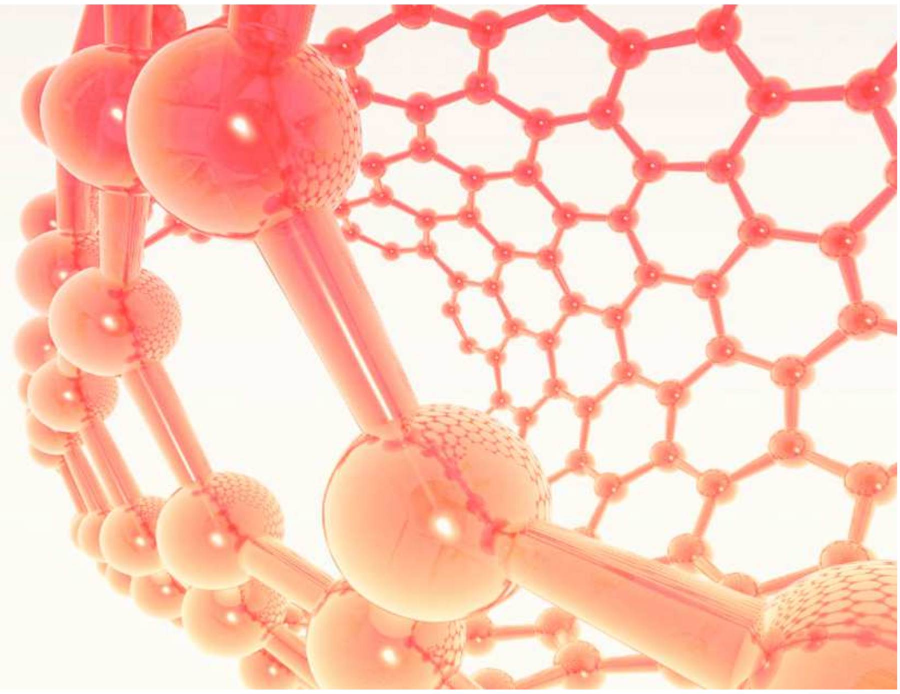
LIFE REACHnano

Development of a web based REACH Toolkit to support the chemical safety assessment of nanomaterials

Guidance on the best practices for environmental risk mitigation



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Guidance on the best practices for environmental risk mitigation

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Contents

1. Introduction

The nanomaterials (NMs) constituent of a product are typically released intentionally in a controlled manner to fulfil the function in the product, remain during its lifecycle within the product to complete their utility. However, during the manufacture, use and disposal of the product, might be also an unintentional release.

To determine whether the liberation (intentional or not) of these NMs can affect the human health or the environment, and how to avoid this release in case of a negative impact, is a task on which is still working nowadays. There are some recommendations[1], although no standard protocol that fulfill the existent gaps has been developed.

In this guide, it has been summarized the best available techniques to control the release of NMs to the environment. This information has been compiled from the ReachNano project's research itself and the experience gained through it.

2. An approach to Risk Management Measures with nanoparticles

Risk Management Measures (RMM) are the necessary actions needed to ensure that exposures to a hazardous NM are minimized. They must cover human health and environment, following the standard hierarchy of controls. In case of some residual risk after RMM have been implemented, it must be addressed and improved.

Risk must be quantified before deciding if a particular risk is critical enough to require resources to manage it. Afterwards, measurements are needed to certify that the management procedure has reduced such risk.

2.1. Nanomaterial hazard and risk evaluation

The **hazard** of a nanomaterial is defined as the inherent capacity of a chemical to cause adverse effects in human or environment under conditions of exposure. Thus, the intrinsic harmfulness of a chemical, which can be different at nanoscale than their known properties at micro- and macro-scale, together with the **dose** received, which accumulates in a specific biological compartment (e.g. skin, lungs, water, soil…) determine the risk of the exposure to a nanomaterial.

Hazard identification, accurate interpretation of the dose-response relationships and exposure evaluation are critical for a correct risk assessment and management. Throughout the life cycle of a nanomaterial there are multiple release scenarios, whose risk can be higher or lower depending on the process involved, use and disposal of such nanomaterial.

Several approaches are proposed to evaluate the risk of a chemical in the nanoscale, although there is no common strategy. They are normally based on step-by-step methodologies, such as the one proposed by the International Organization for Standardization (ISO[2]), based on the following stages:

- Analysis about the hazardous nature of the nanomaterials,
- Analysis about the effectiveness of the control methods,
- Appropriate and accessible procedures to control the release/exposure.

However, the main difficulty of application of this approach to nanomaterial is the fact that the available information about the harmfulness or effectiveness of protective controls may be scarce or incomplete. Likewise, it might occur that is not the nanomaterial composition what poses the risk, but further characteristics such as surface area, shape, agglomeration or other chemicals present.

[1] Health & Safety Authority. Local Exhaust Ventilation: (LEV) Guidance. The Metropolitan Building, James Joyce St., Dublin 1. January 2014

[2] ISO (2011) Nanotechnologies – Nanomaterial Risk Evaluation (ISO/TR 12121:2011)

2.2. Release of nanomaterials to the environment

Accurate determination of the amounts or concentrations from nanomaterials in the environment with analytical measurements is generally complicated due to the following:

- It is likely that the specific NM sought appear only at very low concentrations in the environment.
- Measurement methods do not exist for certain materials or are not sensitive enough.
- Nanomaterials may be converted (coagulate, agglomerate, aggregate, dilute…) in the environment or deposit to the different media (soil, water, air).
- Existing classification methods can hardly differentiate the several sizes, concentrations, shapes and surface modifications in which NMs are present.

Thus, the occurrence of nanomaterials in the environment are hardly measured. Instead, calculation models are applied to estimate the emission amounts and the resulting environmental concentrations relevant for their partitioning between water, soil and air, derived from production volumes approximations and their release rates, used as input to these models.

In principle, it has to be considered that NMs can be released into the environment at any moment of their entire lifecycle, from production, use or intermediate use to manufacture other products or disposal (Fig. 1).

