

Transformation / Dissolution of Titanium Dioxide Grades in Environmental Media

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Introduction & objectives

The assessment of the ecotoxicity of TiO₂ grades is progressing through the REACH evaluation process. The aquatic hazard of metal substances is typically determined by their dissolved ions, and the respective assessment does not take exposures to the undissolved fraction into account. Therefore, the transformation and dissolution (T/D) of six different nano- and micro-TiO₂ grades were investigated according to OECD Monograph No. 29 (1) and under GLP. The test was conducted to determine the rate and the extent to which TiO₂ particles in solution remain dispersed or produce ionic titanium species.



Fig. 1: Transformation / Dissolution test setup

Materials and methods

Six different commercial TiO₂ grades (pg-1, pg-2, pg-3, uf-1, uf-2, uf-3) varying in size, specific surface area and crystal structure were tested with loadings of 1 mg/L at pH 6 and 8 over 28 days. Solutions were sampled after 24, 168, 336 and 672 h (Fig. 1). One subsample was filtered through a polyethersulfone (PES) membrane (pore size 0.2 μm) to obtain the fraction containing dispersed material < 200 nm.

A further subsample was subjected to centrifugal filtration (Fig. 2) through a 3 kDa (approx. 2 nm, 30000xg, 60 min) PES membrane; operationally defined as fraction potentially containing ionic species.

Fig. 2: Centrifugal filtration tube (yellow: Dispersion above membrane; filtrate in the bottom. Colored dispersion for illustration)



Ti concentrations of test solutions were measured by ICP-OES. Mean Ti concentrations are based on duplicate samples of triplicate vessels corrected for Ti background levels.

To derive mean concentrations, Ti concentrations below the LOD/LOQ were estimated as follows: LOD = LOD / √2 and LOQ = LOD + 0.5 (LOQ - LOD).

The applicability of centrifugal filtration was confirmed by analyzing a filtered aqueous Ti standard. Additionally, aqueous dispersions of 1 g/L of the six TiO₂ grades and one control (ultrapure water) were sampled after two days, subjected to centrifugal filtration and the Ti concentrations of the filtrate were measured.

Results

Centrifugal filtration is applicable to collect the (operationally defined) dissolved titanium fraction (Table 1) as already confirmed for Ag ions (2).

Table 1: Validation information for centrifugal filtration

	Ti standard	Control (water)
loading [μg/L]	1	-
[μg/L Ti]	0.981 ± 0.09 (n=3)	< LOD (<0.171)
mean recovery [%]	98.1 ± 8.6	
TiO ₂ test item	pg-3, uf-1, uf-2	pg-1, pg-2, uf-3
loading [g/L]	1	1
[μg Ti/L]	< LOD (<0.171)	< LOQ (<0.512)

Measured Ti concentrations of both fractions of T/D solutions at pH 8 were below the LOD/LOQ. Thus, only measured Ti concentrations of T/D solutions at pH 6 are summarized in Table 2. Ti concentrations of blanks and several samples of T/D solutions at pH 6 were below the respective LOD/LOQ.

Table 2: Ti concentrations of T/D solutions at pH 6 (Means ± standard deviation)

