Impact of nanomaterials on waste water treatment plant functioning and biosolid valorization

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Safe(r) Ecodesign Research and Education applied to NAnomaterial DEvelopment.

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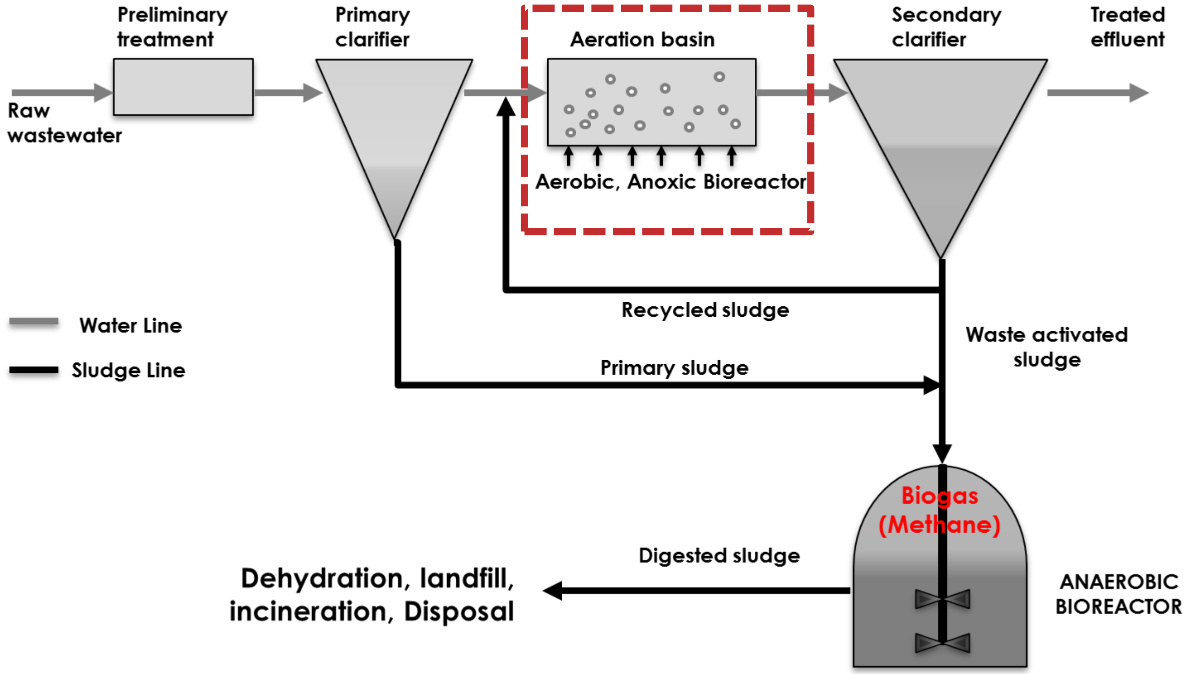
Biological wastewater treatment and sludge upgrading



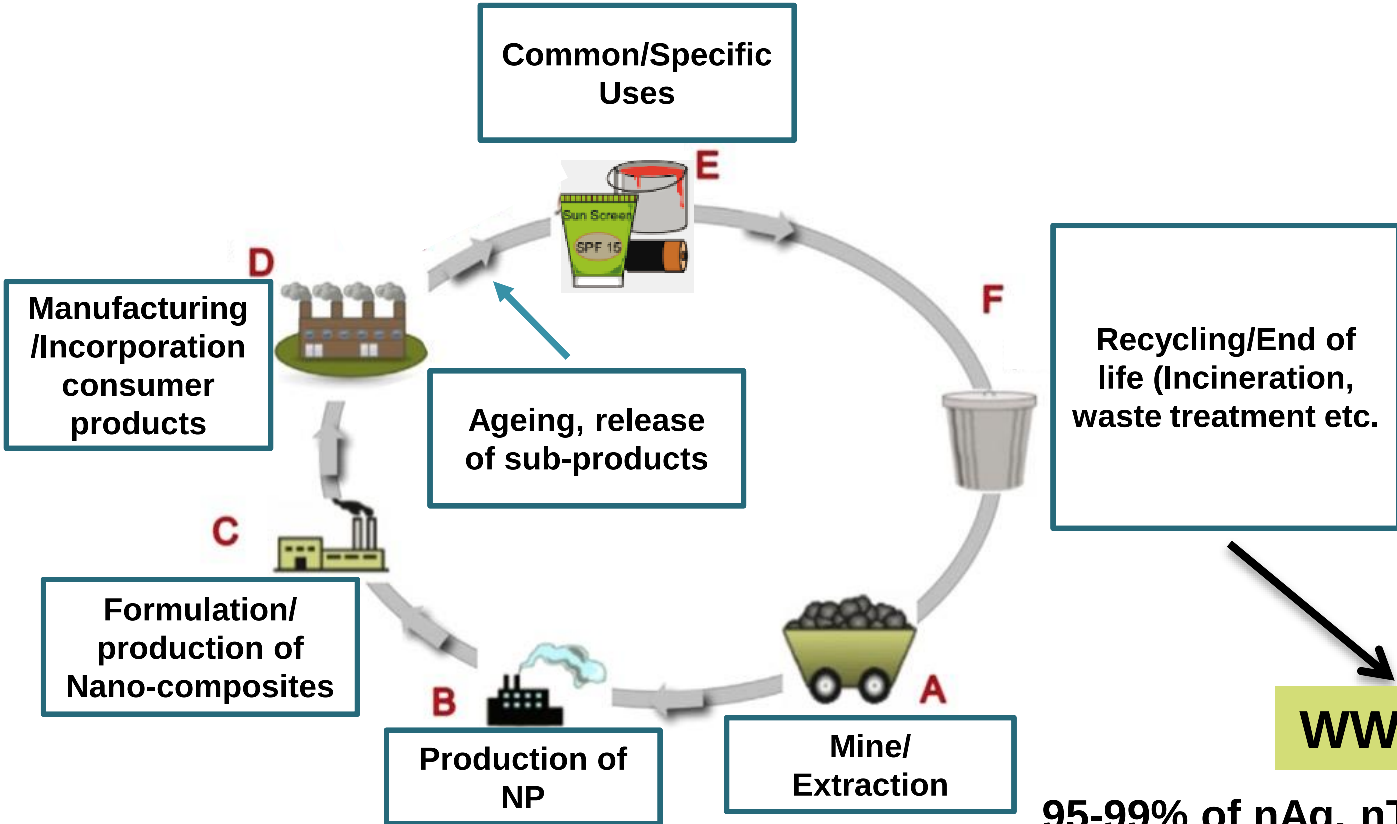
- Activated sludge flocs: consortium of different groups of microorganisms, organic and inorganic particles embedded in extracellular polymeric substance (EPS).

