Nanomaterials in Waste Streams
Current Knowledge on Risks and Impacts

Chapter 5

The fate of engineered nanomaterials in sewage treatment plants and agricultural applications

This chapter investigates the current state of knowledge on engineered nanomaterials (ENMs) and their behaviour in wastewater treatment processes in order to identify areas for future research. It focuses on the processes currently in use for urban sewerage treatment and begins by investigating the presence of engineered nanomaterials in wastewater treatment plants. It the moves on to examine the possible retention and aggregation of engineered nanomaterials in activated sludge and explores the possible transformations that ENMs can undergo in treatment plants and the models that are available to predict these transformations. The chapter also discusses the potential risks of agricultural application of sewerage sludge that is charged with engineered nanomaterials. The chapter concludes by identifying knowledge gaps and areas where additional research would be required.

This report investigates the current state of knowledge on engineered nanomaterials (ENMs) and their behaviour in wastewater treatment processes in order to identify areas for future research.

This chapter first covers the general processes of wastewater treatment and investigates the presence of engineered nanomaterials in wastewater treatment plants. It then examines the possible retention and aggregation of engineered nanomaterials in activated sludge and explores the use of retention, aggregation and sedimentation models. The chapter also looks into the possible impacts of engineered nanomaterials accumulated in sewage sludge bound for agricultural applications. It also identifies current international research around this area. Finally, the chapter highlights knowledge gaps and areas where additional research would be required.

Processes used in urban sewage treatment plants: the role of activated sludge

Sewage treatment plants collect wastewater from urban and/or industrial sources. Urban wastewater arises from human activities (toilets, showers, dish-washing, etc.). The amount of sludge produced is hard to gauge. However, a 2004 report by ADEME (French Environment and Energy Management Agency) confirmed this fact. The produced figures show that, agricultural applications represent significant quantities (Table 5.1).

Table 5.1. **Production and management of sewage treatment plant sludge in France (2000-04)**

			Agricultural recovery
Dry material (tonne/year)	Urban Sludge	887 755	524 290
	Industrial Sludge	950 000	600 000
Raw material (tonne/year)	Urban Sludge	8×10^6 to 10×10^6	5×10^6 to 6×10^6
	Industrial Sludge	3.5×10^6 to 4×10^6	1.9×10^6 to $.3 \times 10^6$

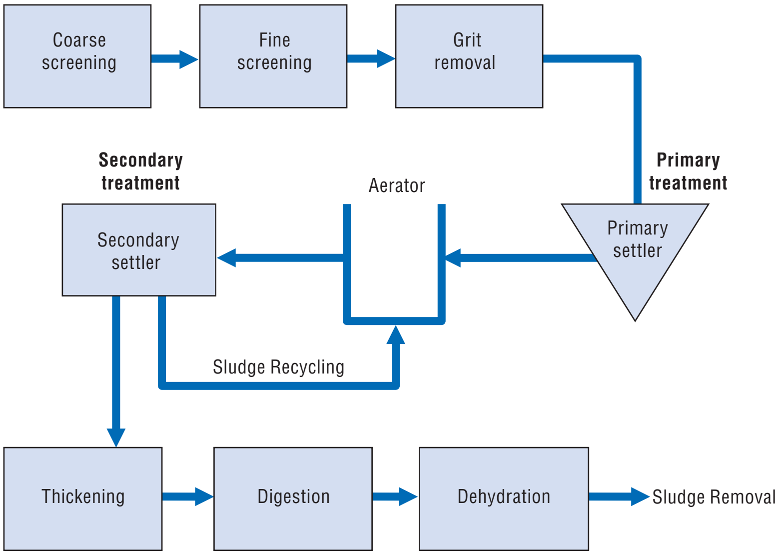
Source: ADEME, 2004.

Most plants are biological treatment plants. They are based on biological processes and are sometimes linked to physical/chemical processes (flocculation, chlorination, etc.). Figure 5.1 shows the stages in a process used in an urban sewage treatment plant.

The first stages are means of removing the largest objects: coarse + fine screening + grit removal.

