

Unraveling the effects of cerium oxide nanoparticles on the metabolism of anaerobic digestion of waste activated sludge

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Supplementary Material

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Section S1. Anaerobic and waste sludge characteristics

Table S1. Physicochemical characteristics of anaerobic sludge and waste activated sludge samples.

Parameter	Unit	Waste activated sludge	Anaerobic sludge
pH	-	7.65	7.78
Temp.	°C	27.40	38.10
TS	mg/L	15820	27900
VS	mg/L	9960	21100
FS	mg/L	5860	6800
Total COD	mg/L	12830	21701
Soluble COD	mg/L	7434	14663
Total Carbohydrates	mg/L	583	1658
Soluble Carbohydrates	mg/L	241	46
NH ₄	mg/L	73	180
TSS	mg/L	14175	24300
VSS	mg/L	10950	18050
FSS	mg/L	3225	6250
VSS/TSS	-	0.77	0.74
Carbon	%	22.76	31.09
Hydrogen	%	3.16	4.54
Nitrogen	%	3.08	3.50
C/N ratio	-	7.38	8.88

Table S2. Elemental composition ($\mu\text{g/L}$) of the anaerobic sludge and waste activated sludge samples. Note: ND means “non-detected” or “lower than detection limit”; sd means “standard deviation”.

Element	Waste sludge (mean $\pm$ sd)	Anaer. sludge (mean $\pm$ sd)
Be	0.15 $\pm$ 0.16	0.10 $\pm$ 0.18
Na	112665.00 $\pm$ 8597.39	26404.17 $\pm$ 1340.4
Mg	13289.07 $\pm$ 1261.06	12913.68 $\pm$ 617.93
Al	1079.84 $\pm$ 23.27	5894.22 $\pm$ 199.8
P	3096539.85 $\pm$ 382013.02	7067980.09 $\pm$ 338410.4
K	25466.46 $\pm$ 1920.32	16799.84 $\pm$ 908.98
Ca	27328.41 $\pm$ 5500.12	65476.61 $\pm$ 2043.86
V	6.36 $\pm$ 0.21	21.25 $\pm$ 1.09
Cr	62.92 $\pm$ 42.35	90.35 $\pm$ 6.2
Mn	191.62 $\pm$ 4.00	477.90 $\pm$ 19.24
Fe	40263.57 $\pm$ 1660.13	85888.51 $\pm$ 4107.36
Co	1.71 $\pm$ 0.26	4.50 $\pm$ 0.23
Ni	21.02 $\pm$ 22.67	30.73 $\pm$ 2.52
Cu	339.19 $\pm$ 9.47	932.42 $\pm$ 40.81
Zn	384.20 $\pm$ 13.17	1436.84 $\pm$ 70.17
As	3.02 $\pm$ 0.25	5.74 $\pm$ 0.41
Se	6.66 $\pm$ 0.22	16.90 $\pm$ 0.22
Mo	9.31 $\pm$ 0.79	17.62 $\pm$ 1.15
Ag	1.56 $\pm$ 0.55	6.06 $\pm$ 0.62
Cd	0.70 $\pm$ 0.05	2.14 $\pm$ 0.03
Sb	1.05 $\pm$ 0.09	3.70 $\pm$ 0.16
Ba	132.15 $\pm$ 0.37	415.69 $\pm$ 17.77
Tl	ND	ND
Pb	4.84 $\pm$ 0.15	20.68 $\pm$ 0.82
Th	ND	0.33 $\pm$ 0.05
U	0.96 $\pm$ 0.04	2.33 $\pm$ 0.08

Table S3. Agilent 7900 operating conditions for CeO₂ NPs determination via spICP-MS.

Parameter	Operation Setting
Reference material	Au NPs 60 nm (100 ng/L)
RF power	1550 W
Carrier gas flow	0.67 L/min
Sample inlet flow	0.346 mL/min
Nebulizer pump velocity	0.1 revolutions per sec
Acquisition time	60 s
Dwell time	100 μ s
Mass monitored	¹⁴⁰ Ce
Analyte mass fraction	0.814
Particle density	7.132 g/mL

Section S2. Data from the experiments

COD initial and final

Treatment	COD Initial (mg/L)	COD final (mg/L)
Control		8440.55
10 mg CeO ₂ /g VSS	17465.77	8050.90
50 mg CeO ₂ /g VSS		7789.55
100 mg CeO ₂ /g VSS		7348.3

Normalized methanogenic activity

Treatment	Normalized Methanogenic Activity	
	Average	SD
Control	100	1.08
10 mg CeO ₂ /g VSS	108.91	0.43
50 mg CeO ₂ /g VSS	111.32	1.80
100 mg CeO ₂ /g VSS	114.2	7.86