  ➔Play crucial role in removal of carbon, nitrogen and phosphorus.

- Interactions between the components of Flocs insure the stability and efficacy of treatment.

Nanomaterials concern in WWTP

Life cycle of nanomaterials



WWTPs

95-99% of nAg, $nTiO_2$, $nCeO_2$, nZnO adsobed on Biosolids

What consequences on flocs microbial consortia and indirectly on biological processes ???

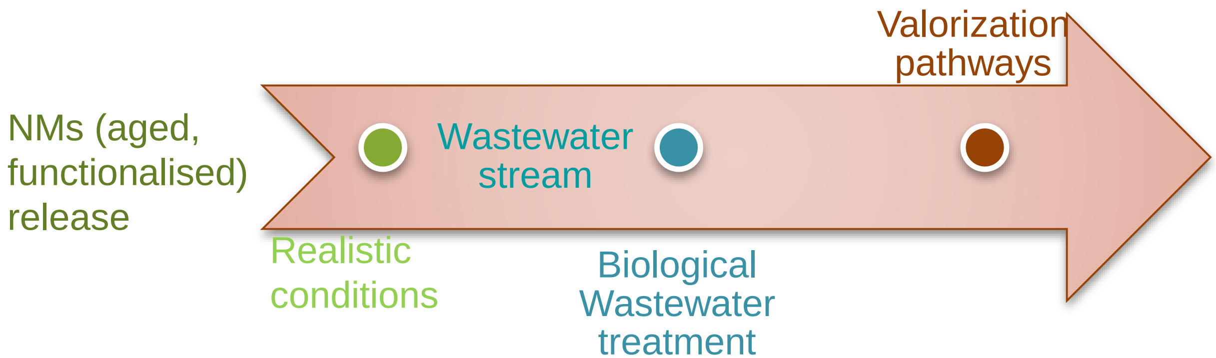
Objectives of project

A. Nanomaterials fate and behaviour

B. Nanomaterials impact on wastewater treatment processes

C. Nanomaterials impact on sludge valorization through anaerobic digestion

Issues and project strategy



Background

Nanomaterials and sludge flocculability

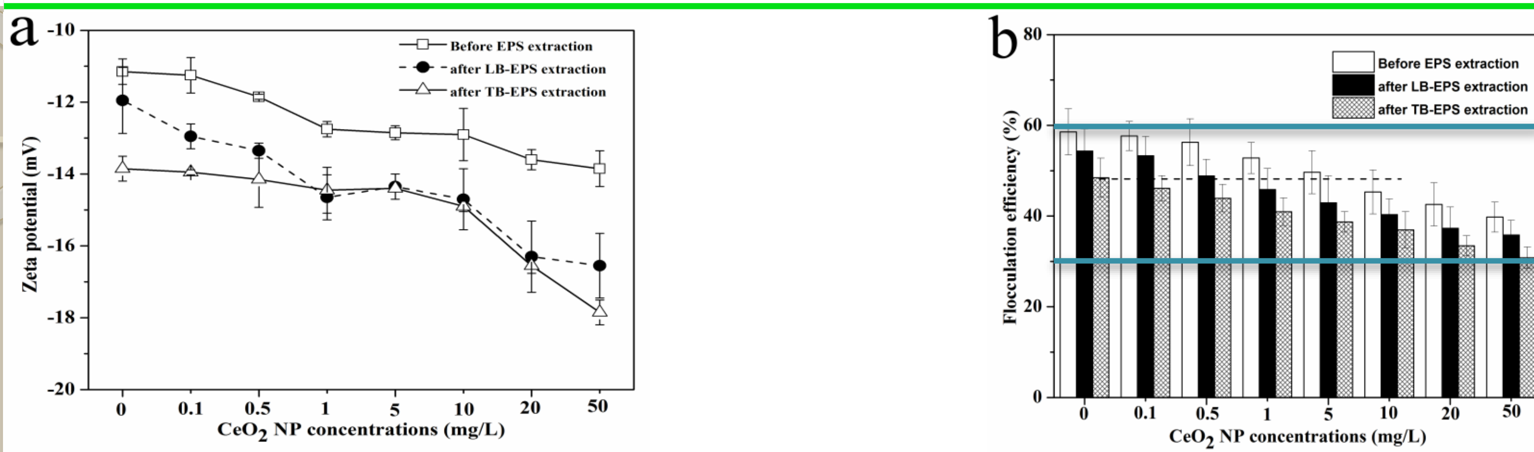


Fig 1. $nCeO_2$ effects on sludge EPS and flocculability ***(You et al. 2016).***

- The short-term exposure experiment with synthetic wastewater (8 h)
- The Zeta potential (ζ) ➔Electrostatic repulsive interactions ➔

highly important for the flocculability of sludge

- Negative charges increase with CeO_2 NP increase, and EPS extraction ➔ negative effect on the ζ

Flocculability : presence of EPS reduce the negative effects of the CeO_2 NPs on sludge flocculability.

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NMs effects on biological nitrogen removal

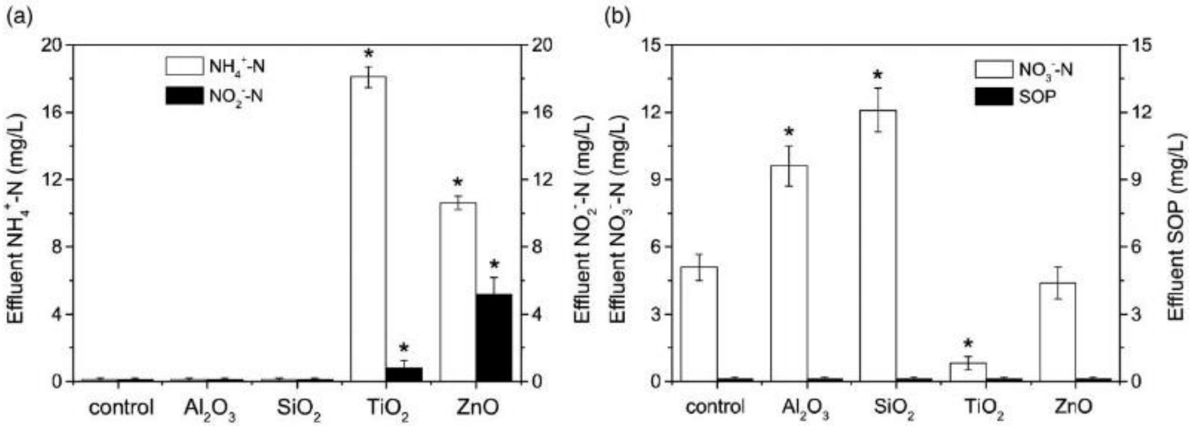


Fig 2. Intermediary compounds concentration after ENMs long term exposure 70 d (50mg/L) *(Zheng et al., 2015).*

