



EVALUATING THE SUSPENSION POTENTIAL OF MANUFACTURED NANOPARTICLES IN LANDFILL LEACHATE

Ceyda Senem Uyguner-Demirel*, Tugce Sakallioglu

Bogazici University, Institute of Environmental Sciences, 34342, Bebek, Istanbul, Turkey

Abstract

Nanoparticles (NPs) have recently been concerned as emerging contaminants. Determination of NPs in different environmental compartments is a revealing topic for researchers studying their impacts in nature. Various methods of analysis have been reported in literature for their measurement and recovery. However, there are difficulties in their quantification in landfill leachate. Taking into account varying landfill components and their possible interactions with NPs, different types of NPs were investigated in this study. Total concentrations of metals from commonly used TiO_2 , ZnO (coated and uncoated), and SiO_2 NPs were quantified in deionized water and in two different types of landfill leachate. Percent recoveries of metals from different NPs i.e., ZnO and TiO_2 added to deionized water ranged between 76%-129%, whereas percent recoveries in leachate were generally less around 45%-99%. On the other hand, the percent recovery results of SiO_2 were quite high in the range of 65%-99% and comparable to those in deionized water. Considering the complex nature of leachate matrix lower results would be acceptable.

Key words: acid digestion, landfill, leachate, nanoparticle, recovery

Received: June, 2016; Revised final: November, 2016; Accepted: December, 2015; Published in final edited form: May 2019

1. Introduction

As a result of improvements in nanotechnology in recent years, commercial nanoproducts have drastically increased in the global market (Boldrin et al., 2014; Dulger et al., 2016). It is estimated that 50% of nanomaterials nano-silver, nano-titanium dioxide and carbon nanotubes, that are used in cosmetics, health, electronic, textile and water treatment sectors, will be sent to landfills for disposal after their lifetimes are over (Mueller and Nowack, 2008). Nanoparticles (NPs) i.e., silicon dioxide (SiO_2), titanium dioxide (TiO_2), aluminum oxide (Al_2O_3) and zinc oxide (ZnO) which are mostly used in coatings, paints, energy and environmental applications, and as catalysts, were reported to dominate the global market with significant mass flow (Gao et al., 2018; Keller et al., 2013).

Within the nanotechnology based consumer products, TiO_2 is among the utmost reported

engineered nanomaterial in the market (Aitken et al., 2006). TiO_2 is commonly added to paints and cosmetics (Weir et al., 2012) and also used in photocatalytic oxidation studies to remediate polluted air and water (Chong et al., 2010; Herrmann, 2005; Lutic et al., 2017). SiO_2 NPs are available in various industrial applications, such as catalysis, pigments, pharmacy, electronic and thin film substrates, electronic and thermal insulators, and humidity sensors (Giesche, 1994). The three NPs used in this study would be found in a large fraction of consumer products that would have a relatively short life span and end up in landfill at some point (Bolyard, 2012; Bolyard et al., 2013).

Potential release of manufactured NPs into waste has become an emerging issue (Brar et al., 2010). A recent review by Bundschuh et al. (2018) explains in detail the scientific advances for the understanding of the sources of NPs focusing on their fate and interactions with biota. Studies related to life

* Author to whom all correspondence should be addressed: e-mail: uygunerc@boun.edu.tr

cycle predictions of NP loadings in the environment (Mitrano and Nowack, 2017) indicate an important role for their removal in wastewater treatment plants (Kiser et al., 2009). The fate of NPs in the course of waste stabilization in landfills is also very crucial in integrated waste management systems (Bolyard et al., 2013; Demirel, 2016; Dulger et al., 2016; Mitrano et al., 2017; Reinhart et al., 2010). Therefore, understanding the behavior and transformation is essential for accurate estimation of those NPs.

Determination of NPs in different environmental compartments is a revealing topic for researchers studying their impacts in nature. Various methods of analysis have been revealed in literature for their measurement and recovery (Bolyard et al., 2013; Hennebert et al., 2013; Yang et al., 2012). However, there are difficulties in the detection and quantification of NPs in landfill leachate. Moreover, for the precise measurement of NPs, sample preparation is a crucial step which requires significant attention. Up to now, no specific method has been defined that can routinely monitor the presence of such particles in the environment or in a complex matrix like leachate (Hennebert et al., 2013). For the determination of NPs, effect of parameters such as particle size, particle shape, surface characteristics, coating properties (Mahmoodi et al., 2017; Mudunkotuwa et al., 2012; Reed et al., 2012; Sakallioglu et al., 2016; Vogelsberger et al., 2008) pH, temperature, ionic strength (Reed et al., 2012) as well as concentration of the dissolution process, have to be considered (Schmidt and Vogelsberger, 2009).

