Environmental Science: Nano

ARTICLE

Toxicity of dimercaptosuccinate-coated and un-functionalized magnetic iron oxide nanoparticles towards aquatic organisms

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ya-Qi Zhang,[a] Ralf Dringen,[b, c] Charlotte Petters,[b,c] Wiebke Rastedt,[b,c] Jan Köser,[a] Juliane Filser,[d] and Stefan Stolte[a,e]

Electronic supplementary information (ESI)

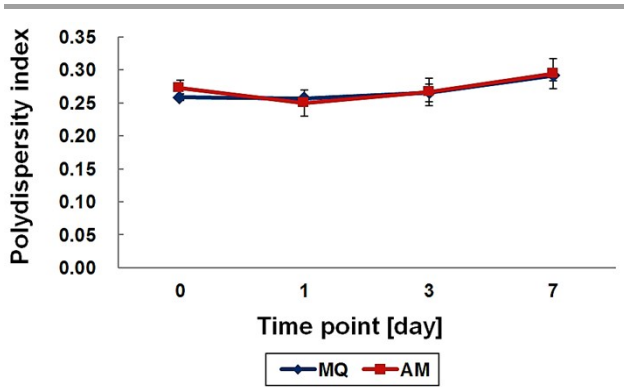

Fig. § 1 Polydispersity index (PI) of DMSA-IONP (1791 µM Fe, i.e. 100 mg Fe/L) dispersed in MilliQ water (MQ) or algae medium (AM). Samples were measured at days 0, 1, 3 and 7. Data shown represent mean values ± SD (n=15).

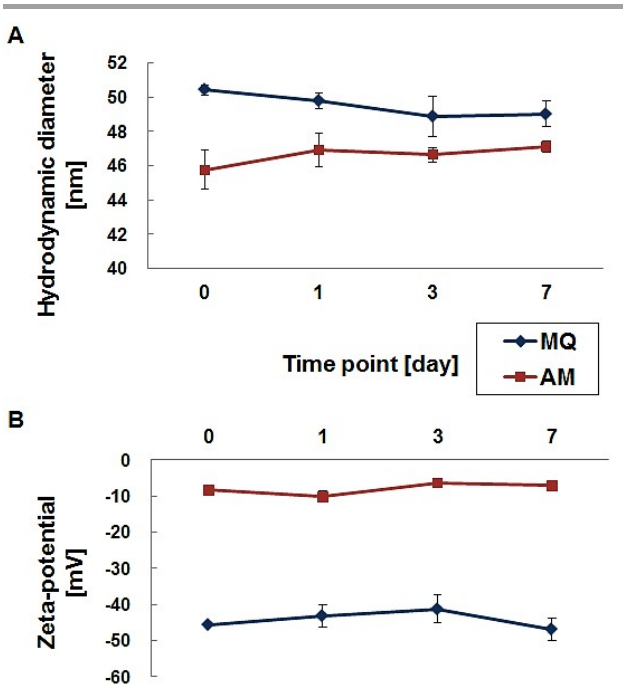

Fig. § 2 Hydrodynamic diameter **(A)** and zeta-potential **(B)** of DMSA-IONP (1791 µM Fe, i.e. 100 mg Fe/L) dispersed in MilliQ water (MQ) or algae medium (AM). Samples were measured at days 0, 1, 3 and 7. Data shown represent mean values ± SD (n=15 or 9).

[a] *UFT - Centre for Environmental Research and Sustainable Technology, Department Sustainable Chemistry, University of Bremen, Leobener Straße, D-28359, Bremen, Germany. *E-mail: stefan.stolte@uni-bremen.de.*
[b] *CBIB - Centre for Biomolecular Interactions Bremen, Neurobiochemistry, Faculty 2 (Biology/Chemistry) University of Bremen, Leobener Straße / NW2, D-28359, Bremen, Germany.*
[c] *UFT - Centre for Environmental Research and Sustainable Technology, Department Neurobiochemistry, University of Bremen, Leobener Straße, D-28359, Bremen, Germany.*
[d] *UFT - Centre for Environmental Research and Sustainable Technology, Department General and Theoretical Ecology, Faculty 2 (Biology/Chemistry) Leobener Straße, D-28359, Bremen, Germany.*
[e] *Department of Environmental Analysis, Faculty of Chemistry, University of Gdańsk, ul. Wita Stwosza 63, 80-308 Gdańsk, Poland.*

Table § 1 Hydrodynamic diameter (*d*) and zeta-potential (z) of uncoated IONP and DMSA-IONP dispersed in MilliQ water or the three test media (447.7 µM Fe, i.e. 25 mg Fe/L) at beginning of the test (t_0) (n=15 or 9).

	Uncoated IONP				DMSA-IONP			
	MQ	**AM**	**DM**	**LM**	**MQ**	**AM**	**DM**	**LM**
***d* (z-average) [nm]**	56.53	5956	5351	5146	63.48	51.03	3857	151.13
	± 1.38	± 1045	± 823	± 1171	± 7.10	± 0.27	± 258	± 6.32
z [mV]	39.83	-16.25	1.40	-12.86	-59.52	-21.20	-14.49	-19.58
	± 4.43	± 0.14	± 0.18	± 0.28	± 1.12	± 1.74	± 0.28	± 0.33
pH	4.3	7.4	6.6	4.7	6.4	6.7	6.5	4.9

To check for the concentration and pH effects on the colloidal properties additional characterizations were done for IONP samples with 25 mg Fe/L (447.7 µM Fe). Scattering intensities for IONP samples below this concentration were expected to be below 10000 cps (counts per second) and therefore likely to cause unreliable data evaluation of the autocorrelation functions.