N removal efficiency was impacted by NP Exposure

Sludge digestion: effects of nanomaterials

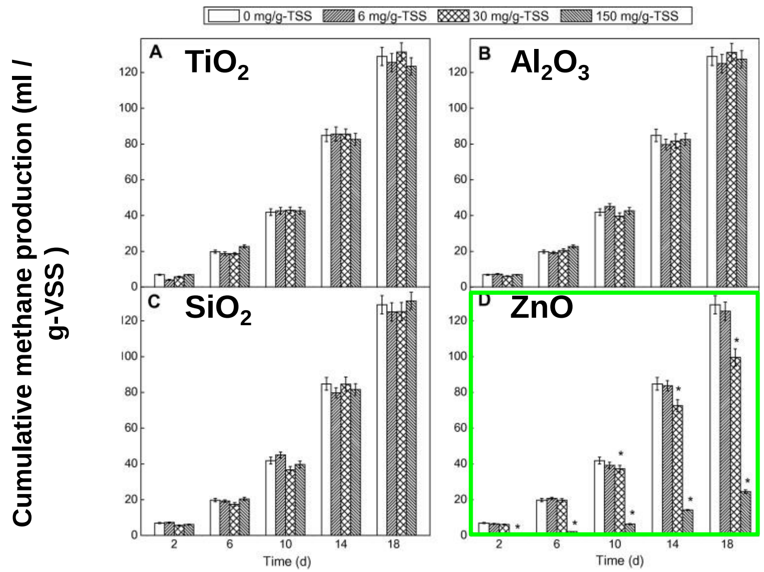


Fig 3. Effects of different dosages (0, 6, 30 and 150 mg/g-TSS) of NPs exposure on methane generation during sludge digestion (*Mu et al., 2011*).

ZnO NPs ➔ dose-dependent inhibition of CH_4 production (up to 80%), consecutive to inhibitory effect on the activities of protease, AK and coenzyme F420 (25.3, 22.9 and 40.9% after 18 d exposure).

Experimental setup and Results

Selected nanomaterial

- Diesel additive containing nanoCeO_2 (Envirox™)
- Combusted to simulate combustion in the engine
- nanoCeO_2 mean size : 19±10.4nm (TEM)
- Ce^{4+} oxidation state (XANES)
- Wastewater treatment experiment : nanoCeO_2 added 3 times a week, final concentration : 2.8 mg/L

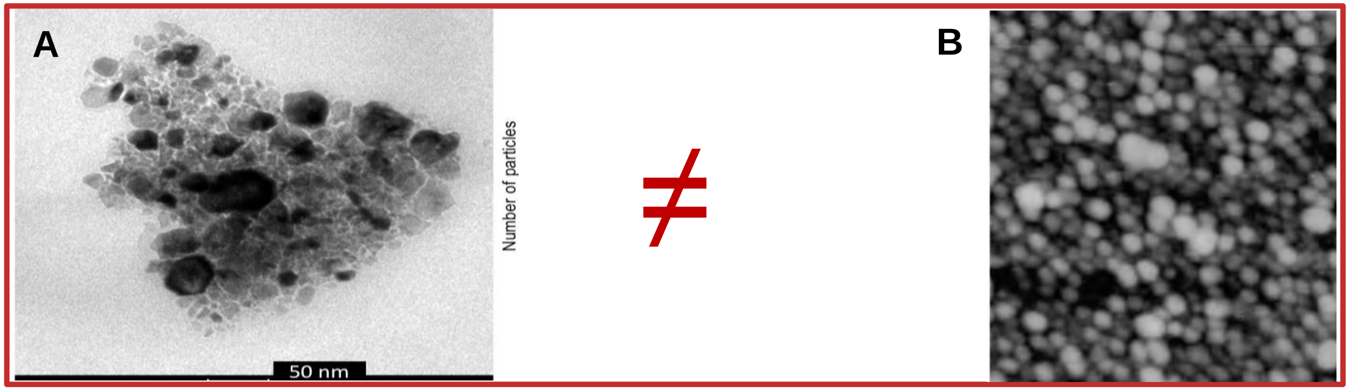
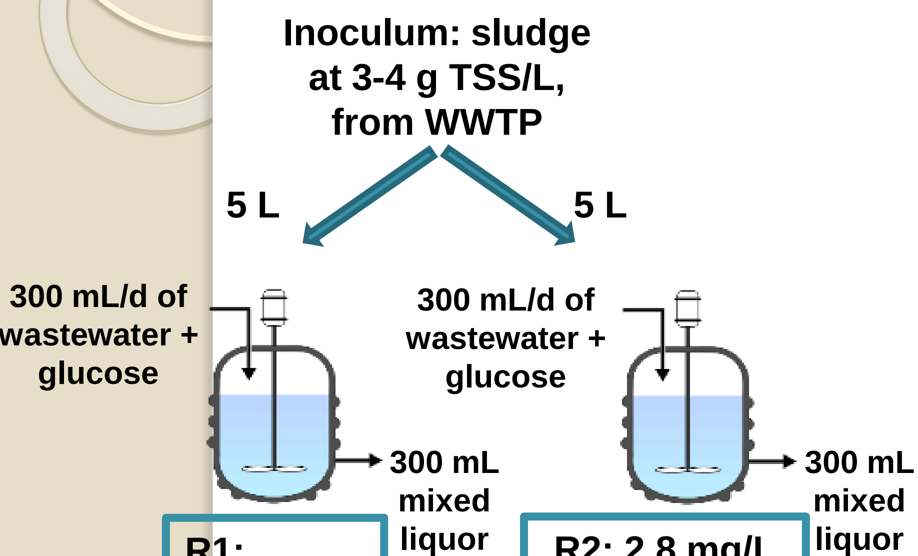


Figure 4: A. TEM image of combusted Envirox™ *(Auffan et al., 2016)* and B.TEM image of manufactured nCeO_2