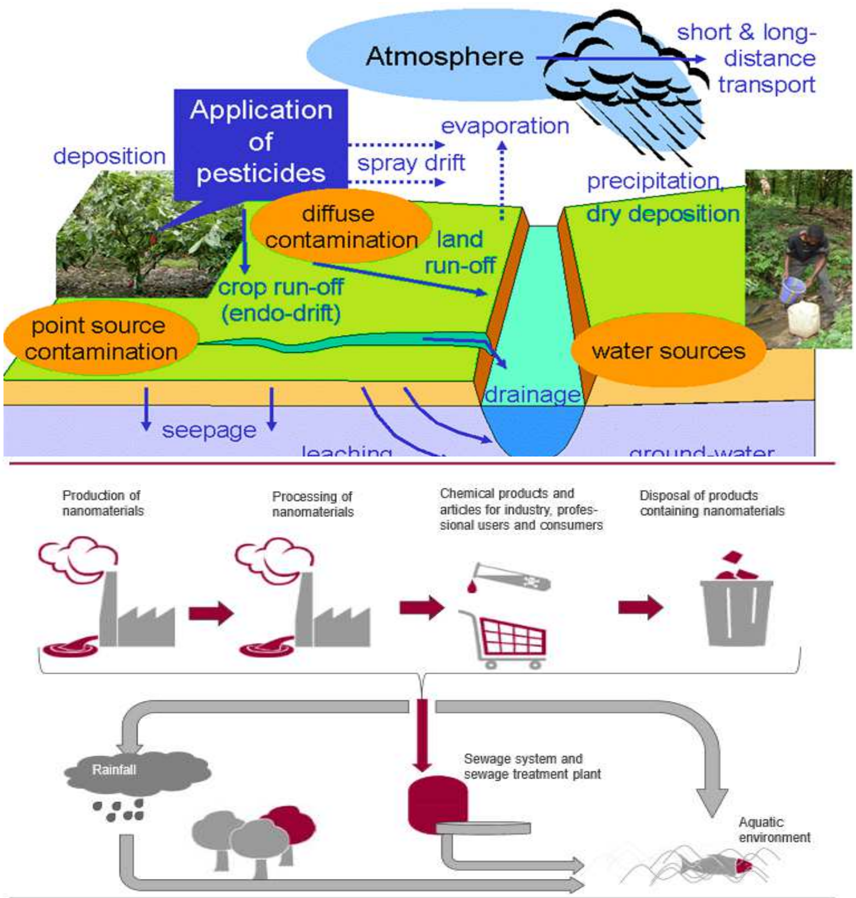

Figure 1. Lifecycle of nanomaterials and emissions sources to the aquatic environment[3].

[3] Antonia Reihlen & Dirk Jepsen. Nanomaterials and Nanotechnologies in the aquatic environment. Okopal. August 2014

2.3. Risk management and best practices

Risk mitigation depends directly on the Risk Assessment analysis and their qualities are straight interconnected: the more precise are the Risk Assessment conclusions, the best the Risk mitigation measures are.

Again methodologies based on tiered approaches are the best techniques to asses and manage the risk mitigation, independently of the position of the company in the supply chain of the nanomaterial. In Fig. 2 is outlined a set of steps that schematize the implementation of the risk evaluation strategy.

Figure 2. Steps for nanomaterial risk management.

Essentially, the guidelines suggest the following analysis of the materials and processes:

1) **Collect** information that identifies and describes the NM when possible (if not, analogous materials might help) and the intended procedures that follow. It is as important to identify the available information regarding to that NM as the lack of it, to fulfill the gaps when possible.

2) **Develop** three sets of material profiles, regarding to:

- main physico-chemical properties,
- (eco)-toxicological properties,
- potential human and environmental exposures through the NM lifecycle.

Again, gaps on information are fulfilled if possible with data from literature or new testing campaigns.

3) **Evaluate** risks information from the profiles to identify the nature and magnitude of the risks, and assess consequences of changes in applications where the risk can be reduced in this way.

4) **Assess** how to manage the risks identified in the previous steps following a hierarchy of controls (Fig.3) adapted to each case under consideration.

5) **Decision making**, appropriate to the product's stage of development and according to the controls fitting each case. Document and share such decisions.

6) **Regularly review** the state of the controls, update risk evaluation, ensure that RMMs are working properly and improve those systems when new information or conditions are provided.

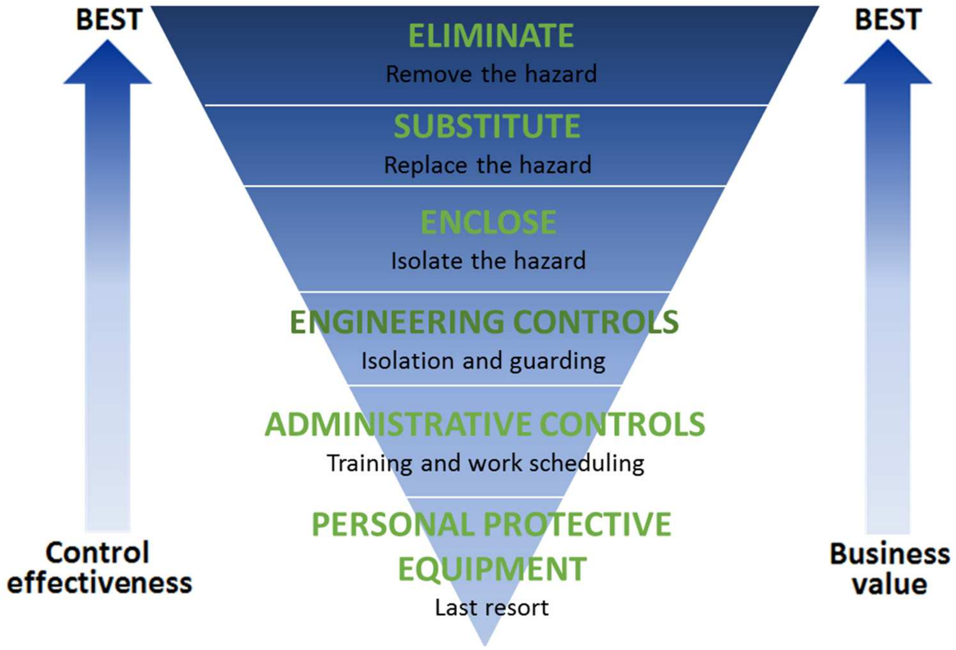

Figure 3. Hierarchy of Risk Management Measures when a hazardous ENM is identified.

3. Best practice recommendations

The capture and control of nanoparticles are important to **prevent unwanted emissions into the environment**. In this sense, **waste management strategies** are thought to reduce the environmental impact by the waste streams containing nanomaterials generated from the **whole life cycle** of a nanomaterial including production, transport, storage and use of nanomaterials.

Waste **reduction and recycling** strategies have to be the first options to reduce the nanowaste production in order to reduce the environmental exposure. Moreover, **end-of-pipe technologies** are the option that have to be implemented to remove the pollutant, nanomaterials in this case, from the air, solid and water streams before the emission to the environment.

During this section a summary of **best available technology (BAT) or best practice recommendations** to control measures will be presented. In addition, a case studies of three different levels, laboratory, pilot and industrial-scale will be presented in order to demonstrate the application of these technologies.

The **three environmental compartments** to which nanomaterials can be released are **water, soil and air**. The priority is to avoid release of nanomaterial within the facilities of the company (indoors), applying the mitigation measures necessary. However, in case there is a part of the process or an incidental release outdoors, or during waste management processes, the following cautions have to be taken into account to avoid contamination of any of the three primary compartments.

3.1. Indoor release management strategies

Following the strategies from Fig. 3, the priority is to eliminate, substitute or confine the risk at its source. Some recommendations must be followed to avoid release to each of the compartments aforesaid.