In general, digestion followed by dissolution in aqueous media is usually applied for the analysis of NPs comprising metals and metal oxides (Hennebert et al., 2013; Khosravi et al., 2012). Open hot-plate, alkaline fusion and microwave digestion methods are frequently used for the analysis of solid samples (Bolyard et al., 2013; Szymczycha-Madeja and Mulak, 2009). In these techniques, the digestion is accomplished with diverse mixtures of mineral acids, such as: HNO_3 , $\text{HNO}_3 + \text{HCl}$, $\text{HNO}_3 + \text{HCl} + \text{HF}$, $\text{HNO}_3 + \text{HF}$, $\text{HNO}_3 + \text{HClO}_4$ (Bolyard et al., 2013; Fabricius et al., 2014; Khosravi et al., 2012; Larrea et al., 1997; Szymczycha-Madeja and Mulak, 2009). The use of hydrofluoric acid, which is able to dissolve silicates, requires the removal of excess hydrofluoric acid to prevent equipment damage or specialized non-glass components during analysis. It is important to note that instrumental tools and applied techniques may not always be suitable for the detection and

analysis of all nanomaterials. Instrumental tools and applied techniques may not always be suitable for the detection and analysis of all nanomaterials. Understanding the properties of coated NPs is also important because the coating can reduce the bioavailability of NPs, and limit their toxicological effects in the environment (Musee, 2011). Considering that some of the applied digestion methods are problematic and with the intention to implement a protocol, it is aimed in this study to practically determine and analyze selected NPs in landfill leachate. It is important to note that once quantification of NPs in landfill leachate is successfully accomplished with verified methods, critical knowledge about their potential transport and ultimate disposition could be attained. In this paper the potential of NPs to be suspended in leachate and deionized (DI) water was evaluated.

Commonly used TiO_2 , ZnO , and SiO_2 NPs were selected and percent recoveries to quantify the total concentrations of Ti, Zn and Si from NPs at different nominal concentrations in DI water and two different leachate samples were investigated. Both coated and uncoated ZnO NPs were tested due to their common use in literature. Overall, the findings of this paper would provide information about the analytical determination of NPs in landfill leachate. However, considering that other engineered nanomaterials may have distinctive properties like density, surface coating etc., further research is required with a large number of different NPs.

2. Materials and methods

All chemicals used were reagent grade. Dilutions were prepared using DI water. The properties of the commercially available NPs that were used in this study are presented in Table 1 as defined by the manufacturer. For the determination of particle size of NPs Philips XL 30 ESEM-GED/EDAX was used (Fig. 1). Before analysis, the samples were dried for one hour at 103 °C and then coated by a Sputter Coating (Quorum Technologies, UK) instrument.

NPs are not stable, they can easily form clusters and precipitate in aqueous solutions, therefore fresh suspensions were prepared each time. Appropriate amounts of NPs were added to 1000 mL of DI water or leachate (1-100 mg/L) and then sonicated for 30 min using a Bandelin Sonorex ultrasonic bath (Weir et al., 2012).

Table 1. Properties of nanoparticles as defined by the manufacturer

<i>Nanoparticle</i>	ZnO (uncoated)	ZnO (coated)	TiO ₂ (uncoated)	SiO ₂ (uncoated)
<i>Commercial name</i>	Sigma Aldrich Zinc oxide	BASF, Zinc oxide, Triethoxycaprylysilane (Z-COTE HP 1), hydrophobic	Sigma Aldrich Titanium oxide	Sigma Aldrich Silicon dioxide
<i>CAS no</i>	1314-13-2	1314-13-2	13463-67-7	7631-86-9
<i>Particle size, nm</i>	<100	<200	21	10-20

