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Fate of Engineered Nanoparticles in Wastewater Treatment Plant

Losy projektowanych nanocząstek w oczyszczalni ścieków

A nanomaterial has at least one dimension in the nanometre scale of approximately 1 to 100 nm. Because of their very small size, nanostructures have different physicochemical properties, compared to the same materials on the macro scale. Engineered nanoparticles (ENPs) are deliberately produced by man using many different materials, such as metals: Ag, Zn, Au, Ni, Fe, and Cu; metal oxides: TiO_2, Fe_3O_4, SiO_2, CeO_2, and Al_2O_3; nonmetals: silica and quantum dots; carbon: nanotubes and fullerene as well as graphene. The nanoparticles are used in all industrial and medicine, pharmacy, cosmetics, agriculture, transport, energy. Fast-growing nanotechnology provides a wide spectrum of applications, but it also brings new and unknown risks to human and environment. In recent years, the environmental release of ENPs has been on the rise because of increase of NPs in commercial products. Moreover, the fate of NPs in wastewater treatment processes may play an important role in determining the pathway their environmental release. The nanoparticles in wastewater treatment plants will experience aggregation, sedimentation, transformation which may affect their concentration in effluents, but also in the sludge. The most laboratory studies focused on fate of nanoparticles in activated sludge process were carried out with SBR reactors with addition of Ag, ZnO, CeO_2 and TiO_2 nanoparticles. Bacteria in biological treatment processes are likely be exposed to nanoparticles that have undergone agglomeration and transformation. These nanoparticles could agglomerate or even get adsorbed to the extracellular polymers during primary and secondary treatment eventually ending up in wastewater sludge. Hence, the fate of engineered nanoparticles during wastewater treatment process should be investigated to help reduce the risk of their potential negative environmental effects. In the article reviews of the recent results in the literature concerning transformation of engineered nanoparticles during treatment process have been shown.

Keywords: nanoparticles, wastewater treatment, sewage sludge

Introduction

Nanoparticles have a long history. The behavior and fate of naturally occurring nanoparticles and colloids has been intensively studied for decades. The existence of naturally occurring nanoparticles in water, air and soil is known from the beginning of earth's history as they have been recorded from 10 000 years old glacial ice cores. These nanoparticles are assumed to be derived from natural combustion processes and deposited into the ice core via atmospheric deposition [1]. Likewise,

the presence of natural nanoparticles has also been recorded from the sediments of Cretaceous-Tertiary (K-T) boundary at Gubbio, Italy [2]. Many geological and biological processes are known to produce natural nanoparticles. Geological mechanisms include physico-chemical weathering, authigenesis/neoformation and volcanic eruptions [3].

The European Commission has recently (2011) adopted a recommendation on the definition of nanomaterial according to which 'nanomaterial' means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range $1 \div 100$ nm. Such applications exploit the properties, distinct from bulk/macroscopic systems, of nanoscale components [4].

In nanometer range, particles exhibit different thermal, mechanical, optical and electrical properties from the bulk material. Large surface area to volume ratio provides various unique and new properties, which are utilized in many fields of nanotechnology.

Daily used articles such as cosmetics skin and hair care products, strain resistant clothes, cleaning agents, nanotextiles etc. containing nanoparticles have become a major concern of nanopollution. These products are released into the municipality collection systems and finally flows into wastewater treatment plants (WWTP). In general, fate and transport processes that act on ENPs during wastewater treatment processes include among others oxidation and reduction, precipitation, settling, adsorption, desorption, biotransformation, agglomeration or aggregation. Nanoparticles are then released into the soil mainly via sewage sludge and WWTP effluent. However, the fate of NPs through the WWTP and in the environment has not been comprehensively explored although research publications are increasingly emerging in this area.

The present work deals with reviewing the fate of selected engineering nanoparticles during wastewater treatment process taking into account their removal efficiency from wastewater as well as accumulation in sewage sludge. The reviewed literature covers the most used ENPs and studies performed in model wastewater treatment plants.

