

ENVIRONMENTAL RESEARCH OF THE
FEDERAL MINISTRY OF THE ENVIRONMENT,
NATURE CONSERVATION AND NUCLEAR SAFETY

Project No. (FKZ) 3710 65 414

Report No. (UBA-FB) 001741/E

Mobility, fate and behavior of TiO₂ nanomaterials in different environmental media Summary

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On behalf of the Federal Environment Agency (Germany)

UMWELTBUNDESAMT

This publication is only available online. It can be downloaded from
<http://www.uba.de/uba-info-medien-e/4568.html>.

The contents of this publication do not necessarily
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ISSN 1862-4804

Study performed by: IUTA e.V., Air Quality & Sustainable Nanotechnology
Bliersheimer Str. 60
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Study completed in: August 2012

Publisher: Federal Environment Agency (Umweltbundesamt)
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Edited by: Section IV 2.2 Pharmaceuticals, Washing and Cleaning Agents
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Dessau-Roßlau, August 2013

1. Abstract

Nanomaterials are nowadays used in increasing amounts in everyday products and special applications. Enhanced release of engineered nanomaterials (ENM) into the environment can hence be assumed. First experimental studies and environmental modelling exercises have been conducted during the last years (Gottschalk et al., 2010; Kuhlbusch et al. 2012; Limbach et al., 2009; Kiser et al., 2009) significantly improving our knowledge on release and environmental behaviour. Still not all necessary test procedures and information are yet available to assess the fate of ENMs in the environment. One major current lack is the knowledge on the stability of the coating of ENM, which determines the environmental behaviour. Another knowledge gap is the information of a possible carrier function of nanomaterials in soils for soil pollutants. Hence methodologies to study coating stability as well as carrier effects were developed and tested for three different TiO₂ nanomaterials, as one of the most used ENM in products, in soils and aqueous media. More precisely,

- The first part of the study dealt with a method development for the stability testing of the coating of two different functionalised TiO₂ nanomaterials. The stability was analysed covering different environmental conditions like pH, ionic strength and dissolved organic carbon concentration.
- The second part of this study analysed the carrier function of P25 for the two different substances, copper and ¹⁴C triclocarban, in three different soil types.

The surface of a material determines its behaviour in the environment (e.g. isoelectric point, adsorption capacity, and repulsion). Hence changes of surface properties and especially of coatings and their stability are of importance. A method determining surface coating stability was developed and tested with two coated titanium dioxide nanomaterials.

Changes of surface coating can be determined in different ways: a) by quantifying the released coating material in e.g. the suspension media, b) by quantifying the coating material on the nanomaterial prior and after exposure to stress conditions, and c) indirectly by determining changes in the behaviour of the ENM, e.g. changes in particle size distributions, the isoelectric point (IEP). The above endpoints were analysed for the suspension of ENMs in deionised water with as little energy input as well as for conditions as can be expected in the environment (pH, IS, DOC) or for test procedures applied in the laboratory to study environmental behaviour. This concept for testing surface coating stability can be applied to any ENMs but the analytical methods have to be chosen

according to the material and media tested. The combined information from the studies are then discussed and interpreted in view of surface coating stability.

The two ENM chosen for evaluation were the hydrophobic coated NM103 (UV Titan M262) and the hydrophilic coated NM104 (UV Titan M212). The materials are produced with two layers of coatings: an Al₂O₃ layer for averting photo-oxidation (around 6 weight-%) and a second layer of dimethicone / glycerol molecules (around 1 – 2 weight-%) on top of the Al₂O₃ layer to ensure hydrophobic / hydrophilic behaviour.

First tests of coating stability were done using stirring of the nanomaterial in deionised water. Measurements revealed that about 88% ± 8% of the glycerol of the NM104 and 95% ± 5% of the silicon of the NM103 were already dissolved by low energy input. These results were confirmed by corresponding analysis of the remaining ENM which showed no significant concentrations of dimethicone or glycerol. Aluminum concentrations, indicating possible dissolution of the inorganic coating, were below detection limit as expected due to its low solubility at pH > 4.5. Measurements of the IEP confirmed this finding with IEPs around pH 8 as expected for an alumina surface. The IEP for TiO₂ is expected at a significantly higher pH around 5-7.

Additionally, different suspension preparation procedures with different energy input were tested to derive further information on coating stability. Tests using mixing (without external energy input), 1 min stirring after suspending the powder, and 1 minute sonication (ultrasonic probe) followed by 1 hour of moderate stirring (SOP) were compared as methods for suspension preparation. It was shown that the release of the organic coating increased with increasing energy input. Nearly all of the second coating was removed using the established SOP. This was confirmed by SEM / EDX and by ToF SIMS analysis, which identified a TiO₂ core and an aluminium oxide and dimethicone coating for the basic material and a TiO₂ core and an aluminium oxide coating without dimethicone after suspension preparation. Glycerol could not be specified with the two techniques.