The section which corresponds to biological treatment is carried out in an aerator (addition of air) followed by sedimentation of the sludge which is recycled to the top of the aeration reactor. The sludge which is not recycled is thickened, then digested (in an anaerobic reactor) which stabilises the organic matter (less odour) and reduces its toxicity (blocking metals and pathogens), breaks down organic carbon and reduces the mass (dry matter) of the sludge to be disposed; from 35 to 40% for dry matter – 40 to 50% for volatile matter.

Figure 5.1. **Wastewater treatment stages**



Source: From ADEME (2004): *www.ademe.fr*.

Biological treatment reduces organic pollution via heterotrophic bacteria which use the organic material as an energy source. The resulting bacterial development is also used to adsorb (absorb) metallic elements and to aggregate any particles which were not removed by the initial screening process.

Biological sewage treatment plants form the majority of liquid effluent treatment plants. This treatment is also known as activated sludge treatment, i.e. by using a collection of bacteria with the aim of breaking down organic contaminants (pesticides, medical residues, etc.), blocking metals and metalloids, and denitrifying effluents, etc. This is a complex process and also involves biochemical reactors and physical processes such as aggregation, sedimentation, etc. Activated sludge is a complex material (Schmid et al., 2003) made up of bacterial aggregates measuring ~500 µm, themselves formed from microaggregates measuring ~10 µm (Snidaro et al., 1997). The fractal structure with a dimension of approx. 2.2 micro meters limits the transfer of water to the core of the aggregate. The bacterial diversity within the aerobic reactor, for example, ensures that there is a wide range of reactivity.

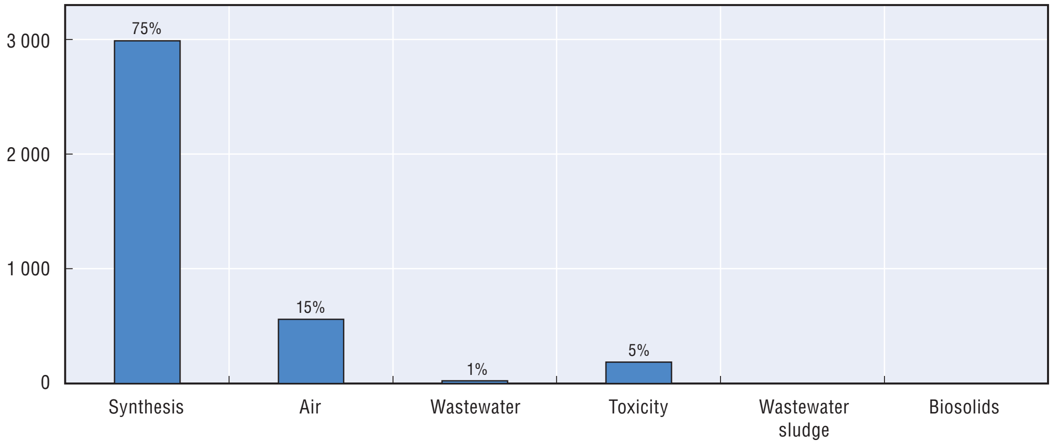
As well as bacteria there are polymers (proteins and polysaccharides) which also have a role to play in "capturing" the various contaminants.

What do we know about the presence of nanomaterials in the sludge from sewage treatment plants?

Although sewage treatment plants receive some wastewater containing metals and nanomaterials (Blaser et al., 2008), very few studies had examined detection of nanomaterials in biological sludge from sewage treatment plants as demonstrated by the exhaustive study carried out by Brar, S. K. et al. (2010) (Figure 5.2).

