



Biodegradability of organic nanoparticles in the aqueous environment

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ABSTRACT

Synthetic nanoparticles have already been detected in the aquatic environment. Therefore, knowledge on their biodegradability is of utmost importance for risk assessment but such information is currently not available. Therefore, the biodegradability of fullerenes, single, double, multi-walled as well as COOH functionalized carbon nanotubes and cellulose and starch nanocrystals in aqueous environment has been investigated according to OECD standards. The biodegradability of starch and cellulose nanoparticles was also compared with the biodegradability of their macroscopic counterparts. Fullerenes and all carbon nanotubes did not biodegrade at all, while starch and cellulose nanoparticles biodegrade to similar levels as their macroscopic counterparts. However, neither comfortably met the criterion for ready biodegradability (60% after 28 days). The cellulose and starch nanoparticles were also found to degrade faster than their macroscopic counterparts due to their higher surface area. These findings are the first report of biodegradability of organic nanoparticles in the aquatic environment, an important accumulation environment for manmade compounds.

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1. Introduction

Nanoparticles are currently receiving an enormous attention from both industry and academia due to their potential in the development of novel highly active materials. Based on chemical composition and morphology, there are several classes of engineered nanoparticles (ENPs) such as metallic nanoparticles (e.g. Au, Pd, Pt) and metal oxides (e.g. TiO₂) but also including organic ones such as fullerenes, carbon nanotubes (CNTs) and cellulose and starch nanocrystals. In addition to ENPs, nature also makes use of nanoparticles such as ferritin, the tobacco mosaic virus and the cowpea chlorotic mottle virus, which are generally referred to as bionanoparticles. These nanoparticles can be chemically modified at the surface to introduce added functionality and such surface-activated nanoparticles are expected to play a major role in the future (Elsner et al., 2009). For example, insoluble particles can be rendered soluble through modification (Fig. 1), opening up further uses (Elsner et al., 2009; Partha and Conyers, 2009), or surface modification can be used to introduce additional functionality such as the ability to absorb high amounts of organic molecules (Morandi et al., 2009). While the nanoparticles receiving the most attention are synthetically derived and either inorganic materials (e.g. metal and metal oxides) or carbon structures such as CNTs and fullerenes, polysaccharide nanocrystals derived from naturally

occurring cellulose, starch or chitin, have proven to be interesting materials to improve the mechanical properties of polymers (Kamel, 2007; Dufresne, 2008; Eichhorn et al., 2010). Other uses as building block for sensor membranes or permselective membranes, reducing agent for metal nanoparticle production and mesoporous silica templating agent have also been reported recently (Bonne et al., 2008; Thielemans et al., 2009; Johnson et al., 2010; Lawrence et al., 2010). An important driving factor for this research comes from the renewable aspect of these nanoparticles, obtained through acid hydrolysis of native plant material or grown by bacteria. In addition, the common claim is made that these materials are biodegradable and benign (Eichhorn et al., 2010), making them even more attractive. However, data to confirm this assumption are missing. Despite the broad interest in developing applications for nanomaterials, knowledge on fate and toxicological issues of nanomaterials in general is almost non-existent (Hart and Hesterberg, 1998; Albrecht et al., 2006; Warheit et al., 2008; Landsiedel et al., 2009; Ben-Moshe et al., 2010; Frimmel, 2010) and even less for fullerenes and carbon nanotubes, even though genotoxicity and other effects (Koike et al., 2008; Wang et al., 2009; Pan et al., 2010) are frequently associated with nanomaterials (Landsiedel et al., 2009). Still less is known as far as their environmental fate is concerned (Kaegi et al., 2008; Gottschalk et al., 2009; Tiede et al., 2009; Frimmel, 2010). A few ecotoxicological studies are available (Barrena et al., 2009; Wiench et al., 2009; Zhu et al., 2010).

It is expected that both inorganic as organic ENPs will be introduced into the environment in increasing amounts over the next

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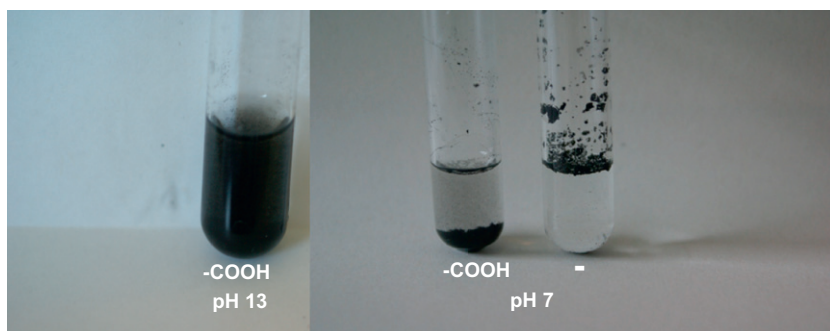


Fig. 1. Solubility of MWCNTs (COOH: COOH functionalized MWCNTs; -: no functionalisation).