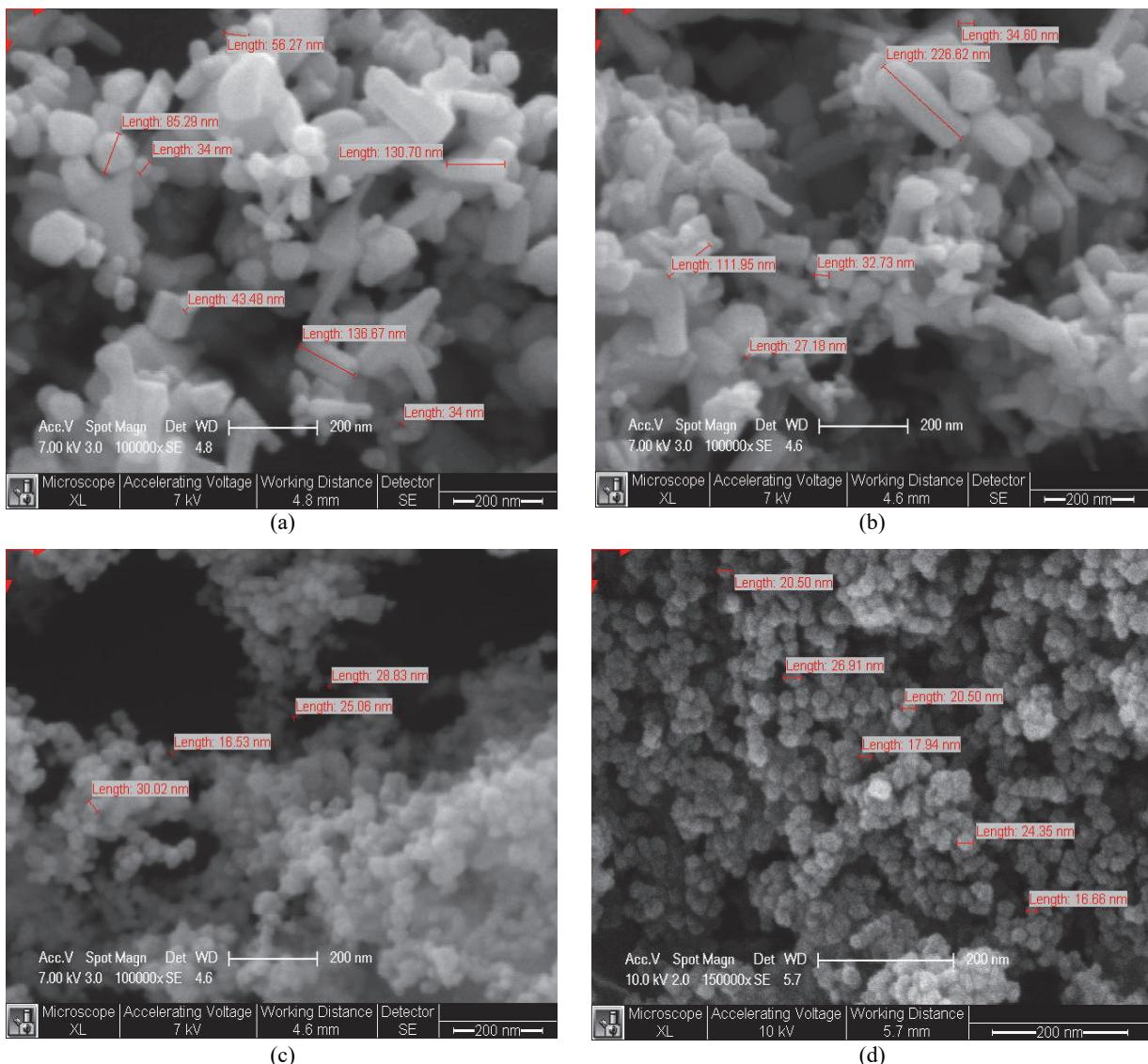


Fig. 1. Average particle size of uncoated ZnO (a), coated ZnO (b), TiO₂ (c) and SiO₂ (d) nanoparticles

Based on literature findings and preliminary tests carried out, for the digestion of TiO₂, ZnO and SiO₂ NPs 5 mL suspension from stock NP solution, 8 mL HNO₃ and 2 mL HCl (1:1) were used for all leachate samples unless otherwise stated. Additionally, for the digestion of sample L1 a different acid combination of HNO₃ (8 mL) and H₂SO₄ (2 mL) was also tested for the calculation of recoveries of selected NPs (TiO₂ and ZnO uncoated).