A study financed by the US EPA ("Targeted National Sewage Sludge Survey Statistical Analysis Report"– EPA-822-R-08-018 – April 2009) indicates the presence of significant concentrations of silver (Ag) or even titanium (Ti) in sludge from urban sewage treatment plants (Figure 5.3). A subsequent study on samples from the EPA's work shows the presence

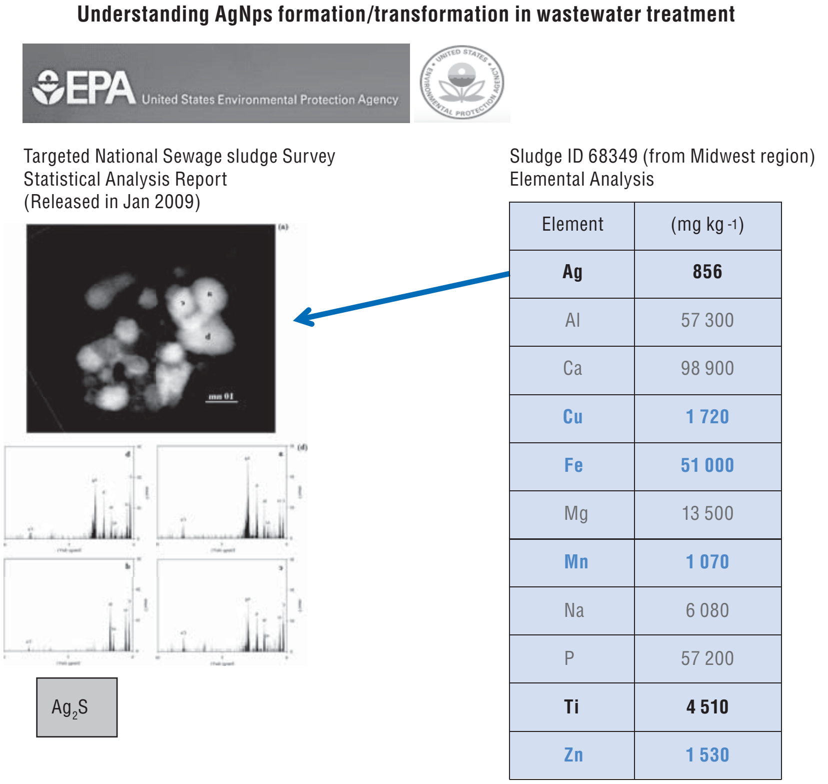
Figure 5.2. **Publications on nanomaterials corresponding to certain research fields**



Source: Brar, S. K. et al. (2010).

of nanoparticles of silver sulphide (Kim et al., 2010). These nanoparticles of silver sulphide result from oxidation of silver metal to form Ag^+ and precipitation of Ag^+ to form Ag_2S which is thermodynamically stable (Figure 5.3).

Figure 5.3. **Concentration of metallic elements and presence of Ag2S nanoparticles in urban sludge**



Understanding AgNps formation/transformation in wastewater treatment

EPA United States Environmental Protection Agency

Targeted National Sewage sludge Survey
Statistical Analysis Report
(Released in Jan 2009)

Sludge ID 68349 (from Midwest region)
Elemental Analysis

Element	(mg kg -1)
Ag	**856**
Al	57 300
Ca	98 900
Cu	**1 720**
Fe	**51 000**
Mg	13 500
Mn	**1 070**
Na	6 080
P	57 200
Ti	**4 510**
Zn	**1 530**

Source: US EPA (2009) and Kim et al. (2010).

Engineered Nanomaterials (ENMs) are bound to be present in sewage treatment plants given that they are to be found in everyday consumer products such as cosmetics, coatings, the agri-food sector, etc. (Brar et al., 2010) and that sewage treatment plants in OECD Member countries are the main channel for wastewater from human activities. In 2010 over 7 billion m^3 (domestic wastewater and rainwater) passed through sewage treatment plants. See Table 5.2 for details.

Table 5.2. **Occurrence of nanoparticles originating from everyday consumer products**

Source	Type of nanoparticle	Quantity used in terms of tonnes	Applications
Metals and alkaline earth metals	Ag	High	Antimicrobials, paints, coatings, medical use, food packaging
	Fe	High	Water treatment
	Pt	High	Catalysts
	Sn	Unknown	Paints
	Al	High	Metallic coating/plating
	Cu	Unknown	Microelectronics
	Zr	High	
	Se	Low	Nutraceuticals, health supplements
	Ca	Low	Nutraceuticals, health supplements
	Mg	Low	Nutraceuticals, health supplements
Metal oxides	TiO_2	High	Cosmetics, paints, coatings
	ZnO	Low	Cosmetics, paints, coatings
	CeO_2	High	Fuel catalyst, Paints
	SiO_2	High	Paints, coatings
	Al_2O_3	Low	Usually substrate bound, paintings
Carbon materials	Carbon black	High	Substrate bound, but released with tyre wear
	Carbon nanotubes	Medium-High	Used in a variety of composite materials
	Fullerenes (C_{60}-C_{80})	Medium-High	Medical and cosmetics use
Miscellaneous	Nanoclay	High	Plastic packaging
	Ceramic	High	Coatings
	Quantum dots	Low	Different compositions
	Organic nanoparticles	Low	Vitamins, medicines, carriers for medicines and cosmetics, food additives and ingredients

