Supplementary Material

Effect of humic acid on phenanthrene removal by constructed wetlands using birnessite as substrates

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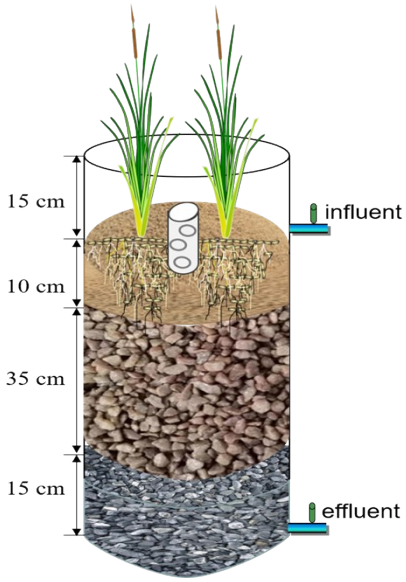

Figure S1. The schematic diagram of constructed wetland.

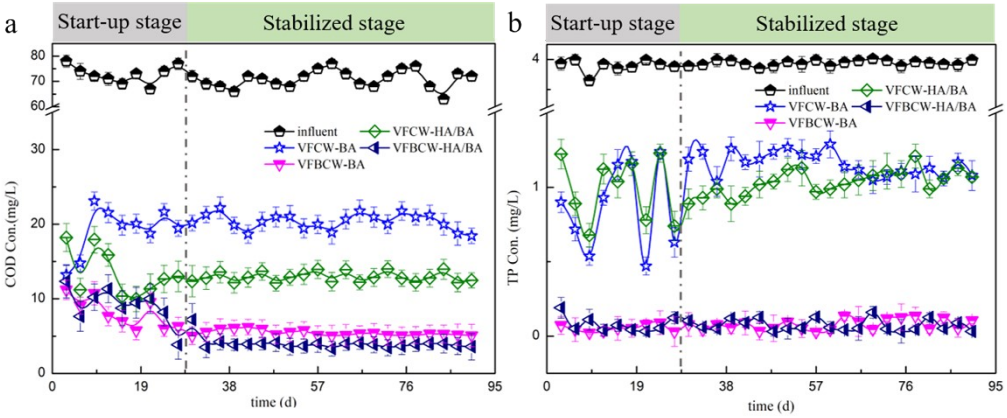

Figure S2. Overall treatment performance of COD (a) and TP (b) in each microcosm.

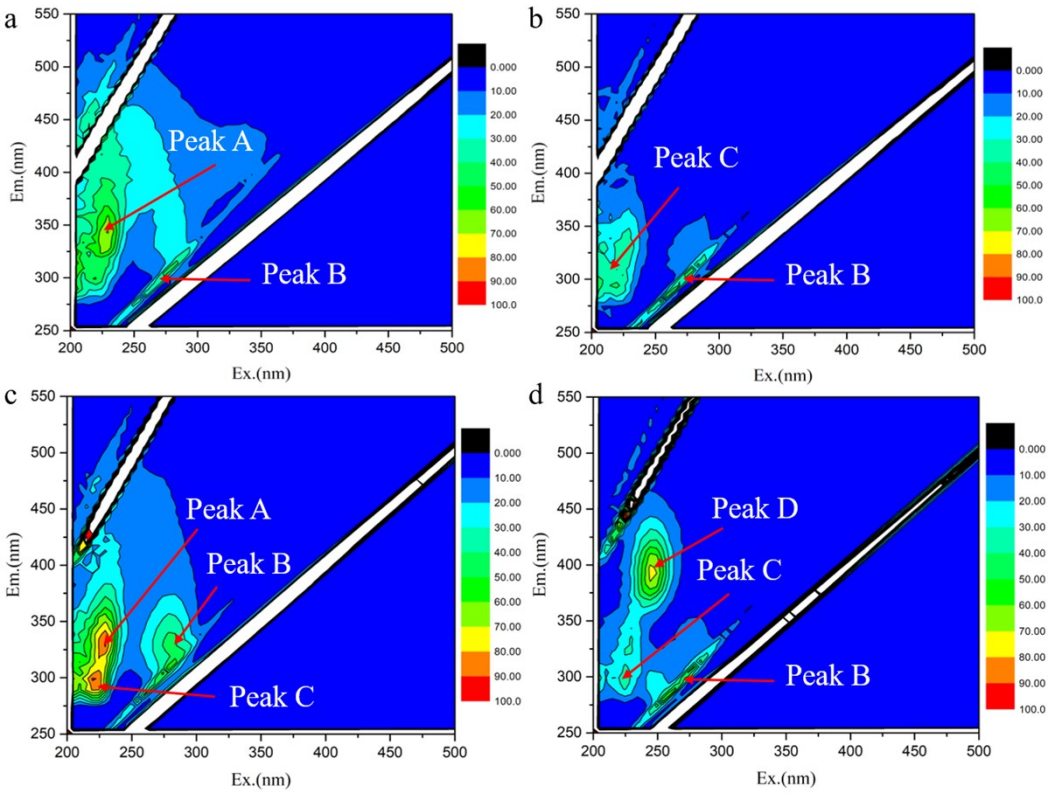

Figure S3. EEM spectra of DOM in different CW units: (a) VFCW-BA; (b) VFBCW-BA; (c) VFCW-HA/BA; (d) VFBCW-HA/BA. Peak A, B, C and D separately represent fluorescence peak of DOM.