1. Nanoparticles

Engineered nanoparticles (ENPs) have been used in many fields from automotive, electronics, building, personal care and health products, clothing and textiles, cosmetics, household, toys, food additives and food packaging, sports equipment up to biotechnology and medicine. Nanoparticles can be categorized by their chemical composition, size and shape, and surface chemistry.

Morphological characteristics to be taken into account are: flatness, sphericity, and aspect ratio. Nanoparticles can be spherical, tubular or irregularly shaped, and can exist in fused, aggregated or agglomerated forms. A simple classification of nanomaterials is based on their structures includes zero dimension, one dimension, two dimensions, and three dimensions (Fig. 1) [5].
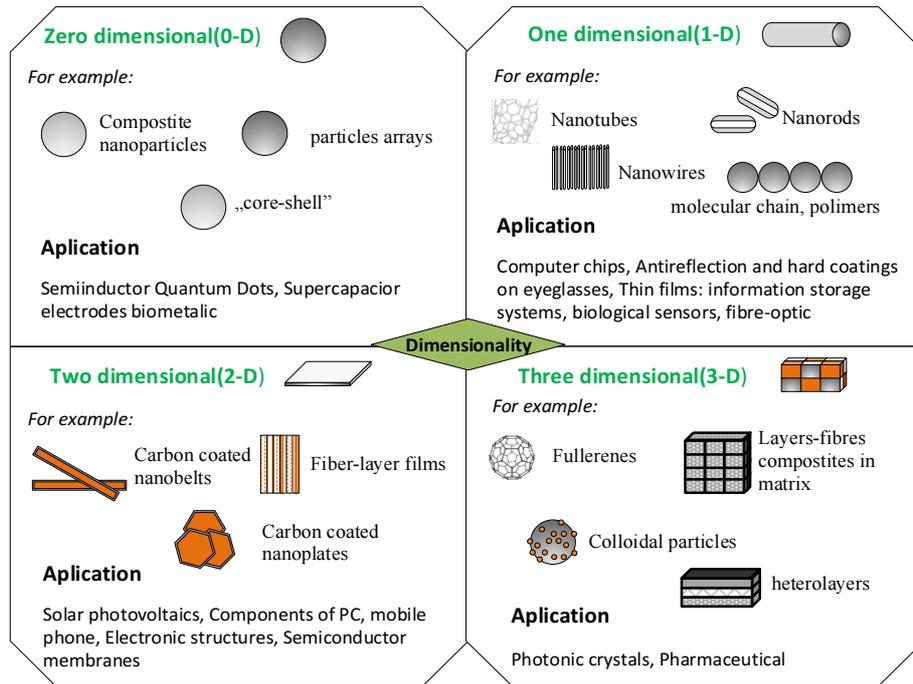
Fig. 1. Main types and applications of nanoparticles [6-8]

The diversity and use of nanoparticles generally referred to as engineered nanoparticles in industrial and consumer product manufacturing is increasing with high speed. For instance, in 2010, the Nanotechnology Consumer Product Inventory (CPI) listed 1012 nanoproducts from 409 companies in 24 countries. While, in 2015 it was 1827 nanoproducts in 33 countries (17 products in Poland). Moreover, Figure 2 shows the number of nanotechnology consumer products available in the CPI over time [9].
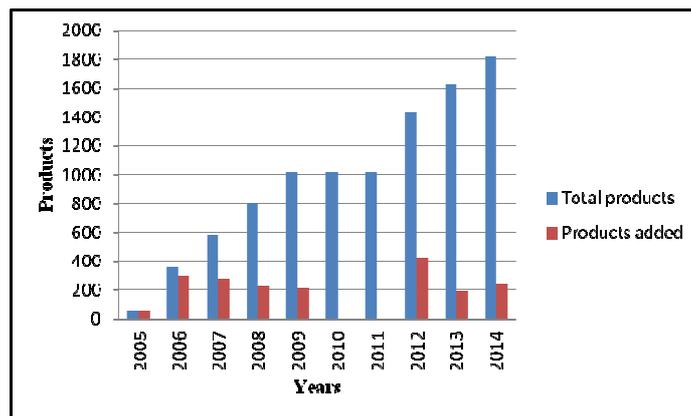
Fig. 2. Number of nanotechnology consumer products available in the CPI (CPI, 2015)

Although the use of ENPs can be beneficial in many areas, unfortunately they are also dangerous for environmental matrix due to their possible toxicity [10]. Because of the risk of releasing ENPs into the natural environment this material threatens human health and ecosystems [11-15]. Released nanoparticles may either remain suspended in the atmosphere or be accumulated or be modified into other dangerous substances. Hence the fate and transport of ENPs should be investigated to help reduce risk their potential negative effect on environmental.