Source: Brar, S.K. et al. (2010).

What transformations can nanoparticles undergo in sewage treatment plants and how does this affect reactor operation?

Physico-chemical transformations of engineered nanomaterials (ENMs)

In the initial stages of sewage treatment plants, nanoparticles resulting from changes in the products containing such particles will experience aggregation, sedimentation in various compartments and also, in some cases, radical transformation which may affect their concentration in effluents, but also in the sludge which will go on to follow different routes such as incineration, storage or agricultural applications. It is therefore important to understand and predict the fate of these ENMs when treating wastewater from industrial or domestic sources. Cosmetics products, for example, include surface-functionalised ZnO and TiO_2 nanoparticles, which may be found in surface water after passing through a wastewater treatment plant (Kiser et al., 2009; Auffan et al., 2010a, 2010b; Westerhoff et al., 2011).

More recent studies on the effects and transformation of nanomaterials or nanoparticles in activated sludge from a sewage treatment plant were generally carried out in a controlled reactor or with a pilot plant in a laboratory. The most extensively studied nanomaterials include nanoparticles of silver metal, followed by ZnO, TiO_2, CeO_2, SiO_2 and carbon nanotubes.

Injected nanomaterials such as TiO_2, Ag°, CeO_2 or Cu are largely eliminated from wastewater through primary and secondary treatment (Kiser et al., 2009 and 2010; Kaegi et al., 2011; Ganesh et al., 2010; Wang et al., 2012; Gomez-Rivera et al., 2012). Nanoparticles are then associated with the solid phases of sludge by over 80% by mass. Mechanisms which lead to such associations include heteroaggregation between nanoparticles and bacteria, plus adsorption and interactions with biological polymers (Wang et al., 2012). Other authors have suggested that physicochemical transformations linked to interactions with living organisms play an important role (Tiede et al., 2010). It appears that the diversity of nanoparticles, their surface functionalisation within products, and their specific surface area etc., will affect their removal in terms of both kinetics and quantity (Kiser et al., 2009 and 2010; Jarvie et al., 2009; Tiede et al., 2010; Barton et al., 2013, 2014a, 2014b). The small proportion leaving the plant would remain in the form of nanoparticles and end up in surface water (Tiede et al., 2010; Kim et al., 2010).

Work on nanoparticles' stability in wastewater during the treatment process (Limbach et al., 2008) has shown that cerium oxide, CeO_2, has an affinity for proteins and in particular for peptides. The zeta potential was modified and increased the stability of the nanoparticles. A similar study with Ag° showed that nanoparticles were very stable and less effectively removed when surface functionalised (Kiser et al., 2010), whereas non-functionalised nanoparticles were associated with the solid phase.

It was demonstrated that nanoparticles associate quickly with the particles present in wastewater and then transformed in the case of Ag° via oxidation and sulfidation (Kaegi et al., 2011; Liu et al., 2011; Doolette et al., 2013; Ma et al., 2012). This sulfidation modifies reactivity insofar as it reduces solubility and toxic potential because Ag_2S is thermodynamically stable and not a biocide nanoparticle (Levard et al., 2011 and 2012). Similar data was obtained for nanoparticles of ZnO (Lombi et al., 2012) using a pilot wastewater treatment plant and compost to analyse the transformations within the sludge. The results show that ZnO is rapidly transformed to ZnS during effluent treatment. ZnS was dissolved in the compost and the Zn^{2+} ions are partially precipitated in the form of zinc phosphate and also combine with iron oxyhydroxides.