Setup of the project processes

Aerobic wastewater treatment



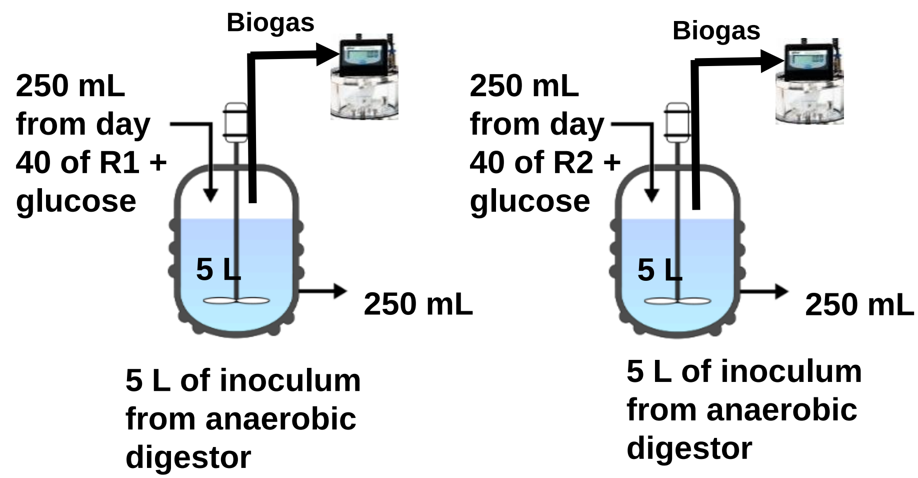
R1: Control

R2: 2.8 mg/L NPs spiked assay

- In R2: NPs spiked 3 times a week to obtain 2.8 mg/L after 40 d of exposure
- At day 40, Sludge with NPs used as substrate in anaerobic phase

Anaerobic Sludge digestion

Agitation : > 180 rpm
pH 6.8 – 7.5
T° C: 37



Control

Assay with Nps

Culture broth sampled everyday is analyzed for Nps fate, consequence of process.

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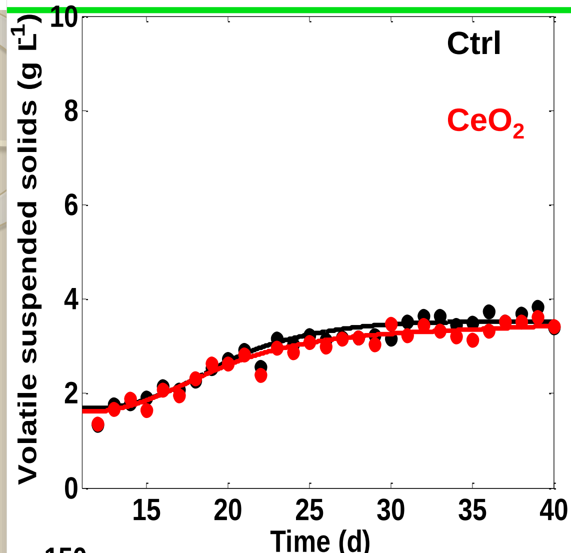
Impacts of $nCeO_2$ on aerobic sludge production (1)



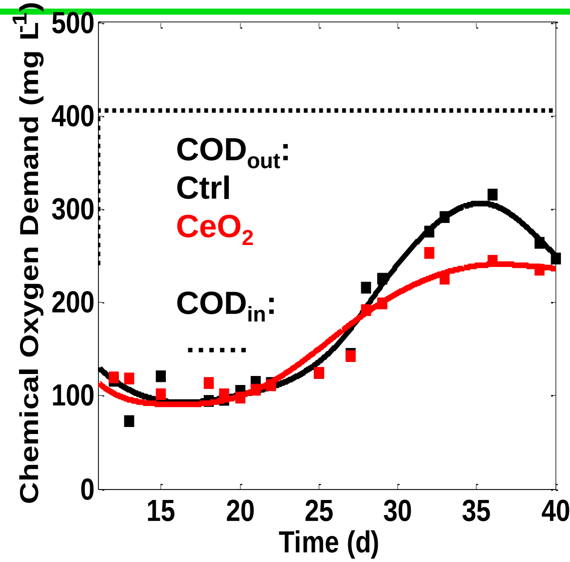
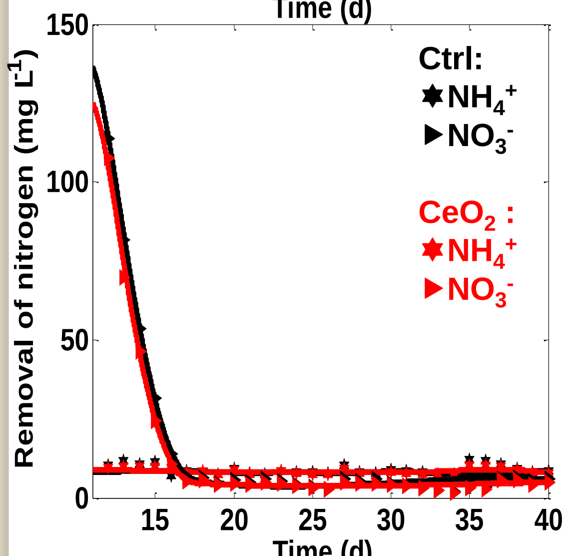


Fig 5: $nCeO_2$ effects on wastewater treatment.



VSS increase until stabilisation ➔ Sludge microorganism growth

COD used as substrate by activated sludge

Total removal of NH_4^+ and NO_3^-

The chronic dosing of CeO_2 showed No effect on nitrogen removal, COD reduction.

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Impacts of $nCeO_2$ on aerobic sludge production (2)