3.1.1. Air Compartment

Nanometric particles, contrary to micrometeric sized ones, can remain suspended in the air up to several minutes and move with air currents. This implies that if a process generates rapidly moving air streams, the finest airborne particles will be transported far away from the source, making aerosol control difficult[4].

In an indoor ambient, such as can be any company that works with nanoparticles, the release of this material to the air has to be controlled to avoid any risk for the human health. The size of particles determines whether they are **inhalable** (sizes below 0.01 µm up to 100 µm of aerodynamic diameter) or **respirable**, particles up to of about 10 µm that can penetrate deeply into the lungs.

Local exhaust ventilation (LEV) belong to the known as Engineering Controls (EC), and is a commonly used method of controlling the fate of airborne NMs in the form of dust, mist, fume, vapor or gas.

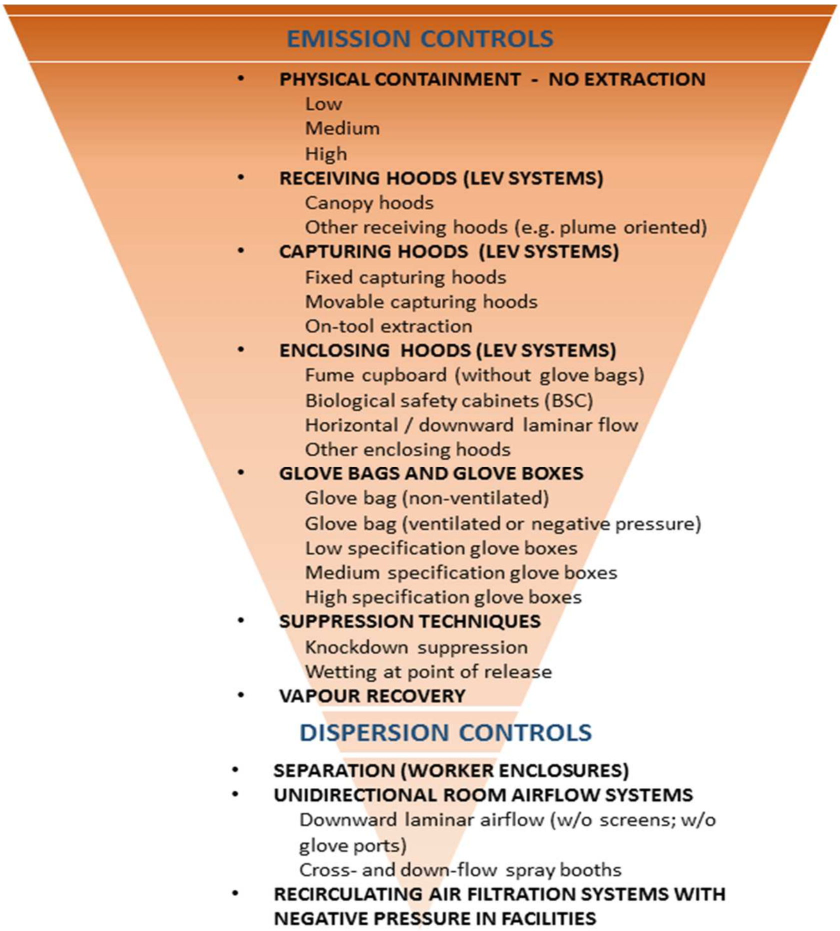

Figure 4. Proposed classification system for engineering controls in air.

The LEV system must be fit for purpose, thus a good understanding of contaminants and process demands is necessary, since they will dictate the type of inlet/enclosure/hood required.

As stated in Figure 4, there are two kind of ventilation controls, to content either emission on first place or dispersion, when the NM releases the workplace. The safest is always turn capture into an enclosure, but not always is necessary, possible or worthwhile.

[4] Health and Safety Executive. Controlling airborne contaminants at work: A guide to local exhaust ventilation (LEV). Second edition 2011

3.1.2. Water Compartment

To prevent or minimize spilt of engineered nanomaterials into water compartments, companies shall develop technologies that perform in the most environmentally friendly way. One of the best available practice is to adhere voluntarily to an Environmental Management Systems (EMS) standard to certify that the company's environmental policy is developed under objectives and action programs and is monitored and improved through continuous evaluation. There are two options to implement an EMS; the rule international ISO 14001[5] or EMAS European system, being the latter more rigorous with regarding to environmental assessment requirements.

In workplaces, optimize water consumption contributes to reduce the environmental impact and to reduce the high consumption of natural resources and pollution and generation of waste associated to it.

It is therefore important that companies install systems and flow control devices, closed loops that reuse wastewater, efficient irrigation systems, pressure limiters, diffusers or timers on taps, among others. Some routines to save water consumption and/or water contamination include:

- Control of counters, pipes and boilers and reduce the use of hot water only when strictly necessary.
- Regular inspection of pipes and joints to detect leaks or excessive consumption.
- Avoid the use of the toilet as a bin.
- Use as little water as possible.
- Recycle and reuse water resources.
- Change to dry-cleaning.
- Limit or avoid spills of contaminants to clean water sources. The use of funnels to transfer, dispensers, siphons or collector trays are recommended.
- Treat waste water to be less harmful after use.
- Update equipment to use always safe tools.
- Consider existing local laws for waste and debris elimination.

Figure 5. Water treatment cycle.

[5] ISO 14001, Environmental management systems. An easy-to-use checklist for small business. Are you ready ? ITC, 2010.

In case of accidental spills, a contingency plan must be ready to use, such as the use of specific products for neutralization and absorption or the confinement of the contaminated area for its later disinfection.

3.1.3. Soil Compartment

Nowadays on of the challenges of the 21st century is the Zero Waste in order to reduce the ecology footprint. Zero waste to landfill address the problem from whole life cycle to get a global perspective and achieve an integrated solution. In this way, zero waste involves from the responsibility and eco-design to reduction, reuse and recycling changing the one-way industrial system into a circular system more sustainable.

Companies send their waste to get dumped in a landfill and pay for this service, implementing a zero waste philosophy they can get significant savings as a consequence of reduce, reuse and recycle the raw materials.

The figure 6 shows the steps that a company have to follow to achieve the landfill free[6].

Waste Data: To reduce waste production its important know what we do and what nanowaste we are producing.

- Identify the flows of matter and energy.
- Identify which nanomaterials are used in these flows.
- Identify the waste produced.

Zero Waste objective: This is the scenario that we want to achieve, stablish the criteria and the objectives.