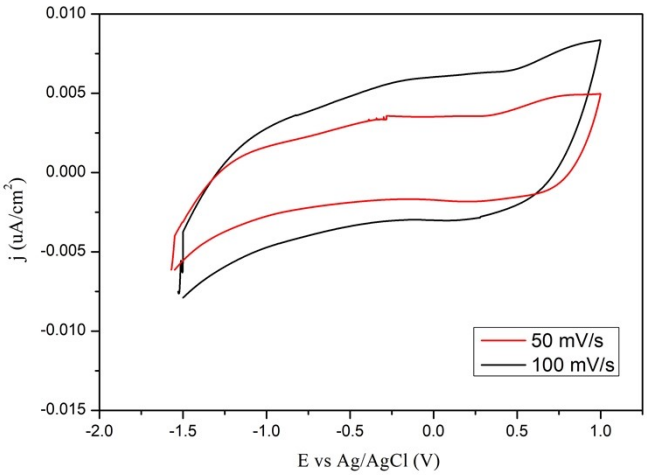

Figure S4. CV curves of HA modified BA on glassy carbon at a scan rate of 50 mV s^{-1} and 100 mV s^{-1}.

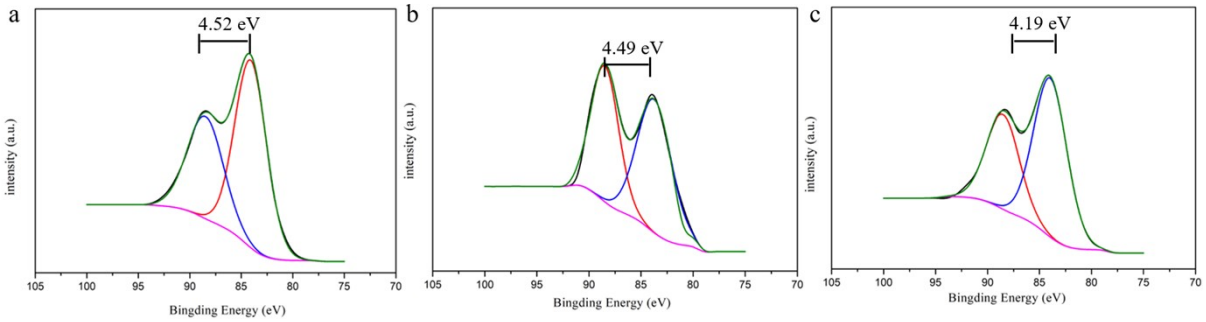

Figure S5. The XPS spectra of Mn3s for birnessite before the experiment (a) and birnessite in different operated CW units: VFBCW-BA (b) and VFBCW-HA/BA (c).

Table S1. EEMs locations, representative EEMs, and fluorescence compounds in CWs.

Peaks	A	B	C	D
EEMs location	Ex: 229 nm Em: 343 (333) nm	Ex: 278 (224) nm Em: 309 (313) nm	Ex: 220 (224) nm Em: 300 nm	Ex: 250 nm Em: 400 nm
Fluorescence compounds	Tryptophan-like	Tyrosine-like	Tyrosine-like	UVC Humic-like

Table S2. The main absorbance bands in FTIR spectra and their assignments.

Bands and peaks (cm^{-1})	Assignments
3400-3200	H-bonded OH groups of alcohols, phenols and organic acids, as well as H-bonded N-H groups
2930-2920	C–H stretching of alkyl structures
1660-1600	Aromatic and olefinic C C, C O in carboxyl; amide (I), ketone and quinone groups
1550	Amides II, aromatic C C
1260-1200	Amide III or aromatic ethers C–O–C
1070-1030	–C–O–C of carbohydrates, aromatic ethers, Si–O–C groupments

Table S3. Relative composition ratios of Mn(II), Mn(III), and Mn(IV) and multiplet split of Mn 3s region (MS) and the average oxidation state of Mn oxides (Mn AOS) in birnessite before the experiment (pristine) and different operated CW units.

Sample	%Mn(IV)	%Mn(III)	%Mn(II)	MS	Mn AOS
pristine	36.67	0	63.33	4.52	3.84
VFBCW-BA	36.11	19.28	44.62	4.49	3.88
VFBCW-HA/BA	34.74	25.01	40.25	4.19	4.22

Table S4. Comparison of diversity and richness estimators of different depths of substrates.

Sample	OTU	Microbial species	Shannon	Simpson	Chao1	ACE	Coverage
VFBCW-BA	40235	3104	7.86	0.98	2049.56	1814.73	0.99
VFCW-HA/BA	66254	2953	7.5	0.97	1903.82	1895.18	0.99
VFBCW-HA/BA	64358	3162	7.53	0.98	1832.53	1810.65	0.99