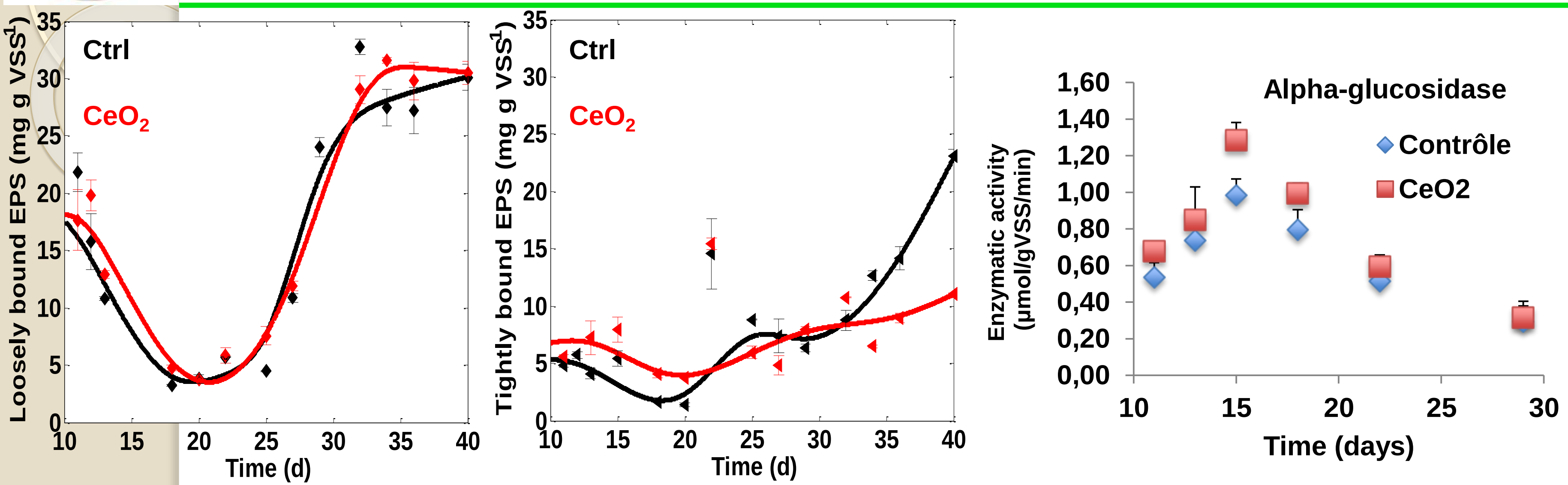

Fig 6. Extracted EPS from cultures with/without $nCeO_2$ during wastewater treatment, Enzyms activity

- EPS play a key role in flocs structure and in protecting microorganisms against environmental stress. In our study, the extracted EPS showed similar trends or at least lower for culture spiked with $nCeO_2$.
- The increase of EPS from day 20 was related to the decrease in α-glucosidase activity that positive effect in presence of $nCeO_2$ (p-value<0.05).

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Impacts of contaminated sludge on anaerobic digestion (1)

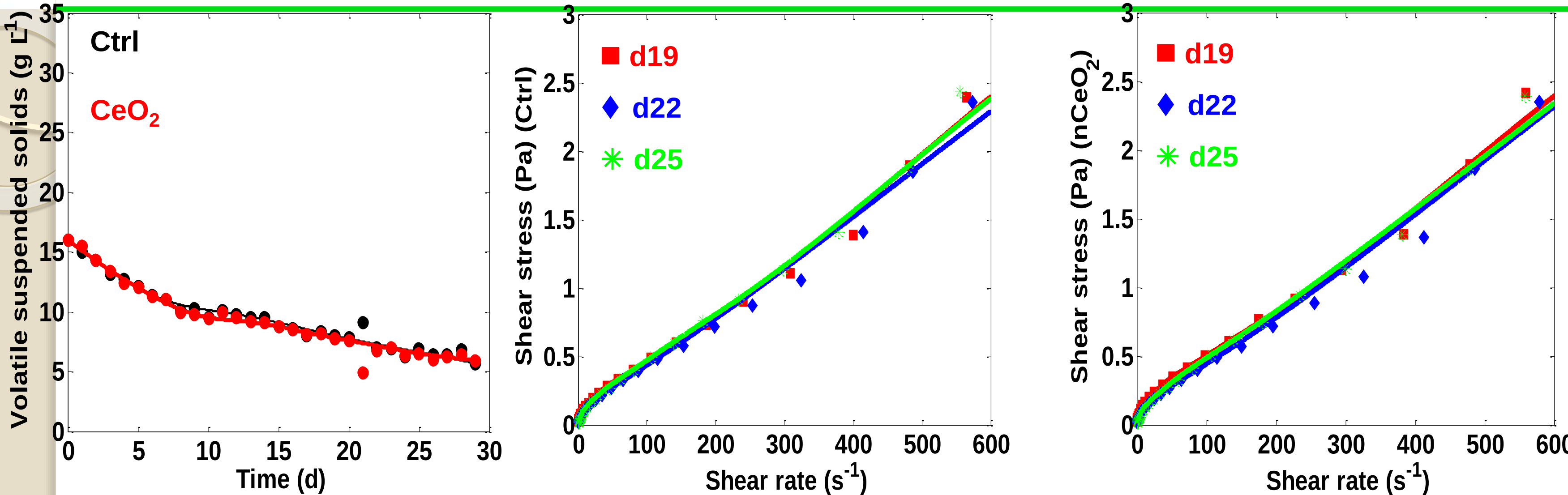


Fig 7. Comparisons of : A. Suspended solids kinetics in anaerobic digestion; B., C. sludge rheology with/without $nCeO_2$

Herschel–Bulkley model

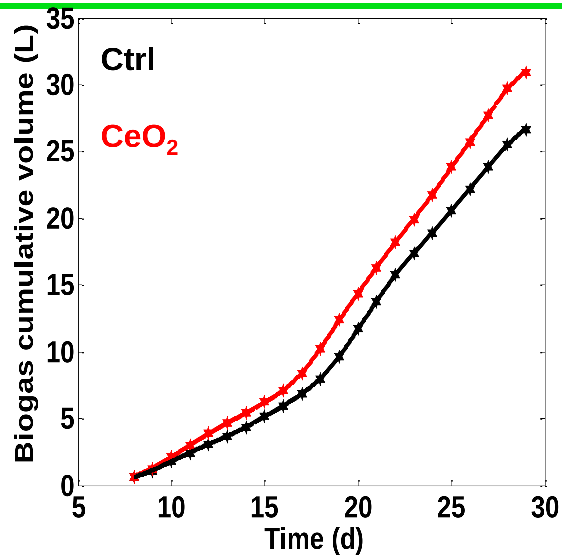
$$\tau = \tau_0 + k\dot{\gamma}^n$$

Parameters displayed in table were obtained from Matlab® fitting.