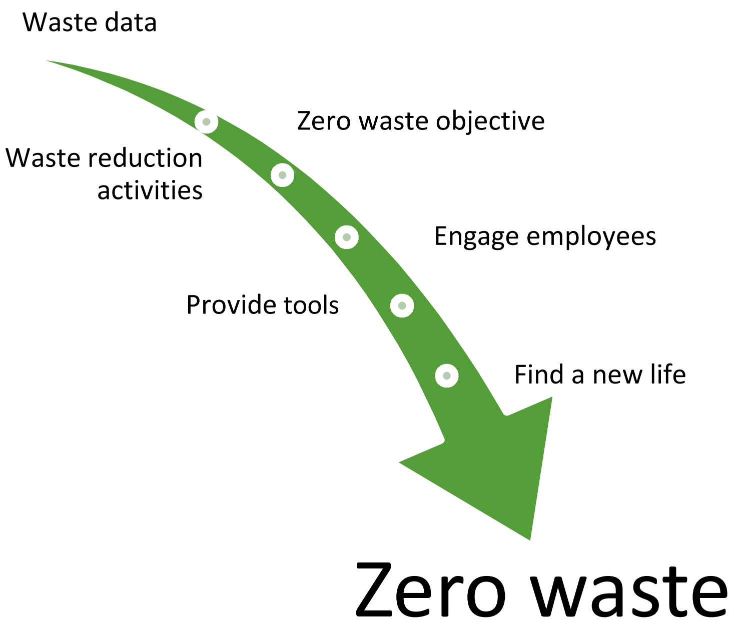

Figure 6. Landfill-free scheme.

[6] GM. The Business Case for Zero Waste. 2012

Waste reduction activities: Prioritize projects which maximizes recycling, minimizes waste, reduces consumption and ensures that products are made to be reused, repaired or recycled back into nature or the marketplace.

- Use as little resources as possible.
- Change the materials used has ones that are more respectful of the environment.
- Separate the nanowaste form the general waste.

Engage Employees: Integrate the employees in the objective of zero waste through formation, courses, suggestions mailbox, etc.

- How to manage the nanopaterials and nanowaste.
- Use specific places to manipulate the nanomaterials
- Check periodically the containers, bottles, bags, etc. in order to prevent leaks

Provide tools: The Company have to provide tools to run the activities.

- Install specific containers to collect the waste along the production chain.
- Install safety work places as a hood cabins or leakproof deposits.
- Install safety storehouse.

Find a new life: Our waste can be the raw material for others.

- Develop a market study to find opportunities.

3.2. Outdoor release management strategies

Once it cannot be contained the release of NM within the confinement, it has to be ensured that the risks reaching outdoors are reduced to the minimum or eliminated. During these last years, numerous studies have been conducted to determine the effectiveness in removing nanoparticles from waste streams using conventional and novel technology. The result obtained are described below.

3.2.1. Air Compartment

3.2.1.1. Electrostatic precipitator

The electrostatic precipitator is used for removing particles, and it has been used satisfactorily for the cleaning of flue gas from large-capacity factories, combustion furnaces, and thermal power plants. It is designed to trap and remove dust particles from the exhaust gas stream of an industrial process charging the dust particles in the gas stream and collecting them and attracted to and deposited on plates or other collection devices. Nevertheless, but the **conventional electrostatic** precipitator cannot remove submicron particles and the collection efficiency drops less than 40 % when the particle size is less than 1 μm[7].

Wet electrostatic precipitator is a modified electrostatic precipitator that collect the charged particles on the wet collecting surface washing the electrodes with liquid. Different configuration can be found in

[7] Vishnu Thonglek1, TanongkiatKiatsiriroat. Improvement of Electrostatic Precipitator for Submicron Particle Collection by Non-Thermal Plasma Pre-Charger. International Journal of Emerging Technology and Advanced Engineering 2013; Volume 3, Issue 10.

literature, wire-to-plate single-stage wet electrostatic precipitator[8] and tubular electrostatic precipitator[9] are two of them reaching **values higher than 90% of removal efficiency for nanoparticles** with diameter of 80 to 600 nm.

The process of collecting particles in electrostatic precipitator depends on the electric force. More electrical charges on the particles could be obtained with high electric field. In this sense the combination of an **electrostatic precipitator with a non-thermal plasma pre-charger[10] increase the removal efficiency on nanoparticles up to 90 %**.

3.2.1.2. Scrubber

A scrubber is a pollution control device that use liquid to wash unwanted pollutants from a gas stream that can be used to remove some particulates and/or gases from industrial exhaust streams.

Newest configurations combined in one unit a high efficiency thermal oxidizer, a novel **nucli-condensation wet electrostatic precipitator** and **a low-temperature PFCs catalytic reactor**[11] reaching high abatement efficiencies, **removal efficiency greater than 99%.**

3.2.2. Water Compartment

3.2.2.1. Waste water treatment plant

The municipal **water treatment plants** (WTP) act as the gateways that control the release of the nanomaterials from industrial and domestic sources to the aquatic environment via treated effluent that is discharged into surface waters[12].

Previous lab-scale investigations on nanomaterials removal (especially nano-Ag and oxide nanoparticles) have shown that about 90% of **nanomaterials are efficiently reduced by biological treatment** and accumulated in the activated sludge or biosolids[13],[14]. According Westerhoff[15], [16], in full-scale activated sludge systems (1500–3000 mg/L), more than 90% removal of most nanomaterials was observed **but** this removal efficiency **cannot be true for all** the nanomaterials. In this sense ZnO, quantum dots or fullerenes which are used in several productive processes have low values of removal efficiency.

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[8] Chen T-M, Tsai C-J, Yan S-Y, Li S-N. An efficient wet electrostatic precipitator for removing nanoparticles, submicron and micron-sized particles. Separation and Purification Technology 2014, 136; 27–35.

[9] Saiyasitpanich P, Keener T.C, Khang S-J, Lu M. Removal of diesel particulate matter (DPM) in a tubular wet electrostatic precipitator. Journal of Electrostatics 2007, 618–624.

[10] Vishnu Thonglek1, TanongkiatKiatsiriroat. Improvement of Electrostatic Precipitator for Submicron Particle Collection by Non-Thermal Plasma Pre-Charger. International Journal of Emerging Technology and Advanced Engineering 2013; Volume 3, Issue 10.

[11] Hsu J-N. Novel Local Scrubber for PFCs, SiH4 and Nanoparticles Industrial Technology Research Institute. 2014.

[12] Li L, Harmann G, Doblinger M, Schuster M. Quantification of nanoscale silver particles removal and release from municipal wastewater treatment plants in Germany. Environ Sci Technol 2013; 47(13):7317-7323.

[13] Liu J, Pennell KG, Hurt RH. Kinetics and mechanisms of nanosilver oxysulfidation. Environ Sci Technol 2011; 45(17):7345-7353.

[14] Limbach LK, Bereiter R, Muller E, Krebs R, Galli R, Stark WJ. Removal of oxide nanoparticles in a model wastewater treatment plant: Influence of agglomeration and surfactants on clearing efficiency. Environ Sci Technol 2008;42:5828-5833.

[15] Westerhoff P, Kiser M A, and Hristovski K. Nanomaterial Removal and Transformation during Biological Wastewater Treatment Environmental Engineering Science. March 2013, 30(3)

[16] Westerhoff P, Zhang Y, Crittenden J, Chen Y. Properties of commercial nanoparticles that affect their removal during water treatment. In: Nanoscience and Nanotechnology: Environmental and Health Impacts (Grassian VH, ed). Hoboken, NJ:John Wiley & Sons, 2008. 71–90.