Acid combinations were added to each Teflon reaction vessel and samples were digested (MARS 6 Microwave Accelerated Reaction System, CEM, USA). The temperature was increased from ambient to 140 °C in 15 min and maintained at that temperature for 5 min. Subsequently, the temperature was raised to 200 °C in 16 min and kept at that temperature for 15 min more. Then, the samples were filtered through 0.45 µm pore size membrane filter, diluted with DI water to a final volume of 50 mL in a volumetric flask and analyzed for total metal concentrations of Ti, Zn and Si using an Inductively Coupled Plasma optical emission spectroscopy (ICP-OES) instrument (Perkin

Elmer OES Optima 2100 DV). Six parallel samples ($n=6$) were tested and the average results were reported. For the analysis metals the limit of detection (LOD) and the limit of quantification (LOQ) were obtained using the standard deviation (SD) of the blank signal multiplied by 3 and 10, respectively. The standard deviation (SD) and the method detection limit (MDL) were calculated as follows: $MDL = t \times SD$, where SD is the standard deviation of the measurements of eight spiked samples for TiO₂ and ZnO, and six samples for SiO₂. t is the Student's t -value at the 99% confidence level ($t = 2.998$ for 7 degrees of freedom, 3.365 for 5 degrees of freedom and 3.747 for 4 degrees of freedom). Relative standard deviation (RSD) which is obtained by multiplying the standard deviation by 100 and dividing this product by the average is expressed as percentage.

2.1. Landfill leachate characterization

The determination of solids, total Kjeldahl nitrogen (TKN), chemical oxygen demand (COD),

total phosphorous, and heavy metals were carried out according to Standard Methods (2012). Conductivity and pH of the samples were measured using Hanna Instruments HI 221 and WTW InoLab pH 7110. Total organic carbon (TOC) contents of samples were acquired using a TOC analyzer (Shimadzu VWP). For the quantification of heavy metal concentrations ICP-OES (Perkin Elmer OES Optima 2100 DV) was used. Anions were measured by an ion chromatography (Dionex ICS-3000).

Detection and quantification of four different NPs in two different landfill leachates were investigated. The first leachate sample (L1) was obtained from a landfill in Izmit and the second one (L2) was from a landfill in Istanbul, Turkey. Characterization experiments were conducted within a couple of days and the rest of the samples were acidified to a pH value of 2 with nitric acid. The leachate samples were analyzed for various physico chemical parameters and the results were given in Table 2. For the validation of heavy metal quantification in leachate samples, LOD and LOQ values were also presented. It has been found that leachate sample L1 contained higher concentrations of organic and inorganic constituents compared to sample L2. High concentrations of NO_3^- (7808 mg/L) and Si (16.40 mg/L) were observed in L1 leachate sample while trace amounts of heavy metals were detected in both of the samples.

It is notable that Si concentrations are quite high whereas low concentrations of titanium and zinc were determined in both of the leachate samples. LOD results ranged between 0.001 to 0.026 mg/L for the elements studied. Considering that LOQ is the level above which quantitative results may be obtained with a specified degree of confidence, the LOQs calculated are adequate for quantitative determinations in DI water as well as in leachate even with low concentration of heavy metals.

3. Results and discussions

Results of average percent recoveries of Zn, Ti and Si NPs in DI water are presented in Table 3. For the percent recoveries of TiO_2 and ZnO (coated and uncoated) three different nominal concentrations (1, 10 and 100 mg/L) were used, whereas for SiO_2 only two concentrations were tested (10 and 100 mg/L). The concentrations of NPs were chosen higher than the typical dosages found in leachate/wastewater to allow an accurate measurement of concentrations with the applied analytical methods.

However, it is also important to note that recent studies emphasized the release of TiO_2 and Ag NPs from cement and paint in rainwater and surface runoff detecting NP concentrations of TiO_2 up to 100 mg/L (Kaegi et al., 2008, 2010).

Table 2. Physico-chemical characteristics of landfill leachate samples

Parameter	Sample		LOD, mg/L	LOQ, mg/L
	L1	L2		
pH	8.05	8.43	ND	ND
Conductivity, mS/cm	69.80	40.80	ND	ND
Total suspended solids, mg/L	1135	665	ND	ND
Total volatile suspended solids, mg/L	835	255	ND	ND
COD, mg/L	27660	4910	ND	ND
Dissolved COD, mg/L	26285	3070	ND	ND
TKN, mg/L	8100	6975	ND	ND
Total phosphorus (P), mg/L	1375	600	ND	ND
TOC, mg/L	10353	1297	ND	ND
Fluoride (F^-), mg/L	ND	4	ND	ND
Chloride (Cl^-), mg/L	4340	3695	ND	ND
Bromide (Br^-), mg/L	ND	16	ND	ND
Sulfate (SO_4^{2-}), mg/L	652	108	ND	ND
Phosphate (PO_4^{3-}), mg/L	400	47	ND	ND
Nitrate (NO_3^-), mg/L	7808	10	ND	ND
Titanium (Ti), mg/L	0.056	0.062	0.005	0.018
Silver (Ag), mg/L	0.009	0.012	ND	ND
Silicon (Si), mg/L	16.40	7.30	0.008	0.028
Zinc (Zn), mg/L	0.040	0.064	0.004	0.014
Aluminum (Al), mg/L	0.180	0.150	0.004	0.014
Cadmium (Cd), mg/L	ND	0.001	0.001	0.004
Cobalt (Co), mg/L	0.013	0.005	0.002	0.008
Chromium (Cr), mg/L	0.163	0.055	0.005	0.016
Copper (Cu), mg/L	0.008	0.009	0.003	0.011
Iron (Fe), mg/L	4.440	0.382	0.005	0.016
Manganese (Mn), mg/L	0.611	0.018	0.003	0.010
Molybdenum (Mo), mg/L	0.004	0.003	0.004	0.012
Nickel (Ni), mg/L	0.087	0.071	0.004	0.014
Lead (Pb), mg/L	0.004	0.004	0.004	0.015