Time (d)	Culture	TSS	EPS	K	n	τ_0	R^2
19	Ctrl	23.45	113.48	0.258	0.509	0.0215	0.995
	CeO_2	21.27	86.99	0.286	0.543	0.0260	0.998
22	Ctrl	21.51	110.90	0.235	0.455	0.0188	0.995
	CeO_2	19.18	77.95	0.237	0.475	0.0192	0.995
25	Ctrl	20.54	87.81	0.237	0.454	0.0206	0.995
	CeO_2	18.49	38.97	0.235	0.443	0.0201	0.991

No Rheological change between control and spiked bioreactor

Impacts of contaminated sludge on anaerobic digestion (2)



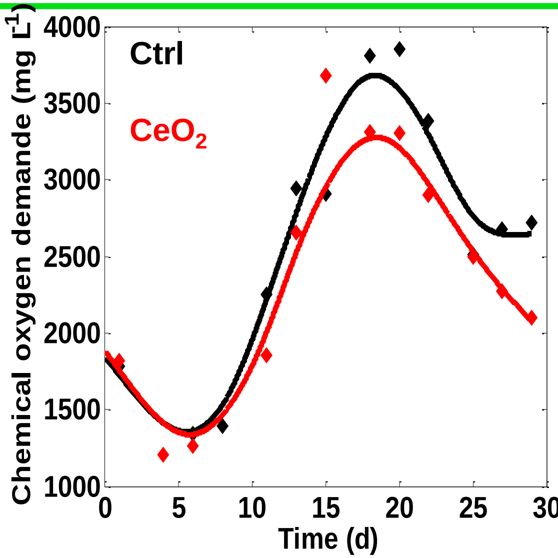


Fig 8. Comparisons of : A. Total biogas production ; B. COD removal with/without nCeO_2

- Using of contamined sludge as influent resulted in higher total biogas production ➔ correlated to higher COD removal.
- However methane production was similar ➔ hydrogenotrophs groups favoured in presence of nCeO_2?

	% vol. CH_4	
Time (d)	**Ctrl**	**nCeO_2**
14	81.4	79.6
18	79.7	80.6
22	77.6	76.1
25	71.8	71.3

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Conclusions and outlook

- **Aerobic process:** Chronic addition of aged $nCeO_2$ up to 2.8 mg/L ➔ No effect on aerobic process in term of EPS production, COD and nitrogen removal efficiency.

- **Sludge digestion:** Aged $nCeO_2$ from aerobic sludge did not disturb the anaerobic digestion process at concentration of 1.5 mg/L.

- **Outlook:**

  $nCeO_2$ distribution in effluent and biosolid: ICP, XAS; Microbial communities analyses.

  Energetic valorization, agronomic valorization.

Acknowledgments

My co-worker, supervisors.

Labex Serenade: funding of the research project.

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Thank You For Your Attention

Nanomaterials in wastewater treatment plants

Table 1: Average predicted concentrations of nanoparticles, considering the market study, A. in effluent and B. in biosolides

A

ENM	New York (μg/L)	Shanghai (μg/L)	London (μg/L)
Ag	0.004−0.26	0.008−0.13	0.003−0.11
Al_2O_3	0.09−7.13	0.25−6.17	0.09−4.56
CeO_2	0.007−1.17	0.024−0.93	0.003−0.49
CNT	0.001−0.19	0.006−0.23	0.001−0.11
Cu + CuO_x	>0.001−0.03	>0.001−0.03	>0.001−0.02
Fe + FeO_x	0.24−14.56	0.54−9.02	0.20−7.22
nanoclays	0.04−1.45	0.09−1.00	0.04−0.93
SiO_2	0.03−5.77	0.20−6.74	0.02−3.20
TiO_2	1.33−43.88	3.13−30.73	1.28−29.18
ZnO	0.37−15.84	0.72−6.43	0.31−7.32

B

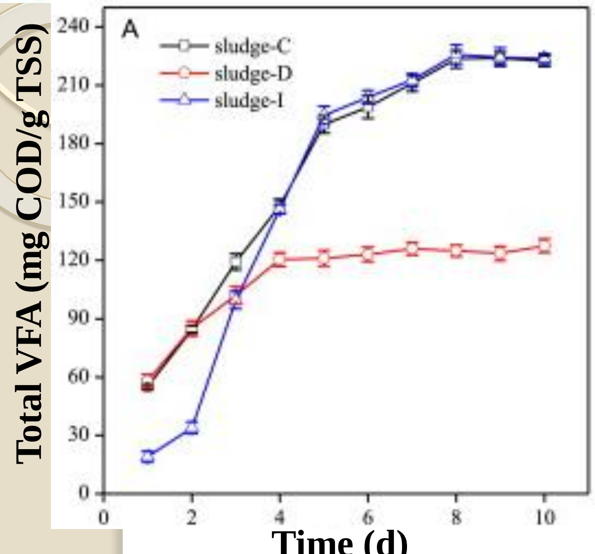
ENM	New York (mg/kg)	Shanghai (mg/kg)	London (mg/kg)
Ag	0.78−2.01	0.18−0.54	0.58−1.37
Al_2O_3	19−56	6−25	18−57
CeO_2	1.39−9.10	0.53−3.74	0.70−6.16
CNT	0.18−1.49	0.14−0.92	0.15−1.34
Cu + CuO_x	0.01−0.24	>0.01−0.12	0.01−0.21
Fe + FeO_x	49−114	12−36	41−91
nanoclays	8−11	2−4	7−12
SiO_2	6−45	4−27	5−40
TiO_2	273−342	70−123	263−367
ZnO	77−124	16−26	64−92

(Lazareva and Keller 2014)

> 90 % of Enginered nanoparticles removed from the wasterwater effluent via sorption to biosolids

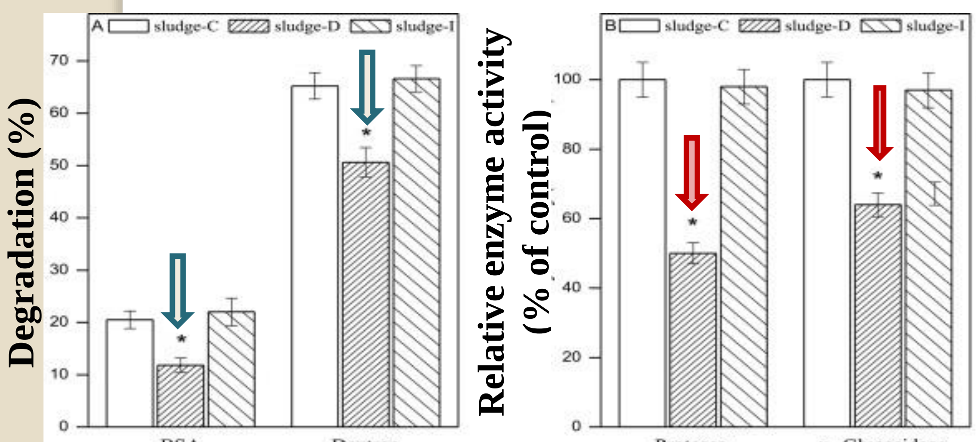
(*Westerhoff et al., 2011, Barton et al., 2014*).