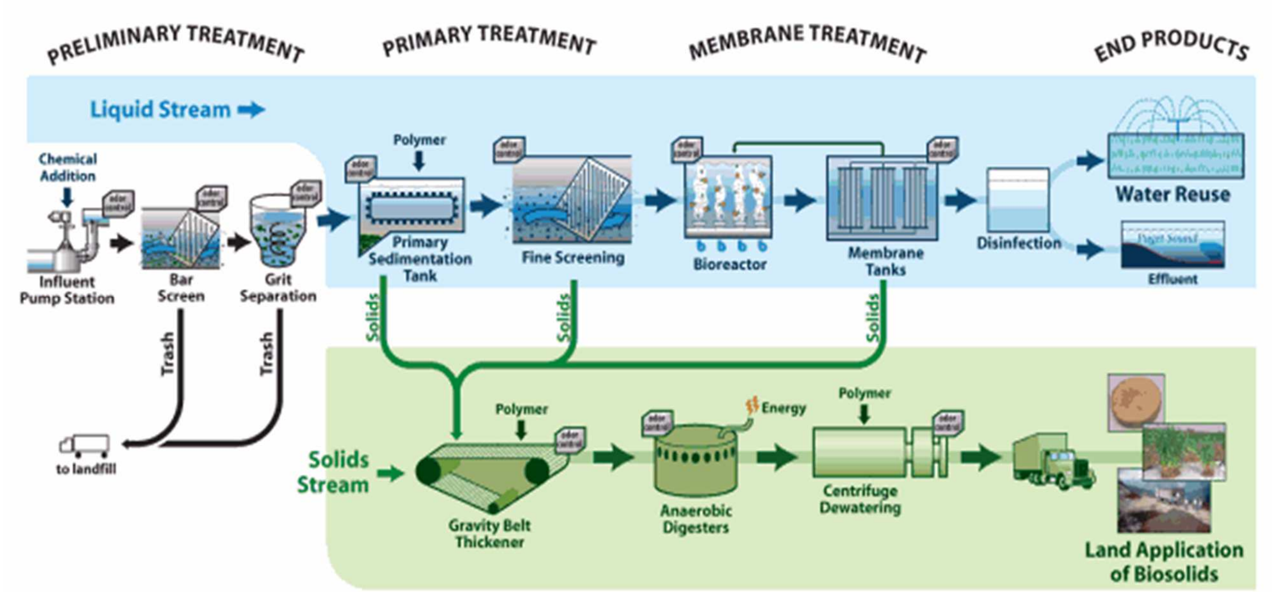

Figure 7. Scheme of water treatment plant.

3.2.3. Activated sludge

The activated sludge is a process to treat wastewater streams using a biological floc composed of bacteria and protozoa in aerobic conditions. These microorganisms are appropriate to remove organic pollutants through three components, a reactor in which the microorganisms are aerated and in contact with the pollutants, liquid-solid separation and a sludge recycling system.

Studies carried out show that **activated sludge treatment also permits the elimination of nanoparticles**. Concretely, the results showed that nano-CeO_2 was highly removed during activated sludge treatment (96.6% total Ce)[17]. In this sense, a study carried out the removal of Ag, TiO_2 and SiO_2 nanoparticles were investigated[18]. Despite of a considerable amount of NPs were removed after exposure to activated sludge, 95 % of TiO_2 and SiO_2 just in 1 hour and 90 % of Ag in 24 hours, the removal efficiencies can be affected by the operating conditions of the activated sludge process and the conditions of the activated sludge.

3.2.3.1. Nanoporous membranes

These technologies consist of a regular organic or inorganic framework supporting a regular and porous structure. The size of the pores is generally smaller than 100 nm. Most nanoporous materials can be classified as bulk materials or membranes. Activated carbon and zeolites are two examples of bulk nanoporous materials, while cell membranes can be thought of as nanoporous membranes[19].

This Technologies **could be used** in the future in the selective **decontamination** of waste water and sludge[20]. It should be noted that a nanoporous material with consistently sized pores has the property of letting only certain substances pass through, while blocking others.

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[17] Gómez-Rivera F., Field J.A., Brown D., Sierra-Alvarez R. Fate of cerium dioxide (CeO_2) nanoparticles in municipal wastewater during activated sludge treatment. Bioresource Technology, 2012. 108, 300–304.

[18] Park H-J, Kim H-Y, Cha S, Ahn C-H, Roh J, Park S, Kim S, Choi K, Yi J, Kim Y, Yoon J. Removal characteristics of engineered nanoparticles by activated sludge. Chemosphere, 2013. 92; 524–528.

[19] Holister P. Nanoporous Materials. Cientifica, 2013.

[20] Tsuzuki T. Nanotechnology Commercialization 2013. Taylor and Francis Group, LLC, 2013. 399.

3.2.3.2. Electrofiltration, microfiltration and nanofiltration

Electrofiltration is a method that combines membrane filtration and electrophoresis in a dead-end process. This is a highly innovative state of the art technique for separation of colloidal substances. This process permits to minimize the film formation on the filter membrane which hinders filtration through the application of an electric field. This improves the filtration performance and increases selectivity in case of fractionation.

Electrofiltration, microfiltration and nanofiltration are three of the processes with higher potential to treat waste water with presence of nanoparticles[21]. This process of electrofiltration could be combined with microfiltration and nanofiltration to maximize the yield of nanoparticle elimination. Microfiltration is a low-pressure cross-flow membrane process for separating colloidal and suspended particles in the range of 0.05-10 µm[22]. For nanoparticles by positively charged the removal efficiency is higher than 99 % even though pore diameters are up to 20 times the nanoparticles diameter. For negatively charged nanoparticles are less well rejected but rejection depend more upon nanoparticles properties than membrane properties[23].

3.2.4. Soil Compartment

3.2.4.1. Incineration

Incineration is one of the most common processes to directly treat nanowaste. Incineration is a process that involves the combustion of organic substances contained in waste materials and converts the waste into ash, flue gas, and heat. The flue gases must be cleaned of gaseous and particulate pollutants before they are dispersed into the atmosphere[24].

Projects carried out on the persistence of CeO_2 nanomaterials in full-scale waste incineration plants show that they bind loosely to the solid residues from the combustion process and can be efficiently removed from the flue gas using current filter technology[25].

Using a post treatment system coupled to the incinerator, a gas cleaning system as filter and acid washing flue gas or electrostatic precipitator and a scrubber, the **removal efficiency reached is higher than 99 %[26].** Nevertheless, the residues to which the nanomaterials bind normally end up in landfills, so the problem of nanoparticles could be transferred to the following stage.

[21] Nee U.H., Byoung-Cheun L., Younghun K. New Paradigm for Nanowastes Treatment. Clean Technology, 2012. 18, 50-258.

