Caption of Supplementary data:

Materials and Methods

Table S1 Composition of inoculum, substrate, and naphthalene.

Table S2 MOE docking profiles of ATPase, amylase, F420, acetyl-CoA, and methylmalonyl-CoA.

Table S3 The abundance of microbial community.

Fig. S1. Changes of SCOD during AD.

Fig. S2. Volume integral results obtained by FRI analysis of EPS.

Materials and Methods

EPS extraction

After the experiment, the sludge (1.2 g) was mixed with 0.05% NaCl solution (6 mL). Then, the mixture was vortexed immediately for 5 min, followed by centrifugation at 4000 rpm. The supernatant filtered with 0.45 μm membranes was regarded as the soluble EPS (SAMP). The sludge was mixed with 0.05% NaCl solution again. The mixture was then sequentially vortexed for 5 min, heated in a water bath at 65 ^{o}C for 2 min and centrifuged at 4000 rpm for 15 min. The supernatant obtained was filtered with 0.45 μm membranes to become the loosely bound EPS (LB-EPS). The sludge mixed with 0.05% NaCl solution was sequentially vortexed for 15 min, heated in a water bath at 65 ^{o}C for 30 min and centrifuged at 10000 rpm for 20 min. The supernatant obtained was filtered with 0.45 μm membranes was regarded as the tightly bound EPS (TB-EPS).

EEM analysis

Three-dimensional excitation-emission matrix (EEM) was obtained by an F-4600 spectrophotometer (Hitachi, Japan) equipped with a 1.0 cm Quartz cuvette for DOM analysis. EEM spectra was obtained by setting the emission (Em) wavelength from 200 nm to 550 nm at 5 nm increments and the excitation (Ex) wavelength from 200 nm to 450 nm at 5 nm increments. Each different fluorophore was characterized by an Ex/Em wavelength pair with parallel factor analysis (PARAFAC). For EPS, the fluorescence regional integration (FRI) was used to calculate the area of every region

Table S1 Composition of inoculum, substrate, and naphthalene

Component	Sludge	Starch	Naphthalene
TS	12.12%	-	-
VS	12.08%	-	-
C	32.05%	44.44%	93.75%
H	5.22%	6.17%	6.25%
O	53.02%	49.38%	-
N	8.01%	-	-
S	1.70%	-	-

Table S2 MOE docking profiles of ATPase, amylase, F420, acetyl-CoA, and methylmalonyl-CoA.

	Site	Ligand	Receptor		Interaction	Distance (Å)	E (kcal/mol)
Na^+K^+-ATPase (Bacteria)	Site 1	6-ring	CB	Arg 268 (A)	pi-H	4.43	-0.9
		6-ring	CB	Arg 268 (A)	pi-H	4.11	-0.9
		6-ring	CD	Arg 268 (A)	pi-H	4.20	-0.6
	Site 2	6-ring	NZ	Lys 235 (A)	pi-cation	4.47	-1.5
	Site 3	6-ring	CB	Asp 714 (A)	pi-H	3.90	-0.6
$Ca^{2+}Mg^{2+}$-ATPase (Methanococcus)	Site 1	6-ring	ND2	Asn 42 (A)	pi-H	3.79	-0.9
		6-ring	N	Gly 43 (A)	pi-H	4.94	-0.7
		6-ring	N	Ser 47 (A)	pi-H	4.73	-0.9
	Site 2	6-ring	NZ	Lys 133 (A)	pi-cation	3.54	-2.9
Amylase (Bacteria)	Site 1	6-ring	CA	Phe 14 (A)	pi-H	4.47	-1.1
		6-ring	N	Thr 15 (A)	pi-H	4.08	-0.8
		6-ring	N	Gly 16 (A)	pi-H	3.51	-0.6
		6-ring	N	Gly 16 (A)	pi-H	4.25	-0.7
	Site 2	6-ring	CD	Lys 211 (A)	pi-H	3.79	-0.6