A recent study (Barton et al., 2013) conducted by using a laboratory reactor with activated sludge in aerobic mode with non-functionalised and functionalised industrial CeO_2 nanoparticles with citrate molecules and low added concentrations (~1mg/L after one month) showed that Ce(IV) had been reduced to form Ce(III) with precipitation of $Ce(III)PO_4$. The reduction kinetics of cerium IV differed for surface-functionalised and non-surface-functionalised CeO_2. The reaction worked faster in the case of non-functionalised CeO_2, reaching 30% within the bacterial aggregates, and ~12% in the case of CeO_2 that was coated with citrate after 24 hours. This shows that direct contact with the bacterial membranes plays an important role with regard to physicochemical transformations of metal oxide nanoparticles (Thill et al., 2006; Zeyons et al., 2010). The presence of surface functionalisation with organic or mineral molecules (Auffan et al., 2010a) reduces the transformation kinetics and toxicity. Surface functionalised nanoparticles can slow down transformation kinetics (e.g. oxidation, reduction) and negatively affect the wastewater treatment process. However, it could also be anticipated from this report that surface functionalised nanoparticles (if the coating is stable) reduce toxicity, which would be a positive effect. A summary is provided in Box 5.1 below.

Box 5.1. **Summary of physico-chemical transformations of engineered nanomaterials (ENMs)**

Chemical transformations in sewage treatment plants, such as solubilisation by reduction (e.g. CeO_2) or oxidation (e.g. Ag°), are important parameters to be taken into consideration in nanometric material balances. These chemical transformations are accompanied by precipitation in the form of mineral species such as Ag_2S or $CePO_4$ which are thermodynamically stable and seemingly less toxic than the original materials. Widespread surface functionalisation in order to introduce nanoparticles into common products may slow down these transformations and maintain the initial oxidation or reduction state for longer by limiting contact with bacterial aggregates.

Operation of the various process stages

Researchers have examined a number of effects:

- the change in dissolved oxygen demand
- nitrification and denitrification
- the impact on methanogenesis in the reactor in anaerobic mode and volatile organic acids during sludge composting
- biological oxygen demand
- bacterial diversity
- the decrease or change in the chemistry of extra-cellular polymers (proteins in particular)
- cell death
- mechanisms by which nanoparticles interact with bacteria
- the influence of sludge sedimentation as a function of changes in sludge structure.

The results do not point to consistent messages. For example:

- A paper on the impact of adding Ag° nanoparticles compared with adding silver salts (Ag+) (Arnaout and Gunsch, 2012) on the denitrification process shows that citrate-coated Ag° nanoparticles were associated with maximum denitrification inhibition at concentrations of ~2 ppm. This data completely contradicts the observations of Kiser et al., 2010. Other authors (Yang et al, 2013) noted that the effects on anaerobic digestion were negligible up to silver nanoparticle concentrations of 40 mg/L.
- Multi-walled carbon nanotubes were tested on samples of activated sludge in an aeration reactor in Massachussetts in order to assess the effects on respiration and the production of exocellular polymers. The authors demonstrate that inhibition is dependent on concentration, but for carbon nanotube concentrations > 0.64 g/L (Luongo et al, 2010).

- A critical review (Yang et al, 2013) of the impact of metallic nanoparticles on anaerobic digestion suggested low or zero effects with regard to bacterial diversity in the absence of oxygen in the case of TiO_2, Ag°, ZnO.
- This is partly contradicted by an article by Z. Liang et al.in 2010 concerning Ag°, which shows that the community of nitrifying bacteria decreases over time.

A summary is provided in Box 5.2 below.

Box 5.2. **Summary of operation of the various process stages**

Work on the operation of the various treatment stages (see Figure 5.1) is still in its early stages and requires a more systematic approach to the development of bacterial communities in aerobic and anaerobic reactors according to nanomaterials' doses and their surface formulation, insofar as these communities are the source of the above-mentioned reactions. Experiments involving high concentrations appear to be of limited credibility.