[22] GEA Process Engineering Inc, 2014. Filtration technologies. Ultrafiltration, Nanofiltration, Microfiltration and Reverse Osmosis for Liquid Separation State-of-the-Art Technology for a Complete Solution. Web: http://www.niroinc.com/filtration/filtration_technologies.asp

[23] Ladner, D.A., Steele, M., Weir, A., Hristovski, K., and Westerhoff, P. Functionalized nanoparticle interactions with polymeric membranes. Journal of Hazardous Materials, 2012. 211, 288.

[24] European Commission. Integrated Pollution Prevention and Control Reference Document on the Best Available Techniques for Waste Incineration. August 2006.

[25] Walser T, Limbach LK, Brogioli R, Erismann E, Flamigni L, Hattendorf B.. Persistence of engineered nanoparticles in a municipal solid-waste incineration plant. Nature Nanotech 2012; 7:520-524.

[26] Amara L. Holder,a Eric P. Vejerano,b Xinzhe Zhoub and Linsey C. Marr, Nanomaterial disposal by incineration. Cite this: Environ. Sci.: Processes Impacts, 2013, 15, 1652.

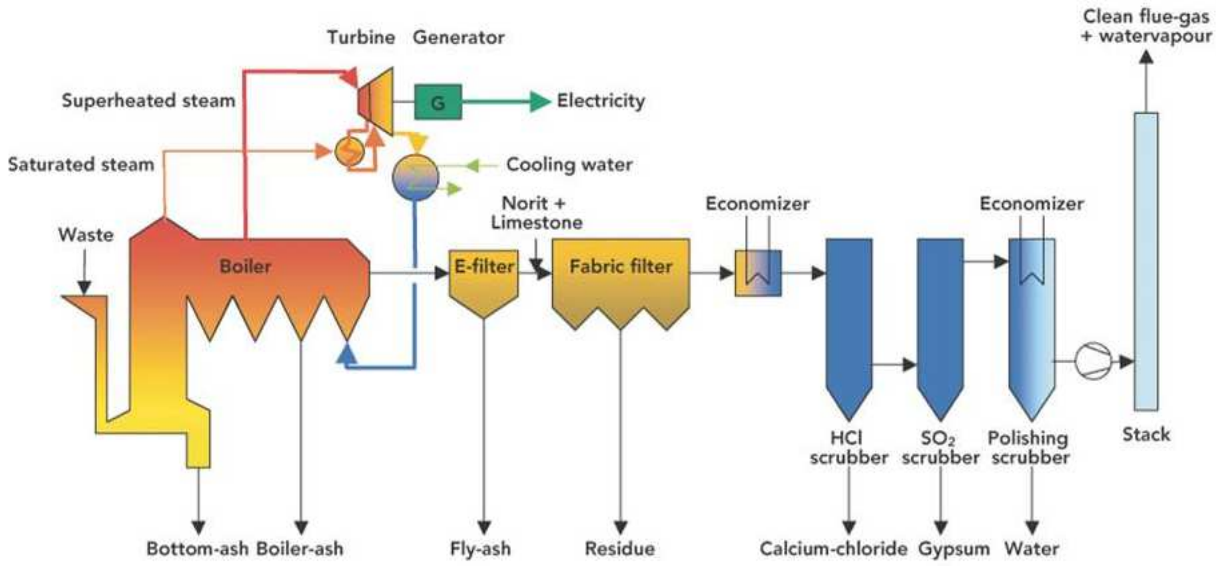

Figure 8. Scheme of waste incineration plant.

3.2.4.2. Landfilling

Is a site for the disposal of waste materials and can be applied directly to untreated residues containing nanowaste as well as for sludge and ashes coming from the prior processes of water treatment and incineration.

The removal reached through is **next to 100 % if no leachate is produced**. Nevertheless, the presence of the nanoparticles in the waste can produce interactions, changing the physico-chemical properties[27] and the inhibition on the microorganism activity[28] THAT could act as continuous releasing source of the nanomaterials to soil and underground water.

3.2.4.3. Fast crystal growth

The process of fast crystal growth **presents an opportunity for the treatment of industrial sludge** containing amorphous/nanophase metal oxides or hydroxides[29]. This technology is presented as an alternative to incineration for the treatment of sludge from industrial water treatment or to immobilize hazardous waste[30] or stabilize ash from the incinerator[31].

Ésta tecnología se presenta como una alternativa a la incineración para el tratamiento de lodos procedentes del tratamiento de aguas industriales o para la inmovilización de residuos peligroso o estabilizar cenizas de incineración.

[27] Bolyard SC, Reinhart DR, Santra S. Behavior of engineered nanoparticles in landfill leachate. Environ Sci Technol 2013; 47:8114-8122.

[28] Yang Y, Gajaraj S, Wall JD, Hu Z. A comparison of nanosilver and silver ion effects on bioreactor landfill operations and methanogenic population dynamics. Water Res 2013; 47:3422-3430.

[29] Zhuang Z, Xu X, Wang Yo, Wang Ya, Huang F, Lin Z. Treatment of nanowaste via fast crystal growth: With recycling of nano-SnO_2 from electroplating sludge as a study case. Journal of Hazardous Materials 2012; 211: 414–419.

[30] Liu WeiZhen, Xu XinJiang, Wang YongJing, He Zhong, Zhou Nan, Huang Feng and Lin Zhang. Treatment of Cr(VI)-containing nanowastes via the growth of nanomaterial. February 2010 Vol.55 No.4-5: 373−377.

[31] P. Kavouras, Ph. Komninou*, K. Chrissafis, G. Kaimakamis, S. Kokkou, K. Paraskevopoulos, Th. Karakostas. Microstructural changes of processed vitrified solid waste products. Journal of the European Ceramic Society 23 (2003) 1305–1311.

3.2.4.4. Phytomining / Phytoremediation

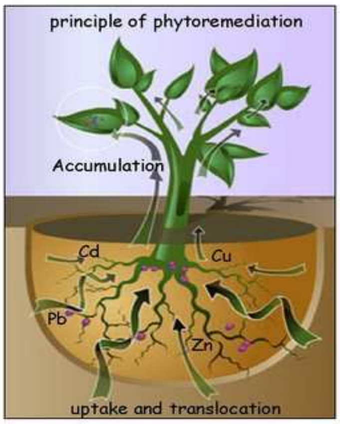

Figure 9. Phytoremediation principle

Phytomining is the planting (and subsequent harvesting) of vegetation that selectively concentrate specific metals from the environment into their tissues, for the primary or subsidiary purpose of commercial exploitation of the extracted metal. Some of these plants are natural hyperaccumulators, and in others the property can be induced. Pioneering experiments in this field might lead to green alternatives to existing, environmentally destructive, opencast mining practices[32].

