands; Electrocatalytic behaviors; Microbial responses