Can we predict the retention and transformation of ENMs by activated sludge? Use of retention, aggregation and sedimentation models

Current data shows that the majority of ENMs accumulate in biological aggregates in sewage treatment plants and these biological solids are then partly recycled in compost. We know that some nanoparticles such as ZnO, Ag°, CeO_2 are transformed and that the transformation kinetics (oxidoreduction + dissolution + precipitation, etc.) are dependent not only on the presence of surface functionalisation, but also on direct contact with biological membranes such as in the case of some biological species which display more active electron transfer behaviour. However, this does not apply in the case of one of the most common ENMs: TiO_2. TiO_2 is not particularly soluble and its photocatalytic activity, which generates powerful oxidising agents, is dependent on the size and extension of certain mineralogical faces (Auffan et al., 2009a, 2009b).

A recent paper by Barton et al., (2014a), written as part of a co-operation between CEINT in the USA, GDR I I-CEINT and Labex SERENADE in France, systematically measures the quantity of nanoparticles associated with biosolids in a pilot urban sewage treatment plant (aerobic and anaerobic reactor) in Durham (North Carolina), and shows that, for brief contact times:

- ~90% of CeO_2, ZnO and TiO_2 nanoparticles were combined with bacterial aggregates
- ~60% of Ag° nanoparticles were combined with bacterial aggregates

after just one hour of contact. See Table 5.3 for details.

Surface-functionalised and non-functionalised nanoparticles were observed to behave differently. At low concentrations (< 10 ppm), non-functionalised nanoparticles were retained to a greater extent in bacterial aggregates than functionalised nanoparticles. Similarly, the energy dissipated in reactors plays an important role in the likelihood of encountering objects and helps to increase the nanoparticles which combine with bacterial aggregates when the mixing energy increases.

Table 5.3. **Percentage of nanoparticles associated with bacterial aggregates in an aerobic and anaerobic reactor of an urban sewage treatment plant**

Sample	Description	Sludge Type	Percent Removal					
			1 ppm		10 ppm		50 ppm	
			Low mixing	High mixing	Low mixing	High mixing	Low mixing	High mixing
Ag 1	40nm Ag PVP	Primary			17	27	52	48
		Secondary			22	42	30	58
Ag 2	8nm Ag PVP	Primary			11	15	40	45
		Secondary			10	40	27	50
Ag 3	40nm Ag PVP	Primary			19	25	48	57
		Secondary			32	59	41	69
Ag 4	25nm Ag GA	Primary			15	13	36	37
		Secondary			27	79	39	75
Ag 5	6nm Ag GA	Primary			14	16	33	43
		Secondary			10	50	30	39
CeO_2 Bare	8nm CeO_2 Bare	Primary	49	55	48	53	79	90
		Secondary	61	90	70	95	88	98
CeO_2 Nanobyk	8nm CeO_2 Citrate	Primary	15	20	23	31	22	35
		Secondary	56	79	70	84	72	82
TiO2 NA	15nm Bare	Primary	60	68	61	69	60	74
		Secondary	81	94	82	96	86	98
TiO2 TINE	20nm Bare	Primary	70	72	70	74	70	75
		Secondary	80	91	82	95	84	97
ZnO Vive	20nm ZnO Na polyacrylate	Primary	25	38	30	39	30	37
		Secondary	20	95	25	76	26	28
ZnO TINE	30nm ZnO Bare	Primary	45	49	49	61	58	65
		Secondary	83	91	85	92	78	92
ZnO NAM	20nm ZnO Bare	Primary	46	47	49	59	58	65
		Secondary	85	91	85	91	83	90

Note: According to initial quantity and energy dissipated in reactors.
Source: Data from thesis research by L. Barton (DUKE University and Aix-Marseille University) (Barton et al., 2014a).

The distribution coefficients, which are a simple way of evaluating the quantities of "soluble" matter retained by a solid phase after a given contact time and with a given initial concentration (eq. 1)

$$\gamma = \frac{\text{Retained Nanomaterials (mg) / Bio-solids (mg)}}{\text{Nanomaterials in Supernatant (mg / L)}}$$

show that the behaviour is dependent on i) the presence of surface functionalisation, the possibility of reduction or oxidation leading to dissolution and solubilisation (Ag°, CeO_2) or even dissolution with a constant oxidation state (ZnO) compared to a chemically stable nanoparticle (TiO_2), ii) the contact time from 1 minute to 60 minutes in the oxidation reactor and the denitrification reactor (anaerobic). For example, Ag° particles measuring < 10 nm display gamma values which reduce over time in both reactors. This is due to faster dissolution kinetics than in the case of larger particles (Ma et al., 2012).