The economics of phytomining basically depends on the metal content in the soil, metal uptake by the plant, plant biomass and most importantly the metal price. Nevertheless, the relative high prices of nanomaterials and especially Au and Ag nanoparticles could permit the use of these techniques with a double objective. Firstly, to carry out the depuration of sludge, soil, water; and secondly, as a green process for the production of gold nanoparticles by simple treatment of gold salts with soybean extracts. The application of phytomining in silver hyperaccumulation is described in Medicago sativa and Brassica juncea.

A summary of the information acquired during the bibliographic review is shown in the following Table 2.

Table 2. Summary of bibliographic information regarding treatment techniques for nanomaterila´s removing.

Treatment technique	Features	Nanomaterials	Removal efficiency
Activated sludge	Lab scale continuous bioreactor	Ag-NP, TiO_2, SiO_2	95% TiO_2, 95% SiO_2 in 1h. Ag-NP: 50% in 1h, 90% in 24h
	Municipal conventional activated sludge wastewater treatment plant. Treats 90% domestic and 10% industrial wastewater	CIT-Ag, PVP-Ag, PVP-Au, Car-Ag, GA-Ag, TA-Au, Car-PS, Sulf-PS, and aq-nC60	CIT-Ag, PVP-Ag, PVP-Au, Car-Ag, and GA-Ag: 39 to 62%; TA-Au, Car-PS, Sulf-PS, and aq-nC60: 92 to 94% of removal
	Full-scaled activated sludge systems	Au, Ag, Cu, CeO_2, TiO_2, SiO_2, C60	> 90% removal of most ENMs. Cu NPs were removed more effectively (~95% for all Cu concentrations) in biomass sludge
Anaerobic digestion	Waste activated sludge (WAS) anaerobic digestion.	ZnO-NP and hydrophobic ZnO-NP	Digestion process removed vast majority of the added Zn
Electrocoagulation / electrofiltration	Simultaneous crossflow electrocoagulation / electrofiltration	Cu-CMP and oxide-CMP wastewaters (CMP = chemical mechanical polishing)	Total solids content, total organic carbon, and silicon for Cu-CMP wastewater were 88%, 64%, and 79%, respectively; whereas 86%, 71%, and 82%, respectively for oxide-CMP wastewater

[32] Brooks R.R., Chambers M.F., Nicks L.J., Robinson B.H. Phytomining. Elsevier Science, 1998. 3, 9, 359-362.

Treatment technique	Features	Nanomaterials	Removal efficiency
Microfiltration and ultrafiltration	Membranes	Silver, titanium dioxide, and gold with diameter of 2 to 10 nm	> 99%
Water treatment plant	Treatment plant: non-aerated, aerated tanks and secondary clarifier	Ag-NPs	60% Ag-NP transformed into Ag_2S
	Bench scale coagulation/flocculation/sedimentation simulated in conventional treatment, microfiltration and ultrafiltration	Ag, TiO_2, ZnO	Ag: 80-98%; TiO_2: 92-97%; ZnO: 1-52% Ag+MF: 98-100%; TiO_2+MF: 96-100%; ZnO+MF: 4-98% Ag+UF: 55-99%; TiO_2+UF: 56-100%; ZnO+UF: 17-64%
	Waste water treatment plant: coagulation (adding different concentration of NaCl, $MgCl_2$, KCl), sedimentation and filtration. Addition of alum (aluminium sulfate)	Hematite, TiO_2, ZnO, Silica, Fe_2O_3, NiO, CdTe Quantum Dots, Fullerene (nC60)	Hematite: < 20%
			TiO_2 : 90%; TiO_2+ 100mM MgCl2:95%; TiO_2 in postsedimentation: 40%; TiO_2 in postfiltration: 95%; TiO_2+alum (postfiltration): > 95%
			ZnO: 5% ; ZnO + 100mMMgCl2: 30%
			Silica: 40%; Silica + 100MmMgCl_2: 50% (sedimentation only)
			Fe_2O_3: 30% ;Fe_2O_3+100mM $MgCl_2$: 35% (sedimentation only)
			NiO: 30% NiO + 100MmMgCl_2: 30% (sedimentation only)
			CdTe Quantum Dots: 0% (sed and filtration); QD+alum: 70% in postsedimentation; QD+alum: 90% in postfiltration
			Fullerene (nC60): 0%; Fullerene (nC60)+10mM NaCl: 40%; Fullerene (nC60)+100mM NaCl: 95%
	WWTPs different biological treatment: activated sludge, microfiltration, membrane biological reactor	Ag-NP	Primary clarification: 10%; Ag-NP: 99,9% removed in biosolids in sludge
	Lab-scale reactors, sequencing batch reactor (SBR). Wastewater treatment plant with activated sludge process and tertiary filtration	TiO_2	Wastewater treatment plant with activated sludge process and tertiary filtration: 82% removal of TiO2; SBR: 70-85% TiO2 in biosolids
Scrubber	High-efficiency thermal oxidizer + nuclicondensation wet electrostatic precipitator + low-temperature PFCs catalytic reactor.	PFCs, SiH_4 and nanoparticles	>99%
Electrostatic	Wet Electrostatic Precipitator / ion generation zone +	Standard monodisperse polystyrene latex	70%–90% for particles of sizes 80–600 nm diameter, for 20–80 nm diameter measured collection efficiency ranged 40%–70%,

Treatment technique	Features	Nanomaterials	Removal efficiency
precipitator	Charging zone + collecing plate	(PSL) particles (91 nm and 150 nm)	
	Wire-to-plate single-stage wet electrostatic precipitator	Nanoparticles	99.2–99.7% when the WESP was operated with fine water mist
	Tubular wet electrostatic precipitator	Diesel particulate matter (20-40 nm)	Removal efficiency was greater than 90% at a 75-kW engine load (residence time of 0.4 s corresponding to 25% of maximum exhaust flowrate). However, at 100% exhaust flowrate (75-kW engine load), the WESP provided an average removal efficiency of 67% for DPM mass and number concentrations. The use of two WESPs in series could offer more than 90% DPM removal at only 400W power consumption.
	Conventional dc-energized ESP	Diesel PM investigated were 99% C, 0.1% Si, 0.07% Fe, 0.1% Ca, 0.4% S, and 0.03% Zn	The conventional dc-energized ESP showed good collection efficiency for particle sizes less than 300 nm where adhesion force was dominated over electrostatic repulsion
	Trapezoidalwaveform-energized ESP (TW ESP)	Diesel PM investigated were 99% C, 0.1% Si, 0.07% Fe, 0.1% Ca, 0.4% S, and 0.03% Zn	TWESP suppressed the particle reentrainment for larger particles but still showed negative collection efficiency
	Electrohydrodynamically assisted ESP (EHD ESP)	Diesel PM investigated were 99% C, 0.1% Si, 0.07% Fe, 0.1% Ca, 0.4% S, and 0.03%	> 90% up to 200 nm / 80% range at 400 nm.
	Combined system of Electrostatic precipitator + Diesel particulate filter	Exhaust gas from a diesel engine/ highest number concentration of particles 69.8 nm	98 to 100 % wo/w ESP
	Non-Thermal Plasma Pre-Charge r+ Electrostatic Precipitator	Exhaust gas supply (diesel burner) / 300-500 nm	> 90% when the NTP precharger was included.
Waste Incineration Plant	Incinerator + electrostatic precipitator + Scrubber	CeO_2	> 99 %
	Incinerator + filter + acid washing flue gas	TiO_2, ZnO, Ag and CNT	>99,9The emissions into water and air are almost not existent
	Incinerator + gas cleaning system	CeO_2	99.6% in the electrostatic precipitator and greater than 99.9% in the wet scrubber