* ND=not determined

Table 3. Average percent recoveries of Ti, Zn and Si in deionized water at different nominal concentrations

Concentration of nanoparticle in suspension (mg/L)	Sample size (n)	Average recovery (%)	Standard deviation	Relative standard deviation (RSD, %)	MDL (mg/L)
ZnO (uncoated)					
1	8	90	0.24	0.26	0.719
10	8	68	0.24	0.35	0.719
100	8	94	0.07	0.07	0.210
ZnO (coated)					
1	8	93	0.21	0.23	0.630
10	8	76	0.14	0.18	0.420
100	8	99	0.19	0.19	0.570
TiO ₂					
1	8	87	0.29	0.33	0.869
10	8	86	0.36	0.42	1.079
100	8	84	0.16	0.19	0.480
SiO ₂					
10	6	129	0.085	0.066	0.286
100	6	76	0.16	0.21	0.538

The concentrations were analyzed by an ICP-OES in individual samples containing 1, 10 and 100 mg/L of NP in DI water resulted in recoveries of 87%, 86%, 84% for TiO₂, 90%, 68%, 94% for uncoated ZnO and 93%, 76%, and 99% for ZnO (coated), respectively. Similar results were reported by Dulger et al. (2016) for Ti recoveries (75%) from TiO₂ NPs in real landfill leachate.

The experiments carried out with SiO₂ yielded recoveries of 129% and 76% for 10 and 100 mg/L of NP in DI water. High concentrations resulted in high recoveries of NPs except for TiO₂. The standard deviations indicate the stability of the measurements and, thus, the precision of data. Considering the average values and standard deviations, best results were obtained for 100 mg/L ZnO and TiO₂. In a similar study by Fabricius et al. (2014) where H₂SO₄ and HNO₃+HCl combination were used for the microwave digestion of TiO₂ and ZnO in DI water, RSD values were reported as 2.2% and 3.2% for TiO₂ and ZnO, respectively. Compared to our findings, RSD values for TiO₂, ZnO in the concentration range of 1-10 mg/L were higher. It has been very well documented that either a mixture of hydrogen peroxide, nitric acid, and sulfuric acid or hydrogen peroxide, nitric acid, and hydrofluoric acid can effectively digest TiO₂ with recoveries greater than 95 percent (Packer et al., 2007; van Bussel et al., 2010).

In another study, the recovery rate for titanium in DI water was tested and the lowest recovery rates (64%- 80%) were reported for the lowest titanium concentration of 10 mg/L while the highest recovery rates were found for the concentrations of 1000 mg/L and 5000 mg/L (103% -149%) (Kuhlbush et al., 2012). In contrast, quite reproducible and repeatable results with high recoveries (84%-87%) were attained with TiO₂ in our case.

Based on acceptable recovery results attained in DI water, tests were repeated with the real leachate samples of L1 and L2. To compensate for variations in the characteristics of leachate, two different types of samples were investigated expressing the changes in the nature of waste with time. The same NP

concentrations and acid combinations were used. Results are presented in Table 4.

It is important to point out that in leachate samples background concentration of Si is quite high, whereas titanium and zinc concentrations are negligible. In calculations of percent recoveries related background concentrations were also taken into account.

