



Nanoparticles and refractory organic matter: Interactions and consequences



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ABSTRACT

The broad application of engineered nanoparticles (ENP) will inevitably lead to their increased discharge into the environment, especially into aquatic systems. There, they meet refractory organic matter (ROM) of the humic type which is ubiquitous. In this contribution, the physical, chemical and microbiological interactions between ENP and ROM were investigated using nanoparticulate maghemite ($\gamma\text{-Fe}_2\text{O}_3$), SiO_2 with positive (e.g. $>\text{Al}^+$) and negative ($-\text{OH}$) surface charge, TiO_2 (P25; ratio of anatase/rutile = 3:1), self-synthesised silver nanoparticles (n-Ag), ROM from a brown water lake and different microorganisms (MO). The physical interaction of ENP and ROM under well-defined conditions followed the Langmuir equation. Zeta potential (ZP) of the (nano)particles changed with ROM concentration and pH value of the solution. Photocatalytically active TiO_2 -NP generated OH^{\bullet} -radicals for the degradation of ROM via low molecular size intermediates. Finally, the toxicity of ENP for microbiological cells was quantified with EC_{50} values. Generally, the presence of ROM led to a distinct detoxification. All these results allow a deeper understanding of the principles of interactions between ENP and ROM. In particular, they are relevant to understand the environmental impact of ENP and to contribute to their beneficial application in technical systems.

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Introduction

Modern technologies leave their footprints in the environment, leading to highly interesting interactions between technogenic matter and the (bio)geogenic one. These interactions are of vital importance regarding the fate and function of the manifold substances in the environment and in the world of technology. In this context, engineered nanoparticles (ENP) and natural organic matter (ROM) are a prominent and well-suited couple to investigate physical, chemical and biochemical principles of mutual influence, especially in aquatic systems [1–3].

ENP are intensively used in industrial products such as pharmaceuticals, cosmetics, dyes and building materials [4–6]. Driven by their broad application, the understanding of ENP and their technical properties has increased significantly [7–9]. Estimates offer production numbers for ENP of worldwide $100,000 \text{ t year}^{-1}$ [10]. However, the knowledge on the actual production of ENP and on their distribution and behaviour in the (aquatic) environment is still poor [11,12]. One of the reasons is the unavailability of sound analytical data especially for the

realistically low concentration ranges in aquatic systems and the complex matrices of polluted waters [1,12].

In such environments, ENP meet the ubiquitous humic matter, which is a complex mixture of biopolymers and their microbial transformation products. Due to generations of worldwide investigations, concentrations were found ranging from 0.5 to 100 mg L^{-1} , given as total or dissolved organic carbon (TOC, DOC) in rivers, lakes and the sea [13,14]. Humic matter is often poorly defined and referred to as natural organic matter (NOM) or refractory organic matter (ROM; used in this paper). In swamps and waste waters, ROM and the operationally defined fulvic acids and humic acids content reaches up to a few tens mg L^{-1} of carbon [13,14]. The given range also holds for soil seepage and pore water. Deposits of solid ROM are ubiquitous. They are wherever they can be dissolved, biotransformed, transported and/or wherever they are in contact with water. Therefore, they have a significant impact on the availability of TOC and DOC in the system concerned [15].

In recent years, it became more and more evident that the interactions between ENP and ROM have to be considered to follow the environmental behaviour of ENP [1]. However, most investigations on ENP and ROM have focused only on the one or on the other. As both types of substances have to be expected to occur simultaneously in environmental and technical aquatic systems, the question arises on the resulting interactions. In this

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contribution, the alterations of ENP in aquatic systems are considered, which has turned out to be key in assessing the hazards of ENP in the aquatic environment. Ageing of ENP is still not thoroughly considered in literature [1].

In this contribution, we highlight the impact of ROM on the physico-chemical properties of ENP and the resulting effects on microorganisms (MO), especially regarding toxicity and disinfection efficiency.

In particular, the aims of the work were to:

- Give basic facts of ROM and selected inorganic ENP to understand the driving forces for their interactions in aqueous systems.
- Identify the major impact of ROM on the physico-chemical properties of ENP.
- Link the influence of the altered physico-chemical properties of ENP on aquatic MO.

We are aware of the fact that the huge variety of the materials involved in natural systems needs to restrict and to focus on typical representatives. Nanoparticulate metal oxides and semiconductors (FeOx, SiO₂, TiO₂) and nanoparticulate silver (n-Ag) were chosen according to their technical relevance. MO (*Escherichia coli*, *Saccharomyces cerevisiae*, *Pseudomonas putida* and *Lactobacillus plantarum*) as target cells were selected with respect to their role in water quality control and water management. The ROM sample was taken from a preserved brown water lake in the Black Forest (Lake Hohloh, HO; Germany), which has been used as source for well-characterised reference material for humic substances of the International Humic Substances Society (e.g. fulvic acid, HO-FA; humic acid, HO-HA).