Treatment technique	Features	Nanomaterials	Removal efficiency
Fast crystal growth	SiO_2 and Na2O as vitrifying and melting agent, respectively	Lead-rich solid industrial wastes	60 wt.% of solid waste, Products with such a high content of solid waste comprise an economically realistic suggestion, but are easily devitrified in conditions of large-scale production due to the difficulty to achieve rapid cooling conditions
	Solid/liquid rate was 1:4, Na-HCO3 amount was 0.4 kg per kg for the original nanowastes, and the mixture was kept for 4 h at 120°C.	Cr(VI)-containing nanowastes ($Mg(OH)_2$, $CaCO_3$)	Cr(VI) removal efficiency is 97.8%
	2,3 kg sludge + 200 g H_2O + 32 g NaOH as a mineralizer	nano-SnO_2 from tinplate electroplating sludge	Nano-SnO_2 could be recycled via dissolving other solid compositions in the sludge by using acid.
Phytorremediation	P. vulgaris (leguminous), T. aestivum (grass), R. crispu (wetland plant), E. canadiensis (aquatic p lant). Roots were rinsed in $CaCl_2$ solution (clean adsorbed metals) and also unrised.	TiO_2	Phaseoulus vulgaris, T. aestivum no difference between rinsed and unrised
			Triticum aestivum (higher concentrations of Ti in roots)
			Rumex crispus (higher concentrations in roots, translocated into the shoots → entering trophic level)
			Elodea canadiensis (oligotrophic systems more difficult than eutrophic systems)
	Production of gold nanoparticles	Au-NPs	Aminoacids→formation of Au-Np
	Using Reed plants to manufacture Au-NPs. Medicago arabiga y Festuca sp.	Au-NPs	M. arabiga manufacter > Au-Np than Festuca sp.
	Water hyacinth plant (Eichhronia crassipes)	Ag-NPs	Manufacture through heavy metals in soils
	Alfalfa plants	Au and Ag-NPs	Production of these NPs within the living plants
Landfill	Interactions between nanoparticles and leachate components	ZnO, TiO_2, Ag-NPs	< aqueous concentrations → low solubility of these NPs; Dispersion of the coated ZnO, TiO_2, Ag NPs in leachate; ZnO in leachate solids natrices; Aqueous NPs retained in solid waste
	General review of landfilling and NMs (a future vision)	NMs	Changing in situ landfill conditions (e.g., leachate characteristics, moisture content, temperature) will likely greatly influence NM behavior
	Landfill anaerobic digestion	Ag-NPs	Inhibited methanogenesis at 10mg/Kg solids. Reduce biogas production
	Landfill	Ag-NP,TiO_2, ZnO	[Ag-NP] = 10mg/kg solid→ inhibited methanogenesis. Majority retained in solid waste.

3.3. Case studies

This section reflects the best available techniques for typical cases of waste management with nanoparticles for three levels of study. Laboratory, pilot and industrial.

3.3.1. Laboratoy-scale case study

Laboratories generate small amounts of nanowastes, usually less than 1 kg per month. Its activities are related to the realization of characterization and performance tests in which the viability and suitability for their pilot scale tests are determined.

The following list shows the work processes which are carried out in a typical laboratory[33].

- Reception of nanomaterials
- Sampling
- Cleaning and maintencance
- Storage
- Analysis/funcionalisation/mixture/formulation
- Waste management

The table 3 shows the nanowastes generated during work processes described and the best available techniques for each case.

Table 3. Application of best available techniques for waste management in a laboratory scale.

Waste	Best available techniques
Contaminated packaging/containers	Waste incineration plant, Landfill
PPEs	Waste incineration plant, Landfill
Waste water	Activated sludge, Electrocoagulation, ultrafiltration and water treatment plants
Contaminated laboratory consumables	Waste incineration plant, Landfill, Activated sludge, Electrofiltration, Water treatment plant
Filters for air emissions	Waste incineration plant, Landfill
Contaminated cleaning tools	Waste incineration plant, Landfill

[33] NanoSafePack Consortium. Best practice guide for the safe handling and use of nanoparticles in packaging industries. 2014

3.3.2. Pilot-scale case study

Pilot facilities generate moderate amounts of nanowastes, usually less than 20 kg per month. Take the data got it in the laboratory scale and test it to check the scalability as a previous step for industrial scale.

The following list shows the work processes which are carried out in a typical pilot plant[34].

- Reception of nanomaterials
- Storage
- Processing
- Cleaning and maintenance
- Waste management

The table 4 shows the nanowastes generated during work processes described and the best available techniques for each case.

Table 4. Application of best available techniques for waste management in a pilot plant.

Waste	Best available techniques
Contaminated packaging/containers	Waste incineration plant, Landfill
PPEs	Waste incineration plant, Landfill
Waste water	Activated sludge, Electrocoagulation, ultrafiltration and water treatment plants
Non valid products	Waste incineration plant, Landfill, Activated sludge, Electrofiltration, Water treatment plant
Filters for air emissions	Waste incineration plant, Landfill
Contaminated cleaning tools	Waste incineration plant, Landfill

[34] NanoSafePack Consortium. Best practice guide for the safe handling and use of nanoparticles in packaging industries. 2014

3.3.3. Industrial-scale case study

Industries generate an important quantities of nanowastes, usually less than 100 kg per month. Take the data got it in the pilot scale and starts the production on the final product.

The following list shows the work processes which are carried out in a typical industry[35].

- Reception of nanomaterials
- Storage
- Processing
- Cleaning and maintenance
- Waste management

The table 5 shows the nanowastes generated during work processes described and the best available techniques for each case.

Table 5. Application of best available techniques for waste management in an industrial plant.

Waste	Best available techniques
Contaminated packaging/containers	Waste incineration plant, Landfill
PPEs	Waste incineration plant, Landfill, Fast crystal growth
Waste water	Activated sludge, Electrocoagulation, ultrafiltration and water treatment plants, Phytorremediation
Non valid products	Waste incineration plant, Landfill, Activated sludge, Electrofiltration, Water treatment plant
Dust/Air emissions	Scrubber, Electrostatic precipitator
Contaminated cleaning tools	Waste incineration plant, Landfill

[35] NanoSafePack Consortium. Best practice guide for the safe handling and use of nanoparticles in packaging industries. 2014

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