NPs effects on AD: Direct vs Indirect spiking



Comparison between CuNPs entering into WWT system and sludge treatment system on VFA production (Chen *et al.*, 2014)

The direct addition of CuNPs led to decrease of maximal VFA production significantly while Cu NPs the entering initially from WWT system had no impact on the fermentative VFA production.



Sudden appearance of CuNPs in sludge anaerobic fermentation ➔ Inhibition of hydrolysis enzymes activities, thus a reduction of the amount of soluble products for acidification

Effect of direct/indirect addition of CuNPs on sludge hydrolysis (Chen *et al.*, 2014)

Analyses of NPs fate and behavior

Analysis		Methods
Aggregation	**Between NPs**	DLS measurements
	Between NPs and wastewater components	
Concentration		ICP-OES on biosolid and supernatant
Speciation		XAS
Ions' released: (seen as indirect cause of toxicity)		After ultrafiltration : ICP-OES or chemical dosages
Adsorption on biosolids		STEM-HAADF/ SEM-EDX/Hyperspectral microscopy
Adsorption on microorganisms		SEM-EDX

Results of NPs behavior in wastewater treatment and sludge digestion: Correlation with observed changes in Biological response and process efficiency?

Nanomaterials release in WWTP

- Nanomaterials are released down the drain during their whole life cycle
- Industrial and urban wastewater

Nanomaterials	Effluent	Biosolids
Ag[1]	0,0164-17µg/L	1,29-39mg/kg
TiO_2[1]	1-100µg/L	100-2000mg/kg
CeO_2[2]	0,007-1,17µg/L	0,53-9,10mg/kg

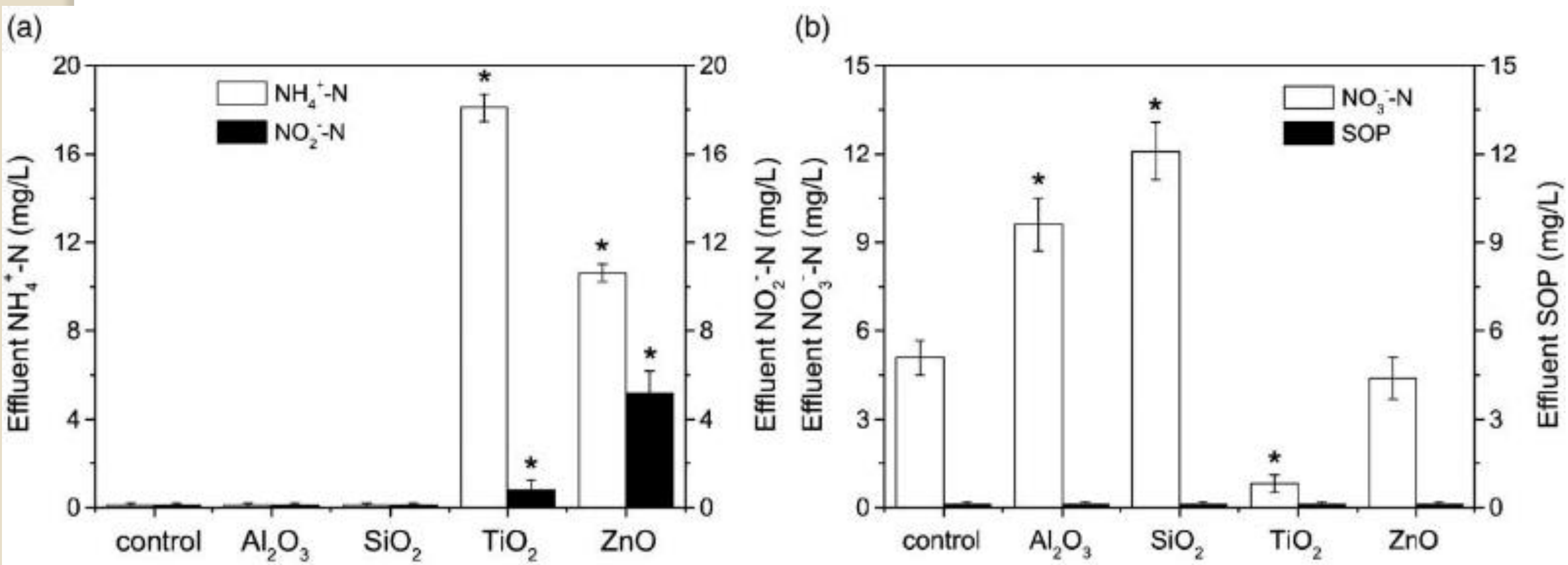
Tableau 1 : predicted environmental concentrations (PECs) of the most product nanomaterials in sewage sludge and effluent water
(Maurer-Jones et al. 2013)[1] (Lazareva and Keller 2014)[2]

Adverse effects of ENMs on N and P removal

- No impact on phosphorus removal

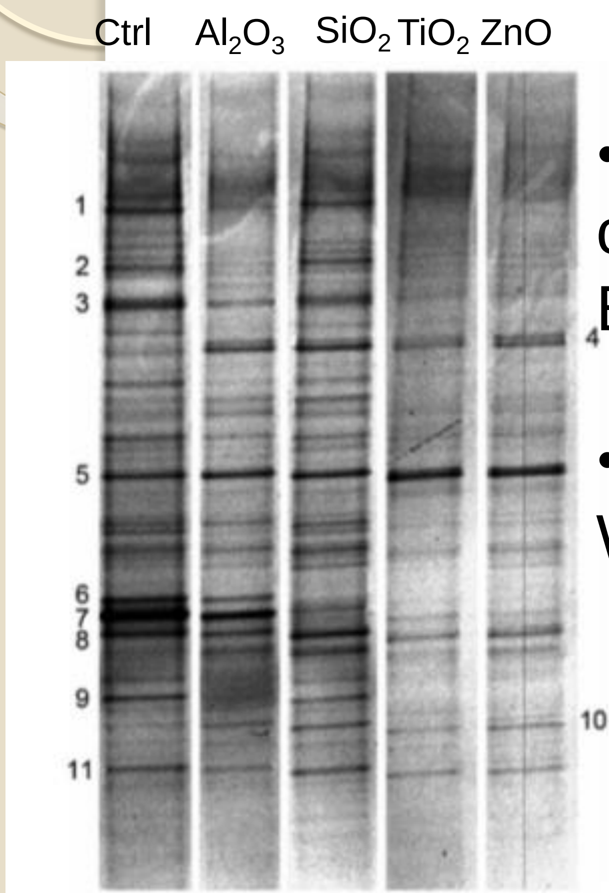
- Impact on nitrogen removal efficiency

-> related with changes in nitrifying/denitrifying bacterial community ?