The presence of dissolved organic matter is well known to increase the stability of both hydrophilic and hydrophobic NPs (Aiken et al., 2011; Bian et al., 2011). Dissolved organic matter interacts with coated NPs, altering the properties of coating and fostering NP dispersion (Bolyard et al., 2013). Moreover, solution conditions such as pH and ionic strength also affect the stability, aggregation, and potential for NPs to dissolve in a leachate matrix (Bolyard, 2012; Mitrano et al., 2017). Considering that leachate L1 has high TOC and COD contents, low recovery percentages of coated ZnO could be explained by the interactions with leachate (Table 4). On the other hand, for L2 sample similar recoveries were attained regardless of ZnO NP being coated or uncoated. In a recent study by Sakallioğlu et al. (2016), it was shown that a large proportion of the added nano ZnO was attached to municipal solid waste while only a small fraction remained in solution. Similar results were also observed by Dulger et al. (2015) who examined the fate of TiO₂ in municipal solid waste. Bolyard et al. (2013) confirmed by high-resolution transmission electron microscopy analysis that ZnO NPs were embedded in solid matrix while dispersed ZnO NPs were likely to form clusters in leachate. As already presented in Table 3, recovery percentages of NPs in DI water range between 76-129%. Complimentary experiments were carried out with selected concentrations of NPs to check the percent recoveries in leachate samples (Table 4). Based on information provided in Table 4, percent recoveries of NPs in leachate are generally less than the values reported in DI water. On the other hand, the percent recovery results of SiO₂ are quite high in the range of 65-99% and comparable to that of DI water.

Table 4. Average percent recoveries of Ti, Zn and Si in two different leachate samples at different nominal concentrations

NP concentration (mg/L)	Sample size (n)	Average recovery (%)	Standard deviation	Relative standard deviation (RSD, %)	MDL (mg/L)
ZnO (uncoated)					
100	5	90 (L1) 46 (L2)	0.07 0.10	0.077 0.22	0.262 0.375
ZnO (coated)					
100	5	45 (L1) 51 (L2)	0.07 0.07	0.15 0.14	0.262 0.262
TiO ₂					
10	5	78 (L1) 70 (L2)	0.15 0.15	0.19 0.21	0.562 0.562
SiO ₂					
10	3	75 (L2)	0.089	0.12	0.620
25	3	65 (L2)	0.080	0.12	0.557
100	3	99 (L2)	0.084	0.085	0.585
200	3	76 (L2)	0.146	0.19	1.017
400	3	61 (L2)	0.043	0.070	0.300

Considering the complex nature of leachate matrix lower results would be acceptable. Agglomeration of the particles in suspension by contact with the leachate could lead to an inhomogeneous distribution of the stock suspensions. In contrast to our findings, previous studies reported unsatisfying recoveries for TiO₂ spiked with sewage sludge (39% for 43.5 mg/L and 42% for 89 mg/L) (Kuhlbusch et al., 2012).

In a recent work of Bolyard et al. (2013) background metal concentrations from ZnO, TiO₂, and Ag nanoparticles in leachate fractions (total, <1500 nm, and <1 nm) were quantified by ICP-OES after digestion of samples in concentrated nitric acid and water/hydrochloric acid solution (1:1). Metal recoveries reported for ZnO, TiO₂ and Ag were 95%, 71% and 79%, respectively. On the other hand, although coated TiO₂ was investigated, similar recoveries were reported by Bolyard et al. (2013) supporting our results.

The digestion of sample L1 using a different acid combination of HNO₃ (8 mL) and H₂SO₄ (2 mL) was also tested and revealed recoveries of selected NPs as 78% for 10 mg/L and 69% and 90% for 1 and 100 mg/L of ZnO (uncoated), respectively. Therefore, the optimum digestion method for TiO₂ could be considered as HNO₃+HCl whereas it is HNO₃+H₂SO₄ for ZnO. The best results were attained using 10 mg/L and 100 mg/L for TiO₂ and ZnO, respectively. Recently, a new method was developed by Khosravi et al. (2012) to digest TiO₂ NPs using ammonium persulfate as a fusing reagent in which high recovery (>95% recovery) of Ti was obtained. Comparable results were also obtained in our study for Ti recoveries.

4. Conclusions

In this paper the potential of NPs to be suspended in two different types of leachate and the ability to quantify the total metal concentration of Ti, Zn and Si from NPs were investigated by determining

percent recoveries. Percent recoveries in leachate are generally less than the values reported in DI water. Considering the complex nature of leachate matrix lower results would be acceptable.

However, other engineered NPs may have different properties like density, surface coating etc. which in turn might affect their determination. Taking into account varying landfill components and their possible interactions with NPs, further research is required with different types of NPs. In order to simulate variations in landfill leachate characteristics over time and their subsequent effect on the fate of NPs, different leachate samples could also be studied in large scale.