2. Performance of nanoparticles in wastewater treatment plant

Particles represent undesired pollutants in most of the wastewater treatment processes. Nevertheless, the removal of particulate matter will be one of the most crucial steps in wastewater treatment. The removal of particles from wastewater, depend of their properties such as size, shape, chemical composition and density etc.

The potential toxicity of nanoparticles and increased their use poses a challenge for wastewater treatment plants (WWTPs) which are the major sources of ENM introduction into aquatic and terrestrial ecosystems. In WWTPs, most of the ENPs are removed from suspension in the primary and/or secondary settling tanks, where solids that are settled or dewatered to form biosolids. Throughout the wastewater treatment process ENPs can be removed from the wastewater streams through several mechanisms in the subsequent stages of the process [16]. These mechanisms can be assigned to one of the following groups: 1) sorption onto large debris and/or other large particles and further gravitional settling; 2) interaction with other pollutans for example: colloids, organic matters, metals; 3) agglomerate/conjugate for example: under the influence of addition of coagulants and flocculants; 4) aggregation 5) adhesion to sludge (microbal cell surfaces); 6) entrapment; 7) complexation; 8) degradation; 9) adsorption and interaction with extracellular polymeric substances [13]. Moreover, nanoparticles can be transformed during wastewater treatment via oxidation (e.g. NPs-silver) or reduction (e.g. NPs-cerium) [16]. Potential removal mechanisms of engineered nanoparticles during wastewater treatment are summarized in Table 1.

The initial stages of wastewater treatment process include screens; grit removal; fats, oils and greases removal and primary sedimentation. All these processes are intended to remove relatively coarse solids and work in relation to a combination of the size and density of the solids they remove. Screens are simple sieve devices that retain material bigger than the mesh size. Typical mesh sizes are down to 2 mm with most screens being larger than that. Therefore, the removal efficiency of nano particles in primary treatment processes will depend on the nature of their relation in the wastewater matrix.

The transport of nanoparticles in general depends largely on their size; for this reason, among others, clusters of engineered nanoparticles will behave quite differently compared to single engineered nanoparticles [17].

Table 1. **Potential removal mechanisms of ENPs during wastewater treatment process**