Table § 2 Hydrodynamic diameter (*d*) and zeta-potential (z) of DMSA-IONP dispersed in MilliQ water or algae medium (447.7 µM Fe, i.e. 25 mg Fe/L) after day 3 or 7 (n=15 or 9).

	Day 3		Day 7
	MQ	**AM**	**MQ**
***d* (z-average) [nm]**	56.55	52.09	57.63
	± 0.33	± 0.39	± 1.71
z [mV]	-36.63	-31.92	-38.82
	± 2.46	± 2.47	± 10.29
pH	6.2	7.2	6.7

Table § 3 The effect of pH in terms of the three test media (pH 5.5, 7.0 and 8.1 for LM, DM and AM, respectively) on the hydrodynamic diameter (*d*) and zeta-potential (z) of IONP dispersed in MilliQ water at 25 mg Fe/L (447.7 µM Fe, n=15 or 9).

	Uncoated IONP			DMSA-IONP		
pH	**5.5**	**7.0**	**8.1**	**5.5**	**7.0**	**8.1**
***d* (z-average) [nm]**	1562	7693	2775	53.32	56.16	54.16
	± 124.39	± 1978	± 1144	± 0.50	± 1.43	± 0.41
z [mV]	26.92	-13.09	-10.85	-42.53	-49.64	-41.18
	± 0.78	± 8.52	± 1.27	± 1.62	± 2.28	± 7.12

Table § 4 Speciation of iron ions (10 µM Fe, i.e. 0.56 mg Fe/L) in the standard (Normal) or iron-free (MQ) algae medium calculated with PHREEQCi (v.3).

FAC: $(NH_4)_5Fe^{III}(Citrate)_2 \cdot 2H_2O$, FAS: $(NH_4)_2Fe^{II}(SO_4)_2 \cdot 6H_2O$, EDTA: Ethylenediaminetetraacetic acid

Scenario	Iron salt	Medium	Iron species [µM]						Precipitation $Fe(OH)_3$ [µM]
			Fe^{2+}			Fe^{3+}			
			Total dissolved	EDTA associated	Citrate associated	Total dissolved	EDTA associated	Citrate associated	
a	FAC	Normal	5.13E-04	1.80E-06	2.86E-04	1.02E+01	1.61E-01	3.25E-04	Not allowed
	FAC	MQ	3.96E-08	-	2.21E-08	1.00E+01	-	3.26E-04	Not allowed
	FAS	Normal	1.00E+01	2.16E-01	-	2.37E-01	9.50E-03	-	Not allowed
	FAS	MQ	1.00E+01	-	-	6.71E-05	-	-	Not allowed
b	FAC	Normal	1.54E-10	5.53E-13	8.59E-11	1.02E+01	1.59E-01	3.26E-04	Not allowed
	FAC	MQ	1.54E-10	-	8.60E-11	1.00E+01	-	1.06E-03	Not allowed
	FAS	Normal	7.05E-11	5.44E-13	-	1.02E+01	2.48E-01	-	Not allowed
	FAS	MQ	7.01E-11	-	-	1.00E+01	-	-	Not allowed
c	FAC	Normal	9.58E-06	1.17E-06	4.70E-06	1.81E-03	9.01E-04	3.03E-08	1.02E+01
	FAC	MQ	5.62E-10	-	3.14E-10	9.12E-04	-	3.03E-08	1.00E+01
	FAS	Normal	1.00E+01	2.29E-01	-	9.70E-04	6.47E-05	-	2.36E-01
	FAS	MQ	1.00E+01	-	-	6.71E-05	-	-	0.00E+00
d	FAC	Normal	1.64E-14	2.18E-15	7.95E-15	1.91E-03	9.94E-04	3.04E-08	1.02E+01
	FAC	MQ	1.42E-14	-	7.94E-15	9.12E-04	-	3.04E-08	1.00E+01
	FAS	Normal	8.71E-15	2.19E-15	-	1.92E-03	1.00E-03	-	1.02E+01
	FAS	MQ	6.51E-15	-	-	9.19E-04	-	-	1.00E+01

In Table § 4 speciation calculations of iron ions (after addition of 10µM of FAS and FAC; pH 8.1) in the presence of EDTA and citrate have been performed for four scenarios:

a) No oxygen is present in the media and precipitation of $Fe(OH)_3$ is not allowed (assumed to be 'infinitely slow').

b) Media are saturated with 8.3 mg/L (0.261 mM) oxygen and precipitation of $Fe(OH)_3$ is not allowed (assumed to be 'infinitely slow').

c) No oxygen is present in the media and precipitation of $Fe(OH)_3$ is allowed.

d) Media are saturated with 8.3 mg/L (0.261 mM) oxygen and precipitation of $Fe(OH)_3$ is allowed.

Some main conclusions from this table:

- the presence of oxygen drastically reduces the concentration of Fe^{2+} which is almost quantitatively converted to Fe^{3+};

- at this pH (8.1) most of the added iron ions should precipitate as $Fe(OH_3)$ (even this was not observed visually in our experiments);
- EDTA as well as citrate do increase the (bio)availability of (in particular) Fe^{3+}, but under these conditions most iron ions are not associated to EDTA or citrate.