Acknowledgements

The financial support provided by TUBITAK Project No:112Y322 is gratefully acknowledged.

References

- Aiken G.R., Hsu-Kim H., Ryan J.N., (2011), Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids, *Environmental Science and Technology*, **45**, 3196-3201
- Aitken R.J., Chaudhry M.Q., Boxall A.B.A., Hull M., (2006), Manufacture and use of nanomaterials: current status in the UK and global trends, *Occupational Medicine: Oxford Journals*, **56**, 300-306.
- Bian S., Mudunkotuwa I.A., Rupasinghe T., Grassian V.H., (2011), Aggregation and dissolution of 4 nm ZnO nanoparticles in aqueous environments: Influence of pH, ionic strength, size, and adsorption of humic acid, *Langmuir*, **27**, 6059-6068.
- Boldrin A., Hansen S.F., Baun A., Hartmann N.I.B., Fruergaard A.T.F., (2014), Environmental exposure assessment framework for nanoparticles in solid waste, *Journal of Nanoparticle Research*, **16**, 1-19.
- Bolyard S.C., Reinhart D.R., Santra S., (2013), Behavior of engineered nanoparticles in landfill leachate, *Environmental Science and Technology*, **47**, 8114-8122.
- Bolyard S.C., (2012), *Fate of coated zinc oxide nanoparticles in landfill leachate*, MSc Thesis, University of Central Florida, USA.