Intermediary compounds concentration after ENMs long term exposure (50mg/L) *(Zheng et al., 2015)*

Effect of long term exposure to ENMs toward AS bacterial community



DGGE profiles of activated sludge bacterial community after long term exposure to 50mg/L ENMs *(Zheng et al., 2015)*

- Adverse effect of ENMs toward AS bacte community (TiO_2 & ZnO ++)
Especially those involved in N removal

- Observed with high ENMs concentration
What would happened with environmental c

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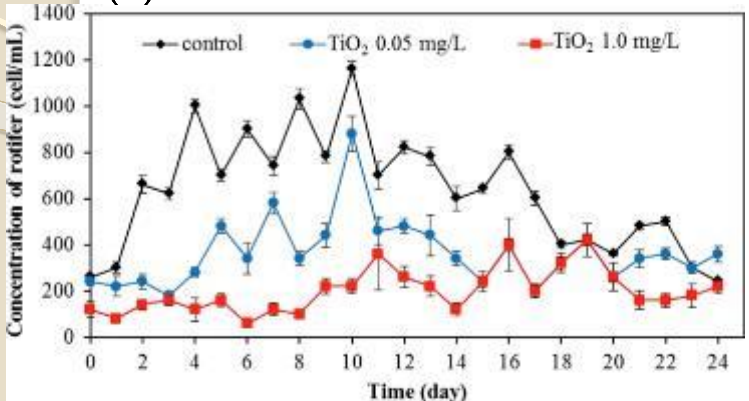
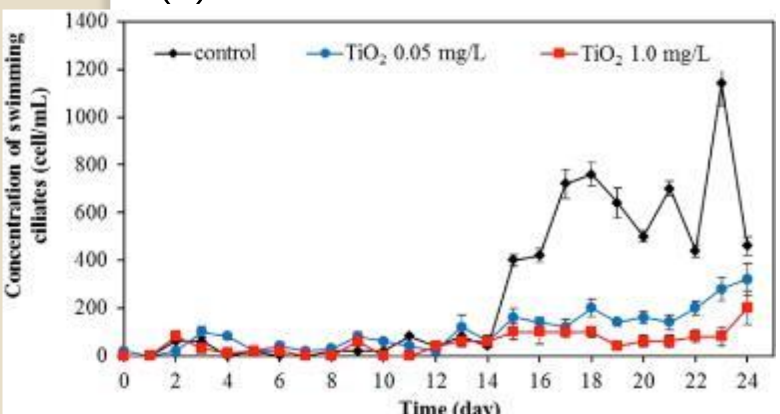
Adverse effects of nanoTiO$_2$ toward protozoa

- Counting using dye and microscop
- The only study about protozoa community
- Low doses of nanoTiO$_2$
- Impact on different protozoa communities involved in wastewater treatment

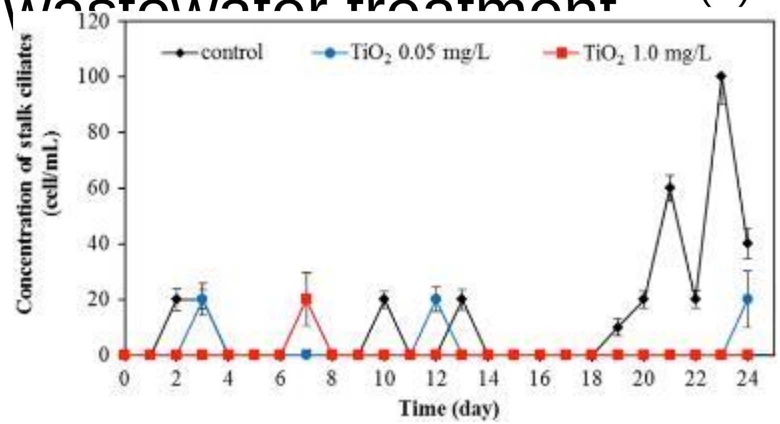
(A)



(B)



(C)



Changes in rotifer (A) and free-swimming (B) or stalkes ciliates (C) concentration with various nanoTiO$_2$ doses (Supha et al., 2015)

Nanomaterials interaction with Sludge EPS

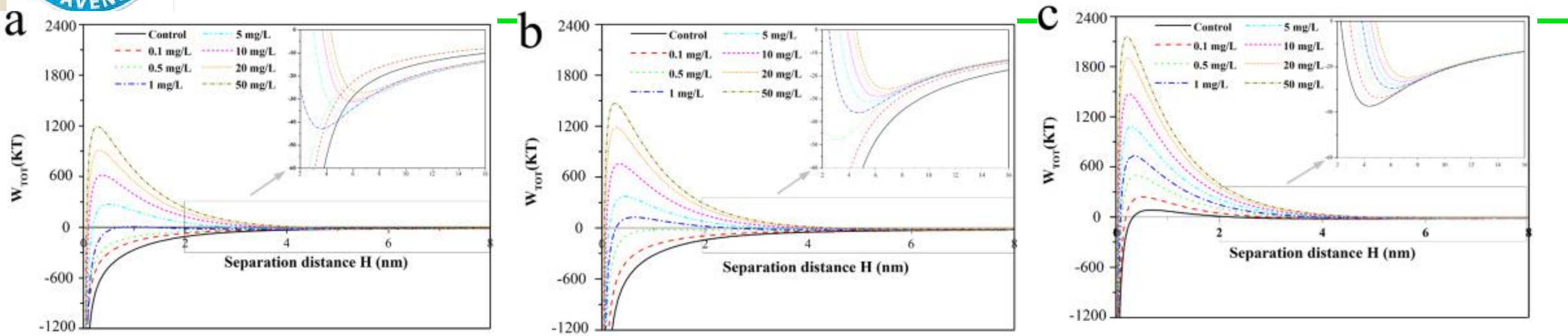


Fig. Effects of CeO_2 NPs on the total interaction energy curves of sludge (a) before EPS extraction, (b) after LB-EPS extraction and (c) after TB-EPS extraction(You et al. 2016).

- After exposure to low [CeO_2](0.1, 0.5 and 1 mg/L), the interaction remains attractive ➔ low concentrations of do not significantly affect the aggregation of the sludge.
- The energy barrier increased after the extraction of the LB-EPS ➔ shifting from attractive to repulsive, to ➔ thermodynamically unfeasible spontaneous adsorption aggregation between microbial aggregates.
- Removing TB-EPS resulted in the shifting of energy barrier to the highest levelthe energy barrier ➔ ~~TB-EPS was more important for high flocculability and aggregation of the sludge~~