Nano-particles	Initial conditions	Treatment process	Operation condition	Comments	Refer.
Ag-NPs	Ag 130 µg/l COD 330 mg O$_2$/L	An aeration tank and a secondary clarifier	Temp. 21°C HRT = 24 h pH = 7.4÷7.5 TSS = 3 g/L	The study suggest that most metallic Ag-NP were transformed into Ag$_2$S during wastewater treatment	[18]
Ag-NPs 20÷40 nm	Ag: 0.5, 5, 10 mg/L	Activated sludge	MLSS = 2 g/L	90% transfer to the sludge	[19]
Ag-NPs 118.5 nm	Ag 1÷5 mg/L COD 400 mg O$_2$/L	Sequencing batch reactor	HRT = 11.7 h SRT = 20 d Cycle 8 h	The major removal road sorption, aggregation, sedimentation onto the sludge. The research revealed that a large portion of Ag (72%) was removed by the activated sludge, of which 48% remained in the mixed liquor and the rest (24%) was removed with the waste sludge.	[20]
Ag-NPs 21 nm	Ag 1 mg/L COD 500 mg O$_2$/L	MLE bioreactor	HRT = 24 h SRT = 20 d TSS = 2.5 g/L	90% associated with biomass	[21]
Ag-NPs 50 nm ZnO-NPs 30 nm	Ag 11 mg/d Zn 124 mg/d	Wastewater treatment plant	pH = 6.4 HRT = 8 h	Chemical transformations Ag-NPs → Ag$_2$S ZnO-NPs → Zn, ZnS, Zn$_3$(PO$_4$)$_2$ biosorption.	[22]
ZnO-NPs 65.7 nm	COD 400 mg O$_2$/L ZnO-NPs 1÷10 mg Zn/L	Membrane bioreactor	HRT = 12 h SRT = 30 d	The permanent increase in Zn in the sludge suggested that biosorption played an important role in ZnO-NPs removal from wastewater. Zn removal by settling accounted for 80% while overall Zn removal was 96%.	[23]
ZnO-NPs 67.32 nm	COD 650 mg O$_2$/L ZnO-NPs 1 mg Zn/L	Sequencing batch reactor	HRT = 11.7 h SRT = 16 d Cycle 8 h	In the influent, effluent and sludge a mass balance of total Zn loading revealed that the primary pathway for this removal was by sorption onto the activated sludge.	[24]
TiO-NPs 40 nm	Ti 2.9 mg/L	Sequencing batch reactor	HRT = 10 h SRT = 6 d Cycle 8 h TSS = 3.3 g/L	Just 12% of the Ti passed through the SBR, when 88% was associated with the biosolid fraction.	[25]
CeO$_2$-NPs 50 nm	COD 248 ± 50 mg/L Ce 55.0 mg Ce/L	Aeration tank and settler	Temp. 27.5°C pH = 7.4 HRT = 10.50 ± 0.96 h TSS = 3 g/L	Elimination occurred mainly by aggregation and settling of CeO$_2$ particles, promoted by circum neutral pH values and by nanoparticle interactions with organic and/or inorganic wastewater constituents.	[26]
ZnO-NPs 10÷130 nm	ZnO: 5, 10 and 20 mg/L COD 543 ± 159 mg/L	Aerated tank reactor and a clarifier	pH = 7.0 HRT = 6 h TSS = 2÷3 g/L	A big percentage of the ENPs settled out into the sludge. Most of ENPs aggregated were attached to the biomass and, therefore, were removed from influent through adsorption processes. Low zinc concentrations (less than 3%) in the effluent. Also, a high efficiency of removal of ZnO ENPs (> 96%) from effluent wastewater was observed.	[27]
5 cyclic (D3 to D7) and 12 linear (L3 to L14) siloxanes	∑cyclic siloxanes 5.14 µg/L ∑ linear siloxanes 15.12 µg/L	Wastewater treatment plant	HRT = 9 h	The prevailing compounds in wastewater were linear siloxanes L11 (24%), L10 (16%), and cyclic siloxanes D5 (13%), while in sludge were D5 (20%) and L10 (15%) of the total siloxane concentration.	[28]

A major determinant for particle mobility is the stability of its suspension. If destabilized, a particle suspension will aggregate, which in turn may lead to massive deposition [29]. The nanoparticles will need to be present in the relevant form or aggregation, through chelation and complexation with soluble components in the wastewater.

Moreover application of coagulants can lead to the higher adsorption of NPs and their further settling in secondary sedimentation tank. Diffusion, gravitational settling and agglomeration determine the transport of NPs toward microorganisms. Activated sludge processes are the most used processes for municipal wastewater treatment plants. Activated sludge includes heterotrophic bacteria and autotrophic nitrifying bacteria which are responsible for BOD and nutrients removal. It is well known that toxic compounds affect the activity of these bacterias [30]. However, there are not enough research reports on the fate of engineered nanoparticles during wastewater treatment processes which are important for accurate environmental risk assessments of nanomaterials [31].

As NPs enter wastewater streams they inhibit some bacterial species in the activated sludge and result in a reduction in the wastewater treatment efficiency [32]. Nanoparticles have different effects on bacteria colonizing the activated sludge. A recent study on the effects and transformation of nanomaterials or nanoparticles in activated sludge were generally carried out in a lab-scale reactor. The most widely studied nanomaterials include nanoparticles of silver metal, followed by ZnO, CuO, TiO_2, CeO_2, SiO_2 and fullerenes.