	Site 3	6-ring	CA	Phe 14 (A)	pi-H	4.48	-1.0
		6-ring	N	Thr 15 (A)	pi-H	4.07	-0.7
		6-ring	N	Gly 16 (A)	pi-H	4.20	-0.7
F420	Site 3	6-ring	CA	Pro 136 (B)	pi-H	4.26	-1.0
		6-ring	CA	Pro 136 (B)	pi-H	4.04	-1.0
Acetyl-CoA	Site 1	6-ring	CE	Lys 55 (B)	pi-H	4.34	-1.0
Methylmalonyl-CoA	Site 2	6-ring	CG2	Thr 122 (E)	pi-H	3.59	-0.6

Table S3 The abundance of microbial community.

Group	ACE	Chao1	Shannon	Simpson	Goods-coverage
N0	725.862	720.273	6.252	0.957	0.996
N1	731.264	715.11	6.314	0.96	0.996
N3	782.737	791.192	5.968	0.943	0.996
N4	720.812	712.278	6.043	0.95	0.996

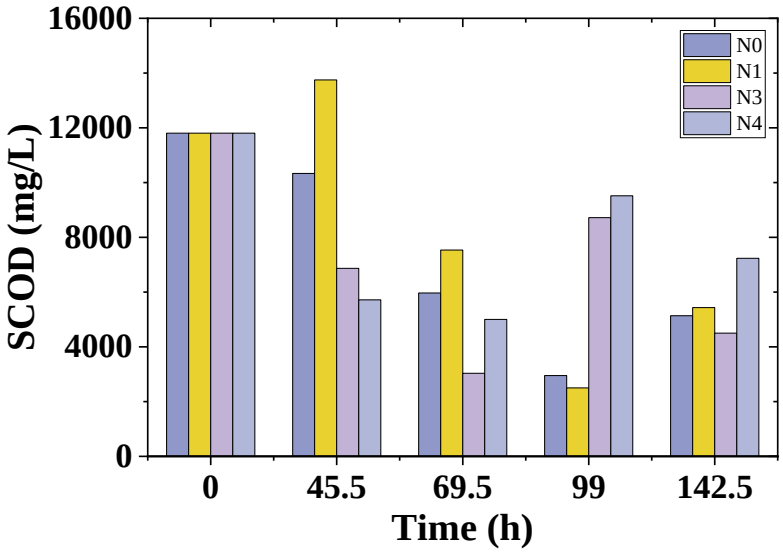

Figure S1. Changes of SCOD during AD.

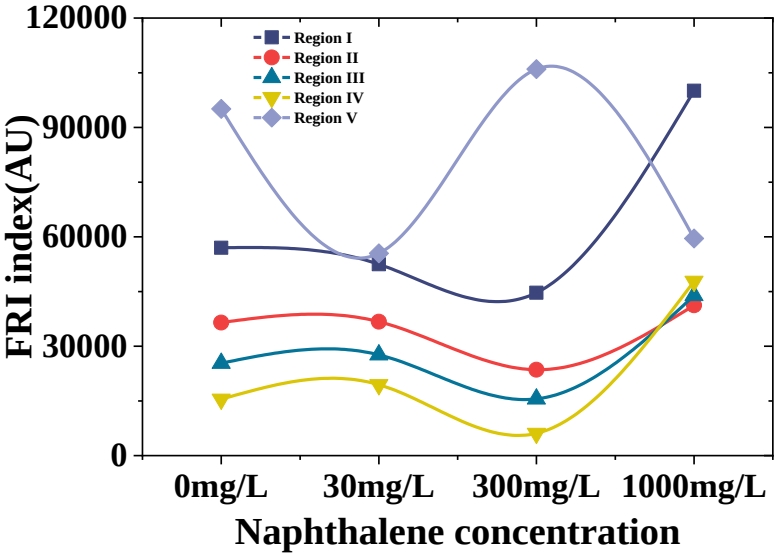

Figure S2. Volume integral results obtained by FRI analysis of EPS.