On the other hand, TiO_2 nanoparticles display a regular increase in γ over the contact time irrespective of the primary reactor (aerobic) or secondary reactor (anaerobic).

CeO_2 nanoparticles display γ values which regularly increase as the contact time increases and with high values due to the fact that reduction of cerium oxide remains low with contact time of less than 1 hour.

It is thus possible to differentiate between the nanoparticles which undergo rapid transformations depending both on their chemistry and their size, such as Ag° (Ma et al., 2012). Similarly, the presence of surface functionalisation enabled by organic molecules on the surface, which are used to mix these ENMs within a product, has a part to play with respect to their affinity for bioaggregates at least over short periods. A summary is provided in Box 5.3 below.

Box 5.3. **Summary of the use of retention, aggregation and sedimentation models**

A research paper by Barton et al. (2014b) provides initial predictions of the retention capacities of nanomaterials by bacterial aggregates. The distribution coefficient (γ), which is measurable from experiments, expresses the distribution of nanoparticles or nanomaterials between the aqueous phase where they are very mobile and the solid phase in the form of bacterial aggregates. The γ parameter, which can be subsequently derived mathematically, expresses the affinity of nanomaterials for bacteria present in the sludge. This affinity also depends on the affinity of soluble organic molecules present in the waste water which can adsorb onto nanomaterials and delay the retention onto bacteria. These affinities are also dependent on the chemical nature of the nanoparticles and the presence of surface functionalisation enabled by additional organic molecules on the surface of a product (these are frequently used to incorporate ENMs into cosmetics, plastics, etc.). This can also be modeled using the aggregation theory developed long ago and applied to water treatment using coagulation-flocculation, etc. (Thill et al., 1998).

What risks are involved in agricultural applications?

The vast majority of ENMs will be found in dried and composted sludge. These solid phases will in some cases be used as fertilisers in agriculture. The rare studies which do exist are either data from models showing transfer to surface water (Blaser et al., 2008), or laboratory research concerning the effects on plants or terrestrial organisms such as worms or bacteria in the rhizosphere. A recent paper demonstrates the stability of Ag_2S when composted (Lombi et al., 2013). However, the one criticism which can be made is that it appears that these tests have never been carried out with products containing ENMs and transformed under real-life conditions, thus releasing complex ENMs. Similarly, the rare studies are conducted outside real-life conditions, i.e. wastewater which has undergone all stages of the treatment process and generates sludge for composting containing ENMs, whether transformed or not. We have already seen that transformations within sewage treatment plants are important for ENMs such as ZnO, Ag°, CeO_2, CuO, etc., but not of course for TiO_2. Indeed, the mobility of these products which have been transformed within the treatment plant, their potential transformations in soil after application and interactions with plants and bacteria in the rhizosphere, along with transfer to surface water, have never been studied in depth.

Current research overview: location of teams involved in this field throughout the world

There are very few teams throughout the world investigating the efficiency of biological treatment of wastewater containing ENMs. In Europe, these are based in Great Britain, France and Switzerland for the most part. Teams in Switzerland and France take a similar approach to studying the mechanism associated with transformations in greater depth.

There is also the US consortium CEINT, which works alongside with France (GDRI I-CEINT, Labex SERENADE), and also with researchers in the United Kingdom, Austria, and others (the TINE – Transatlantic Initiative for Nanotechnology and the Environment – project). This US-backed project aims to assess transformations and the impact on processes involving nanomaterials which are present in an urban sewage treatment plant, as well as the effects on terrestrial organisms and plants. Nevertheless, this approach does not anticipate the direct use of composted sludge containing nanomaterials which has been treated in a sewage treatment plant.