Sorption to activated sludge is a main removal mechanism for manufactured nanoparticles, in conventional activated sludge process. Furthermore, biosorption removes different types of NPs from wastewater with different efficiency. Generally for all types of NPs tested, with increasing biomass concentration to which NPs were exposed, the higher NPs removal efficiency was observed. Kiser et al. studied ENPs removal efficiency with activated sludge process with biomass concentration (TSS) of 400 mg/L [33]. It was found that 97% of silver nanoparticles were removed, probably in part by aggregation and sedimentation, whereas biosorption was predominantly responsible for the removal of 88% of aqueous fullerenes, 39% of functionalized silver NPs, 23% of nanoscale titanium dioxide, and 13% of fullerol NPs. Although Tiede et al. [19] reported that approximately 90% of nano-Ag added to wastewater will transfer to the sludge, however the form of silver adsorbed to the sludge solids was not characterized in this study. However many studied showed that Ag-NPs in sewage sludge were presented in nano-sized Ag_2S form [34, 35].

The effects of zinc oxide nanoparticles (ZnO-NPs) on system performance and bacterial community dynamics of biological wastewater treatment in a lab-scale was also studied [24]. It was found that nitrogen and phosphorus removal efficiencies were severely affected by ZnO-NPs over time. Bacteria community in the activated sludge was affected by ZnO-NPs; a higher concentration of *extracellular polymeric substances* (EPSs) produced by the bacteria after exposure to NPs was observed. However, instead of loosely enveloping the sludge and enhancing

agglomeration, the EPS protected the sludge from NPs by forming a dense protective matrix around the cells. ZnO-NPs were removed effectively from the wastewater. A mass balance of total Zn loading in the influent, effluent and sludge revealed that the main pathway for this removal was via sorption onto the activated sludge.

Ganesh et al. [36] investigated the removal efficiency and toxicity of copper nanoparticles (Cu-NPs) and copper ions in activated sludge biomass. The obtained results indicated that, copper nanoparticles were removed more effectively ($\sim$95%) than copper ions (30÷70%) from the wastewater. The predominant mechanisms of copper removal appear to be aggregation and settling (Cu-NP) or precipitation (copper ion) rather than biosorption.

Wang et al. [32] investigated NPs removal efficiency in the sequencing batch reactors (SBRs). It was found that carboxy-terminated polymer coated silver nanoparticles were removed less effectively (88% removal) than hydroxylated fullerenes (> 90% removal), nano TiO_2 (> 95% removal) or aqueous fullerenes (> 95% removal). Moreover major fraction of carboxy-terminated Ag-NTs were associated with colloidal material.

Gomez-Riviera et al. investigated the fate of nanoparticles CeO_2 (with concentration of 55.0 mg Ce/L) during municipal wastewater treatment by means of activated sludge process (A/S). A high removal of nano-CeO_2 (96.6%) was maintained over 63 d with effluent concentrations of CeO_2 particles < 200 nm on the level of 0.11 mg Ce/L nanoparticles removal occurred mainly by aggregation and settling of CeO_2 particles as well as by sludge biosorption [25].

Barton et al. studied fate of pristine and citrate-functionalized CeO_2 nanoparticles with lab-scale activated sludge bioreactor [37]. I was found that 90% of introduced nanoparticles were associated with biosolids which was accompanied by reduction of the Ce(IV) NPs to Ce(III). Moreover the study showed that the majority of CeO_2-NPs entering waste wastewater treatment plant will be present as Ce(III) and will be associated with the solid phase. At maximum, 10% of the CeO_2 will remain in the effluent and be discharged as a Ce(IV) phase, governed by cerianite (CeO_2). The kinetics of cerium IV reduction were different for surface-functionalised and non-surface-functionalised CeO_2. The reaction was 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 [38, 39]. The presence of surface functionalisation with organic or mineral molecules 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 [40]. However, it could also be anticipated from this report that surface functionalised nanoparticles reduce toxicity, which would be a positive effect.