decades as their use in industrial processes and consumer products increases (Kaegi et al., 2008). They can reach the environment via production processes (emissions into air and water, waste) or, even more likely, as a result of the routine use of products containing nanoparticles (e.g. TiO_2 in sun screens). Other introduction routes into the environment are the result of wash off, e.g. from facades of buildings (Kaegi et al., 2008). This study found evidence that synthetic nanoparticles detach from new and aged facade paints under natural weather conditions and are then transported by facade runoff and discharged into natural, receiving waters. In addition to the unwanted introduction into the environment, some ENPs are used for the remediation of environmental pollution as well such as the treatment of effluents and waste water (e.g. photocatalysis by TiO_2). In such cases the introduction of nanomaterials into the environment is intended. As a result of increased nanomaterials use, the predicted environmental concentration (PEC) of fullerenes in water arising from their use in consumer products was estimated to be about 310 ng L^{-1} (Tiede et al., 2009). Gottschalk and co-workers (2009) calculated PECs based on a probabilistic material flow analysis from a life-cycle perspective of ENP-containing products. The simulated modes (most frequent values) for fullerenes were found to be 0.003 ng L^{-1} in surface waters and about 4 ng L^{-1} in sewage treatment effluents. The discrepancy in these data demonstrates that there is still only little knowledge on usage, introduction into the environment and even less on the fate of ENPs in the aquatic environment and its expected accumulation in the environment. Moreover, the aggregation of ENPs plays an important role in the environmental fate and effects because the size and shape of nanoparticles, their physico-chemical characteristics such as surface properties and polarity, as well as the dimensions of aggregates, will determine the magnitude of any potential toxic effect. Aggregation is affected by pH, ionic strength, and ionic identity (inorganic and organic) of aqueous suspensions (Sharma, 2009) and surface properties such as polarity and presence of functional groups. This is of special importance for chemically modified ENPs. To complicate matters even more, knowledge is limited due to the lack of analytical methods (Frimmel, 2010). Often a combination of methods such as field flow fractionation, electron microscopy and chromatographic and other methods is necessary which makes analysis expensive. Furthermore, within the sample treatment coagulation has to be prevented. Therefore, it can be assumed that as a result of their widespread use, the exposure of the human body to ENPs, e.g. via drinking water, will increase unless proper elimination occurs. This can be done by sorption methods in sewage treatment or even better through use of biodegradable nanoparticles which will mineralize after they reach sewage. In contrast to the wide area of anticipated applications of nanoparticles, the body of knowledge on their fate in the aquatic environment is extremely limited to non-existing.

The significant lack of knowledge in relation to unknown toxic effects, degradability, and bioaccumulation of ENPs in the aquatic

environment made Baun et al. (2009) conclude that it is impossible to set limit values for ENPs in surface waters now and in the foreseeable future. This might become problematic in Europe when certain ENPs are labelled “priority substances” under the Water Framework Directive (WFD), responsible for maintaining a good chemical and ecological status of surface waters. Despite, or even due to, this lack of knowledge, there is an increasing concern over the safety of ENPs to humans and the environment, and it is likely that the environmental risks of these particles will have to be tested under regulatory schemes such as REACH.

If organic materials are fast and fully degraded, no exposure takes place. Without any exposure there will be no effects and risk is absent. However, this holds only if (bio)degradation results in full mineralisation. If recalcitrant transformation products are the result of incomplete degradation even higher risks may result. Therefore, it is extremely important to determine how fast and to what degree organic nanoparticles that can reach the aquatic environment are degraded and mineralized and whether size and/or surface modification is of importance. Furthermore, according to the principles of green (Anastas and Warner, 2000) and sustainable chemistry and pharmacy (Kümmerer and Hempel, 2010), a full life cycle assessment is indispensable for the sustainable use of nanoparticles. Furthermore, knowledge on the biodegradability of ENPs can be used to design new entities accordingly to avoid persistence by benign design (Kümmerer and Hempel, 2010) from the very beginning. This is a key issue on the road to successful application and use of these new chemical entities in the long run (Kümmerer, 2007; Anastas, 2008). As they are new products still under development, such data should be available as soon as possible to be used for a proper sustainable design of new compounds (Anastas, 2008; Kümmerer, 2007; Boethling et al., 2007) to avoid later problems that may negatively impact on the acceptance of such new materials.

To the best of our knowledge, no studies have been presented to date that investigate the environmental fate of fullerenes and CNTs of different size and surface functionalisation. No studies are available that compare the aqueous biodegradability of highly crystalline starch and cellulose nanowhiskers to the biodegradability of the macro-fibres of polysaccharides they are constituted of. While native cellulose and starch fibres are biodegradable to some degree, the crystallinity of nanoparticles of cellulose and starch may significantly delay biodegradation, while their increased surface area may enhance it. As for ENPs with chemically modified surface it is of interest to know how surface functionalisation impacts the biodegradability of functionalized nanoparticles. If this would be the case, an easy assessment of these types of functionalized ENPs would be possible and a simple rule could be established for their benign design (Kümmerer, 2007). Therefore, we start this study with non-carboxylated and carboxylated (6%) CNTs, fullerenes of different size (C_{60} and C_{70}) and crystalline nanoparticles of cellulose and starch in order to compare their

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