A project by I-CEINT (France-USA) seeks to assess the impact and transfer of the nanomaterials present in sludge from sewage treatment plants whilst considering i) dispersivity and transfer to surface water by using CEINT mesocosms, ii) quantifying phyto-availability with respect to plants intended for human consumption, and iii) quantifying the direct and indirect effects of application with respect to bacterial communities in the rhizosphere.

Finally, teams throughout the world are working on the effects of nanomaterials on the diverse range of bacterial communities both in aerobic and anaerobic reactors. The latter are subject to particular attention in that they represent an essential stage in preparing the final material, especially for agricultural applications.

What research still needs to be carried out?

Current state of knowledge

The current state of knowledge can be summarised as follows:

1. Chemical transformations in sewage treatment plants, such as solubilisation by reduction or oxidation are important parameters to be taken into consideration in nanometric material balances. Widespread surface functionalisation by introducing nanoparticles into common products may slow down these transformations and maintain the initial oxidation or reduction state for longer by limiting contact with bacterial aggregates.
2. Work on the operation of the various treatment stages is still in its early stages and requires a more systematic approach to the development of bacterial communities in aerobic and anaerobic reactors according to nanomaterials' doses and their surface formulation. Experiments involving high concentrations appear to be of limited credibility.
3. Initial predictions of the retention capacities of nanomaterials by bacterial aggregates can be made by the distribution coefficient ( ) expressing the affinity of nanoparticles or nanomaterials between the aqueous phase and bacterial aggregates.
4. The mobility of ENMs which have been transformed within the treatment plant, their potential transformations in soil after application and interactions with plants and bacteria in the rhizosphere, along with transfer to surface water, have never been studied in depth.

Areas for further research

Current research often involves the use of activated sludge reactors; the anaerobic stage has not yet been fully explored. It also involves non-functionalised nanoparticles, whereas they are all surface-functionalised in consumer products (cosmetics, plastics, agri-foods, clothing, paint, etc.). There has been no research on the deterioration of products containing ENMs and studies on surface changes in nanoparticles in a sewage treatment plant do not exist. In order to remedy this, it seems essential to:

1. Use sufficiently large pilot plants incorporating all the relevant stages so that data can be extrapolated to a full-scale plant.
2. Work with the residues of various products, obtained in a reproducible manner (see the European NEPHH programme, for example) but which are widely used: cosmetics, paint, agri-foods, etc. under realistic conditions, which thus enable to monitor the changes in ENMs from the point at which they are discharged into water (well diluted) and at the different treatment stages in the plant. Studies have been conducted on changes in surface functionalisation of cosmetics (Botta et al., 2011; Labille et al., 2010; Auffan et al., 2009a, 2009b, 2010 etc.) under mild conditions and of Nanobyk (CeO_2 formulated with citrate molecules) in an aerobic reactor and a laboratory pilot (Barton et al., 2013). Such research is still very limited.
3. Assess the impact of agricultural sludge application and develop a similar test to the RHIZOtest, for example, which assesses the risks of metals being transferred to plants (ADAME, 2007). These experiments will need to be performed with transformed sludge under conditions close to real-life conditions and not with high concentrations of nanomaterials. The use of isotope tracing for nanomaterials would be extremely useful when monitoring the transfer process. 3D visualisation tools such as X-ray nano and microtomography are still not widely used in laboratories, but allow heavy elements to be located in a variety of tissues (plants, living organisms, etc.) in relation to observable effects. Finally, work is needed with actual soils for which precise details are available on their texture and component types as a function of the kinds of tested cultures.

In all these methods, the interdisciplinary aspect is paramount. The effects on living organisms (plants, bacteria, etc.) cannot be studied without considering biological diversity, growth, etc., and having some knowledge of transformation and transfer mechanisms which are the preserve of physico-chemists and specialists in transfers in porous media.

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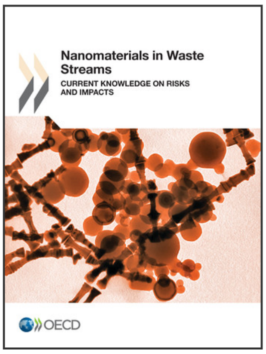

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