Some of nanoparticles will be adsorbed on the debris and large practices within preliminary treatment. However, the majority of ENPs proceeds to the secondary treatment process. It estimated to be approximately 80% of ENPs are associated

with sewage sludge. Thus, further land application of those sewage sludge may cause a serious environmental risk via contamination both of soil as well as aquatic environmental and affect plants and bacteria in rhizosphere.

Conclusion

The increase in the use of nanomaterials in products in many sectors of society have resulted in uncertainties regarding environmental impacts. Nanoparticles products are released into the municipality collection systems and finally flows into wastewater treatment plants.

In the article shown review of the current scientific publications related with fate of nanoparticles in wastewater streams. The fate and transport processes that act on ENPs during wastewater treatment processes including: oxidation and reduction, precipitation, settling, adsorption, desorption, biotransformation, agglomeration or aggregation. Nanoparticles are then released into the soil mainly via sewage sludge and WWTP effluent.

Most of publications cited in this article were focused on the unit operation or process, such as e.g. impact of NPs on: nitrification and denitrification, physical and biological properties of activated sewage sludge, interaction of NPs with bacterial or extracellular polymers. While, still is lack of publication concerning fate of ENPs during whole wastewater treatment process in WWTPs. Therefore, the extension of knowledge about transformation, and behavior of ENPs during wastewater treatment process is very important because it allows to understand and reduce the negative impact of nanoparticles on the environment.

Acknowledgements

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Streszczenie

Nanomateriał zawiera co najmniej jeden wymiar w skali nano w przybliżeniu od 1 do 100 nm. Ze względu na małe wymiary nanomateriały wykazują odmienne właściwości fizyko-chemiczne w stosunku do tych samych materiałów w makroskali. Projektowane nanocząstki (ENPs) są celowo wytwarzane przez człowieka przy użyciu wielu różnych materiałów, tj.: metali: Ag, Zn, Au, Ni, Fe i Cu; tlenków metali: TiO_2, Fe_3O_4, SiO_2, CeO_2 i Al_2O_3; niemetali: krzemionka i kropki kwantowe; węgla: nanorurki i fulereny. Nanocząstki wykorzystywane

są w medycynie, farmacji, kosmetyce, rolnictwie, transporcie i energetyce. Szybko rosnące spektrum zastosowania nanotechnologii przynosi nowe i nieznane zagrożenia dla człowieka i środowiska. Ze względu na zwiększone wykorzystanie ENPs w produktach komercyjnych wzrasta uwolnienie projektowanych nanocząstek do środowiska. Poza tym przemiany ENPs w procesach oczyszczania ścieków mogą odgrywać ważną rolę w przedostawaniu się ich do środowiska naturalnego. Nanocząstki w oczyszczalniach ścieków ulegają agregacji, sedymentacji czy transformacji, co może wpływać na ich stężenie w ściekach, ale także w osadach. Badania nad wpływem i transformacją nanocząstek w osadzie czynnym prowadzano najczęściej w laboratoryjnych reaktorach porcjowych SBR. Najwięcej badań przeprowadzono na nanocząstkach Ag, a następnie ZnO, CeO$_2$ i TiO$_2$. Jak wykazują liczne badania, bakterie w biologicznych procesach oczyszczania mogą być narażone na działanie nanocząstek, które ulegają zarówno aglomeracji, jak i transformacji. W dostępnej literaturze podkreśla się, że te aglomeraty nanocząstek mogą zostać zaadsorbowane na zewnątrzkomórkowych polimerach podczas oczyszczania ścieków, a następnie przedostać się do osadu. Dlatego też drogi przemian nanocząstek w trakcie procesu oczyszczania ścieków powinny być intensywnie badane przede wszystkim w celu ograniczenia ryzyka ich potencjalnego negatywnego wpływu na środowisko. W artykule przedstawiono przegląd literaturowy dotyczący badań nad transformacją inżynieryjnych nanocząstek w procesie oczyszczania ścieków.

Słowa kluczowe: ścieki, osad czynny, oczyszczanie, osady ściekowe, nanocząstki