Materials and methods

Materials and substances

As NP, commercially available NP were used without additional cleaning or NP were self-synthesised in the laboratory as described in [16,17] (Table 1). Chemicals used were of analytical grade (Merck, Germany) if not stated otherwise.

In brief, Fe oxide NP were synthesised according to [16]. For this purpose, FeCl₂ and FeCl₃ (molar ratio 1:2) were dissolved in acidified and deoxygenated distilled water (ultrapure water, Milli-Q; Millipore). Cautious dropwise addition of oxygen-free NaOH (*c*(NaCl)=1.5 mol L⁻¹) formed magnetite (Fe₃O₄) which was magnetically separated, resuspended and centrifuged under exclusion of air (3 times, 4000 × g, 30 min). The third resuspension was done under agitation (18 h) in hydrochloric acid (*c*(HCl)=0.01 mol L⁻¹). The supernatant of the last centrifugation, containing colloidal magnetite, was oxidised with air (100 °C, 30 min) yielding maghemite (γ-Fe₂O₃) of red-brown colour.

Ag NP (n-Ag) were synthesised via reduction of aqueous AgNO₃ by NaBH₄ (*c*(Ag)=0.2 mmol L⁻¹, *c*(NaBH₄)=1 mmol L⁻¹). The

Table 1
Details and origin of the ENP used.

Material	Details	Remarks
FeOx	Fe ₃ O ₄ → 3γ-Fe ₂ O ₃	Synthesis according to [16]
SiO ₂	—SM TM (—OH; “—”)	Ludox [®] GRACE Davison
SiO ₂	—CL TM (>Al ⁺ ; “+”)	Ludox [®] GRACE Davison
TiO ₂	P25; anatase/rutile (3:1)	Evonik Industries AG
n-Ag	2Ag ⁺ + 2NaBH ₄ + 6H ₂ O → 2Ag + 2B(OH) ₃ + 2Na ⁺ + 7H ₂ ↑	Synthesis according to [17]

Table 2
Properties of ROM and FA from Lake Hohloh [14].

ROM	Elemental content (% of dry weight)					
	C	O	H	N	S	ash
ROS	47	40.5	3.8	1.4	2.1	≈5
FA	52	40.4	3.6	0.7	0.7	≈1

suspension was agitated for 24 h and turned out to be stable for several months [17].

ROM originated from the Lake Hohloh, a protected bog lake in the Black Forest, Germany. It is being used as representative ROM (HO series from the International Humic Substances Society). Details of sampling, sample treatment and characterisation are given in [14]. Samples were from the 27th sampling campaign (HO 27).

The membrane filtered (<0.45 μm) ROM concentration of the lake water (HO 27) amounted to ρ(DOC)=25 mg L⁻¹ and the isolated FA (HO 27 FA) content was around 50% (w/w). Specific UV absorption (SUVA, λ = 254 nm) at pH 7 and colour at λ = 436 nm were 5.2 and 0.42 L mg⁻¹ m⁻¹, respectively. Elemental analyses of ROM and FA isolates are given in Table 2. Proton capacities (H-Cap) for pH < 7 and for pH > 7 were 11 μmol mg⁻¹ (DOC) and 3 μmol mg⁻¹ (DOC), respectively, reflecting mainly the amount of acidic carboxylic groups and the phenolic groups, respectively [14].

The microorganisms (MO) used for the investigations are listed in Table 3.

Analytical characterisation methods

In the following, the analytical methods to characterise the ENP, the MO and their interactions with ROM were briefly described; further details are given in [18–20].

Determination of zeta potential and hydrodynamic size distribution

Zeta potential (ZP) of the MO and the NP and their hydrodynamic size distributions were determined using Laser Doppler Electrophoresis and Dynamic Light Scattering, respectively (Zetasizer Nano ZS, Malvern Instruments Ltd.). ZP was calculated using the Smoluchowski approach. For particle size, z-average (Z-A) values are given.

Scanning electron microscopy (SEM)

Selected ENP and MO samples were analysed at the Laboratory for Electron Microscopy (LEM) at the KIT using a LEO Electron Microscopy Ltd., Gemini 1530.

Quantification of metals and organic carbon

Metal ions in the liquid samples were quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES; VistaPro-CCD, Varian, Australia). DOC was determined using a Total Carbon Analyzer (TOC 5000, Shimadzu).

Table 3
Microorganisms, their character and origin (CGSC: Coli Genetic Stock Center; DSMZ: Deutsche Sammlung von Mikroorganismen und Zellkulturen, German Collection of Microorganisms and Cell Cultures).

Species	Type/relevance	Origin
<i>Escherichia coli</i> K-12 d21	Faecal indicator	CGSC
<i>Escherichia coli</i> K-12 DSM 498	Faecal indicator	DSMZ
<i>Pseudomonas putida</i>	Gram(–), ubiquitous	DSMZ
<i>Lactobacillus plantarum</i> DSM 20174	Gram(+), not pathogenic	DSMZ
<i>Saccharomyces cerevisiae</i> DSM 70459	Eucaryotic (yeast)	DSMZ

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