Amino acids, organic acids and nucleobase/side/tide content

Units (mg/L) amino acids	Control 96 h	10 mgCeO ₂ /g VSS 96 h	50 mgCeO ₂ /g VSS 96 h	100 mgCeO ₂ /g VSS 96 h
Glutamic acid	900.63	1455.17	1567.51	2006.97
Aspartic acid	539.03	979.30	1039.55	1286.13
Alanine	517.55	1037.87	1012.21	1159.05
Leucine	507.10	1075.10	1032.35	734.80
Lysine	342.36	727.08	753.32	890.10
Isoleucine	319.46	676.80	696.08	858.05
Phenylalanine	301.64	593.57	575.08	707.82
Valine	268.26	542.86	539.85	664.29
Glycine	226.27	399.36	378.49	582.58
Threonine	217.81	416.44	435.18	490.29
Methionine	191.58	360.80	364.50	443.99
Serine	179.06	311.34	290.36	328.72
Arginine	174.64	163.53	165.58	173.35
Histidine	130.25	178.80	181.56	243.47
Citrulline	125.92	278.37	306.88	317.10
Tyrosine	108.92	253.33	237.38	268.12
tryptophan	56.23	122.54	114.48	185.68
Ornithine	22.93	53.57	68.37	75.43
Homoserine	6.04	33.81	22.30	27.88
Proline	0.00	240.81	208.67	250.12
Cysteine	0.00	0.00	0.00	0.00
Glutamine	0.00	0.00	0.00	0.00
Asparagine	0.00	0.00	0.00	0.00

Organic acids at 96 h. Unit: mg/L	Control	10 mgCeO ₂ /g VSS	50 mgCeO ₂ /g VSS	100 mgCeO ₂ /g VSS
malic acid	0.04	0.15	0.14	0.25
Citric acid	0.02	0.02	0.03	0.05
ascorbic acid	0.07	0.07	0.07	0.06

Unit: mg/L Nucleobase/side/tide	Control 96 h	10 mgCeO ₂ /g VSS 96 h	50 mgCeO ₂ /g VSS 96 h	100 mgCeO ₂ /g VSS 96 h
Uracil	1.52	1.45	1.46	1.27
Thymine	1.01	1.13	1.05	0.99
Xanthine	0.61	1.04	0.95	0.63
Hypoxanthine	0.58	0.68	0.63	0.49
Inosine	0.50	0.05	0.05	0.07
Thymidine	0.32	0.42	0.24	0.24
Uridine	0.30	0.03	0.04	0.06
Guanosine	0.25	0.05	0.05	0.06
Guanine	0.19	0.15	0.11	0.20
Cytidine	0.14	0.06	0.04	0.06
Adenosine	0.05	0.03	0.03	0.02
Adenine	0.00	0.00	0.00	0.00

Enzymatic activity

Treatment	Enzymatic Activity		Enzymatic Activity	
	Mean	SD	Mean	SD
Protease Relative Activity			Protease Relative Activity	
Control	0.177	3.39E-17	Control	100.00% 0.00%
10 mg CeO ₂ /g VSS	0.146	0.00057	10 mg CeO ₂ /g VSS	82.49% 0.33%
50 mg CeO ₂ /g VSS	0.134	0	50 mg CeO ₂ /g VSS	75.71% 0.00%
100 mg CeO ₂ /g VSS	0.131	0.00057	100 mg CeO ₂ /g VSS	74.01% 0.33%
Acetate Kinase Relative Activity			Acetate Kinase Relative Activity	
Control	0.092	0.00057	Control	100.00% 0.63%
10 mg CeO ₂ /g VSS	0.106	0	10 mg CeO ₂ /g VSS	115.22% 0.00%
50 mg CeO ₂ /g VSS	0.088	1.69E-17	50 mg CeO ₂ /g VSS	95.65% 0.00%
100 mg CeO ₂ /g VSS	0.089	0.00057	100 mg CeO ₂ /g VSS	96.74% 0.63%
F420 Relative activity			F420 Relative activity	
Control	0.049	0.00057	Control	100.00% 1.18%
10 mg CeO ₂ /g VSS	0.026	0.00072	10 mg CeO ₂ /g VSS	53.06% 1.58%
50 mg CeO ₂ /g VSS	0.025	0.00177	50 mg CeO ₂ /g VSS	51.02% 3.62%
100 mg CeO ₂ /g VSS	0.018	0	100 mg CeO ₂ /g VSS	36.73% 0.00%

Cerium concentration

		(Ce) Particle Conc. (mg/L)	(Ce) Ionic Conc. (mg/L)
Control	Mean	0.248618867	0.022448056
	SD	0.001360608	0.004712255
10 mg CeO ₂ /g VSS	Mean	5.422207811	3.059743655
	SD	0.021614372	0.005972421
50 mg CeO ₂ /g VSS	Mean	31.44369676	10.93186724
	SD	0.130048118	0.101633603
100 mg CeO ₂ /g VSS	Mean	67.61942902	17.83382696
	SD	0.166557753	0.056406939