The Al₂O₃ coating was proven to be stable and independent of the type of energy input and even after longer sonication. Zeta potential measurements indicate an isoelectric point of the coated TiO₂ nanomaterials around pH 8-9, which is comparable with the isoelectric point of alpha aluminium oxide and different from the isoelectric point of TiO₂ (Kosmulski, 2006). Furthermore EPR analyses showed no ROS formation even when the material was illuminated in the UV light. This results support the previous results of an intact aluminium oxide layer on tested TiO₂ materials after suspension in deionised water. Therefore we conclude that the aluminium oxide coating will be the actual surface of the two materials.

Effects of different environmental conditions on the ENM behaviour were then mimicked by varying the ionic strength using Ca²⁺ as one of the major cations in surface waters (von der Kammer et al., 2010) and the dissolved organic carbon content (here different concentrations of humic acid - AHA). Zeta potential measurements were conducted as well as the size of the materials under these varying conditions as an indicator of possible changes in environmental behaviour.

The variation of the ionic strength (CaCl₂ concentration) showed an impact on the interfacial properties, in particular in basic media. No isoelectric point below pH 10 could be identified in freshly prepared suspensions (CaCl₂ solution > 0.001 M). With increasing ionic strength the agglomeration of the ENM increased. A gradual change of the zeta potential was observed with IEPs moving back to lower pH values. This change may be explained by low kinetics and possible uptake of CO₂. The latter influences the ion balance.

A different situation occurs if the ENMs were suspended in aqueous systems containing DOC (humic acid). DOC adsorbs on the ENM surface. It seems that this adsorption is quite stable since changes in pH and ionic strength had only a small influence on the zeta potential. The surface charge was strongly negative e.g. for DOC concentrations ≥ 2.5 mg/L, also in the presence CaCl₂.

The tests clearly show that coating stability can vary significantly. Stable coating can alter the environmental behaviour significantly. This is shown by the change of the IEP for Al₂O₃ coated TiO₂. The coating has an influence on the zeta potential which has influence on soil ENM interactions and hence soil transport of ENM. Influences of the ionic strength as well as of DOC on the zeta potential were clearly shown. It seems that especially DOC is of importance. The humic acid used in this study lead to a (steric) stabilisation of the ENMs and a negative zeta potential. Both lead to higher ENM mobility in negatively charged soil environments.

The possible carrier effect of P25 for soil pollutants was the second research topic to be investigated. Recent studies indicated that mobile nanomaterials can act as carrier for pollutants (Hofmann and Kammer, 2009; Fang et al., 2011). Trichlocaban (TCC) and a copper salt (CuSO₄) were chosen as soil contaminants to be tested due to the relevance and analytical advantages. Three different natural soil types were employed. Only low soil mobility was observed for P25 in this study in agreement to a previous study (Kuhlbusch et al., 2012). The transport of isolated agglomerates down to the last segment of the soil column could only be observed using electron microscopy coupled with a chemical analysis (SEM / EDX) independent on the soil type. The low mobility of P25 is probably affected by the positive zeta potential of the material in the expected pH range

of the soils. With the positive zeta potential a higher adsorption on negatively charged surfaces, like soil minerals, is likely, which reduces the mobility of the material in the system. Hence no carrier effect of P25 was expected.

For copper a low and pH dependent mobility with and without P25 was detected. The soil types with the lowest pH (soil type G03 and A01) showed a significant higher mobility whereas the soil type with the highest pH and highest cation exchange capacity (soil type A02) showed the lowest mobility. This is in agreement with previous results showing the pH dependent mobility of copper in soils, higher mobility at lower pH.

A similar soil type dependent mobility, but overall a lower mobility of copper was observed when TiO₂ nanomaterial was added to the first centimetre in the soil column. This may be explained by the adsorption of the copper onto the P25 surface. The low mobility of P25 would then also lead to a lower mobility for copper. Results of Fang et al. (2011) agree with this hypothesis, but it should be noted that Fang et al. tested a TiO₂ nanomaterial with a negative zeta potential.

Comparable results were also shown for the experiments with TCC, which was employed at very low concentrations. Radioactive labelling of TCC with ¹⁴C allowed the use of these low concentrations. TCC soil mobility was lower than for copper in all tested soil types. Anyhow, the presence of P25 diminished the mobility of TCC even more but not significantly, also in the sandy soils at low pH.

Even though the results were similar for TCC and copper, it has to be noted that the results probably differ for other nanomaterials, e.g. showing increased soil pollutant mobility when ENM is added.

Overall, reduced mobility of soil pollutants may lead to an accumulation in the upper soil layers. The formation of accumulation layers with high concentrations of pollutants can be hazardous for soil organisms like lumbricidae which live in the upper soil layer.

On the other hand, ecotoxicological tests conducted in the framework of this study show that the presence of TiO₂ leads to higher fractions of TCC in the gut of a common earthworm and lower negative effects of the compound towards this organism. It is hypothesised that the adsorption of TCC on the TiO₂ surface may facilitates its excretion leading to lower negative effects. Only few similar investigations have been published so far, and hence, more research is necessary to enable some generalisations on the overall influence of (inorganic) nanomaterials on the bioavailability of organic compounds.

Nevertheless, both tests, the soil leaching experiments and the bioavailability tests, proof that ENMs, here TiO₂ might have a significant influence on the fate of environmentally important pollutants.

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