	pg-1 [μg Ti/L]	pg-2 [μg Ti/L]	pg-3 [μg Ti/L]
0.2 μm filtered and background corrected			
24h	4.02 ± 0.54	0.65 ± 0.12	1.12 ± 0.26
168h	1.54 ± 0.93	0.42 ± 0.16	0.71 ± 0.31
336h	0.56 ± 0.28	<LOQ (<0.36)	0.33 ± 2.1
672h	0.49 ± 0.18	<LOD/LOQ (<0.10/<0.30)	LOD/LOQ (<0.11/0.34)
centrifugally filtered and background corrected			
24h	<LOQ (<0.51)	<LOD/LOQ (<0.17/0.51)	<LOQ (<0.51)
168h	<LOD/LOQ (<0.11/0.34)	0.09 ± 0.05	<LOQ (<0.34)
336h	<LOD/LOQ (<0.11/0.32)	<LOD/LOQ (<0.12/0.36)	<LOD/LOQ (<0.11/0.32)
672h	<LOD/LOQ (<0.11/0.34)	<LOD/LOQ (<0.10/<0.30)	<LOD/LOQ (<0.11/0.34)
	uf-1 [μg Ti/L]	uf-2 [μg Ti/L]	uf-3 [μg Ti/L]
0.2 μm filtered and background corrected			
24h	5.72 ± 2.06	<LOQ (<0.42)	0.94 ± 0.70
168h	0.27 ± 0.18	1.02 ± 0.44	0.76 ± 0.62
336h	<LOD/LOQ (<0.11/0.32)	0.55 ± 0.27	0.24 ± 0.15
672h	<LOD/LOQ (<0.11/0.34)	1.13 ± 0.71	<LOD/LOQ (<0.10/0.30)
centrifugally filtered and background corrected			
24h	<LOD (<0.14)	<LOD (<0.14)	<LOD (<0.14)
168h	<LOD (<0.11)	0.05 ± <0.01	0.10 ± 0.02
336h	<LOD (<0.11)	<LOD/<LOQ (<0.12/0.36)	<LOD/LOQ (<0.12/0.36)
672h	<LOD (<0.11)	<LOD (<0.10)	<LOD/LOQ (<0.10/0.30)

Conclusions

- Centrifugal filtration can be applied to collect an operationally defined fraction assumed to contain dissolved Ti species.
- Low levels of dispersed TiO₂ < 200 nm are present under environmentally relevant conditions at pH 6 but a decrease is observed over 28 days for most of the TiO₂ grades.
- All six different commercial nano- and micro-TiO₂ grades do not release detectable soluble ionic Ti species in aqueous media under standard T/D conditions. Therefore it can be assumed that the limit of solubility for ionic Ti is <0.3 μg/L

References

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Acknowledgements

We thank TDMA / TDIC for funding this research. The study may not be freely used to comply with regulatory requirements like REACH without the formal agreement of TDMA/TDIC.

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Keywords: bioaccumulation, PBT assessment, earthworms, terrestrial oligochaetes

The assessment of the ecotoxicological potential of titanium dioxide grades is progressing through the REACH evaluation process. Conventionally, the aquatic hazard classification schemes for metal substances are primarily determined by the hazards elicited by their dissolved metal ions, and typically do not take exposures to metal substances that are not dissolved in the water column into account. Therefore, the transformation and dissolution of 6 different nano- and micro-TiO₂ grades were investigated according to OECD Monograph No. 29: Guidance Document on Transformation / Dissolution (TD) of Metals and Metal Compounds in Aqueous Media (2001 and under Good Laboratory Practice. The T/D protocol, including conditions and media representative of those generally occurring in the aqueous environment, was applied to determine the rate and extent to which TiO₂ grades in solution remain dispersed or produce ionic Ti species.

The six different commercial TiO₂ grades tested varied in size, specific surface area and crystalline structure. Six T/D studies were performed with a loading of 1 mg TiO₂/L of each grade at pH of 6 and 8 for 28 days, respectively. Solutions were sampled for the analysis of Ti concentrations after 1, 7, 14 and 28 days. Samples were filtered through polyethersulfone membranes with a pore size of 200 nm and 3-kDa membranes via centrifugal filtration (corresponding to a pore size of approximately 2 nm) to separate the operationally-defined dispersed and dissolved fractions. The feasibility of the method was validated with a commercial standard containing a certified dissolved Ti concentration; titanium in the respective filtrate was fully recovered (100 ± 15 %). ICP-OES was used to quantify aqueous Ti concentrations since calcium contained in the standard T/D media may interfere with ICP-MS measurements.

Titanium concentrations of all solution samples after centrifugal filtration were below the limit of quantification or detection (< 300 ng/L). Dispersed Ti concentrations up to 5 µg/L were measured for some materials at pH 6 whereas dispersed Ti concentrations of solutions at pH 8 were below the detection limit. The results indicate that all 6 different commercial nano- and micro-TiO₂ grades do not release detectable soluble ionic Ti species in aqueous media under standard T/D conditions.