- Brar S.K., Verma M., Tyagi R.D., Surampalli R.Y., (2010), Engineered nanoparticles in wastewater and wastewater sludge – evidence and impacts, *Waste Management*, **30**, 504-520.
- Bundschuh M., Filser J., Lüderwald S., McKee M.S., Metreveli G., Schaumann G.E., Schulz R., Wagner S., (2018), Nanoparticles in the environment: where do we come from, where do we go to?, *Environmental Sciences Europe*, **30**, 1-17.
- Chong M.N., Jin B., Chow C.W.K., Saint C., (2010), Recent developments in photocatalytic water treatment technology: A review, *Water Research*, **44**, 2997-3027.
- Demirel B., (2016), The impacts of engineered nanomaterials (ENMs) on anaerobic digestion processes, *Process Biochemistry*, **51**, 308-313.
- Dulger M., Sakallioglu T., Temizel I., Demirel B., Copty N.K., Onay T.T., Uyguner-Demirel C.S., Karanfil T., (2016), Leaching potential of nano-scale titanium dioxide in fresh municipal solid waste, *Chemosphere*, **144**, 1567-1572.
- Fabricius A.L., Duester L., Meermann B., Ternes T.A., (2014), ICP-MS-based characterization of inorganic nanoparticles-sample preparation and off-line fractionation strategies, *Analytical and Bioanalytical Chemistry*, **406**, 467-479.
- Gao K., Lin K.L., Hwang C.L., Tuan B.L.A., Cheng T.W., (2018), Elucidating the effects of nanosilica on the characteristics of alkali-activated thin-film transistor liquid-crystal display waste glass, *Environmental Engineering and Management Journal*, **17**, 293-306.
- Giesche H., (1994), Synthesis of monodispersed silica powders. I. Particle properties and reaction kinetics & II. Controlled growth reaction and continuous production process, *Journal of the European Ceramic Society*, **14**, 189-214.
- Hansen S.F., Heggelund L.R., Revilla Besora P., Mackevica A., Boldrin A., Baun A., (2016), Nanoproducts – what is actually available to European consumers? *Environmental Science: Nano*, **3**, 169-180.
- Hennebert P., Avellan A., Yan J., Aguerre-Chariol O., (2013), Experimental evidence of colloids and nanoparticles presence from 25 waste leachates, *Waste Management*, **33**, 1870-1881.
- Herrmann J.M., (2005), Heterogeneous photocatalysis: state of the art and present applications, *Topics in Catalysis*, **34**, 49-65.
- Kaegi R., Sinnet B., Zuleeg S., Hagendorfer H., Mueller E., Vonbank R., Boller M., Burkhardt M., (2010), Release of silver nanoparticles from outdoor facades, *Environmental Pollution*, **158**, 2900-2905.
- Kaegi R., Ulrich A., Sinnet B., Vonbank R., Wichser A., Zuleeg S., SimmLer H., (2008), Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment, *Environmental Pollution*, **156**, 233-239.
- Keller A.A., McFerran S., Lazareva A., Suh S., (2013), Global life cycle releases of engineered nanomaterials, *Journal of Nanoparticle Research*, **15**, 1-17.
- Khosravi K., Hoque M.E., Dimock B., Hintelmann H., Metcalfe C.D., (2012), A novel approach for determining total titanium from titanium dioxide nanoparticles suspended in water and biosolids by digestion with ammonium persulfate, *Analytica Chimica Acta*, **713**, 86-91.
- Kiser M.A., Westerhoff P., Benn T., Wang Y., Pérez-Rivera J., Hristovski K., (2009), Titanium nanomaterial removal and release from wastewater treatment plants, *Environmental Science and Technology*, **43**, 6757-6763.
- Kuhlbusch T.A.J., Nickel C., Hellack B., Gartiser S., Flach F., Schiwy A., Maes H., Schäffer A., Erdinger L., Gabsch S., Stintz M., (2012), Fate and behaviour of TiO₂ nanomaterials in the environment, influenced by their shape, size and surface area, Umweltbundesamt, Germany, On line at: https://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/texte_76_2013_mobility_fate_and_behaviour_of_tio2_summary.pdf
- Larrea M.T., Gomez-Pinilla I., Farinas J.C., (1997), Microwave-assisted acid dissolution of sintered advanced ceramics for inductively coupled plasma atomic emission, *Journal of Analytical Atomic Spectrometry*, **12**, 1323-1332.
- Lutic D., Coromelci C.G., Juzsakova T., Cretescu I., (2017), New mesoporous titanium oxide-based photoactive materials for the removal of dyes from wastewaters, *Environmental Engineering and Management Journal*, **17**, 293-306.
- Mahmoodi N.M., Khari F.A., Khatibzadeh M., Gharanjig K., (2017), Synthesis of alginate amide composite using microwave and its dye removal ability, *Environmental Engineering and Management Journal*, **16**, 1859-1866.
- Mitrano D.M., Mehrabi K., Dasilva Y.A.R., Nowack B., (2017), Mobility of metallic (nano)particles in leachates from landfills containing waste incineration residues, *Environmental Science: Nano*, **4**, 480-492.
- Mitrano D.M., Bernd Nowack B., (2017), The need for a life-cycle based aging paradigm for nanomaterials: importance of real-world test systems to identify realistic particle transformations, *Nanotechnology*, **28**, 1-23.
- Mudunkotuwa I.A., Rupasinghe T., Wu C.M., Grassian V.H., (2012), Dissolution of ZnO nanoparticles at circum neutral pH: a study of size effects in the presence and absence of citric acid, *Langmuir*, **28**, 396-403.
- Mueller N.C., Nowack B., (2008), Exposure modeling of engineered nanoparticles in the environment, *Environmental Science and Technology*, **42**, 4447-4453.
- Musee N., (2011), Nanowastes and the environment: Potential new waste management paradigm, *Environment International*, **37**, 112-128.
- Packer A.P., Lariviere D., Li C.S., Chen M., Fawcett A., Nielsen K., Mattson K., Chatt A., Scriven C., Erhardt L.S., (2007), Validation of an inductively coupled plasma mass spectrometry (ICP-MS) method for the determination of cerium, strontium, and titanium in ceramic materials used in radiological dispersal devices (RDDs), *Analytica Chimica Acta*, **588**, 166-172.
- Reed R.B., Ladner D.A., Higgins C.P., Westerhoff P., Ranville J.F., (2012), Solubility of nano-zinc oxide in environmentally and biologically important matrices, *Environmental Toxicology and Chemistry*, **31**, 93-99.
- Reinhart D.R., Berge N.D., Santra S., Bolyard S.C., (2010), Emerging contaminants: nanomaterial fate in landfills, *Waste Management*, **30**, 2020-2021.
- Sakallioglu T., Bakirdoven M., Temizel I., Demirel B., Copty N.K., Onay T.T., Uyguner-Demirel C.S., Karanfil T., (2016), Leaching of nano-ZnO in municipal solid waste, *Journal of Hazardous Materials*, **317**, 319-326.
- Schmidt J., Vogelsberger W., (2009), Aqueous long-term solubility of titania nanoparticles and titanium (IV) hydrolysis in a sodium chloride system studied by adsorptive stripping voltammetry, *Journal of Solution Chemistry*, **38**, 1267-1282.

- Rice E.W., Baird R.B., Eaton A.D., Clesceri L.S. (Eds.), (2012), *Standard Methods for the Examination of Water and Wastewater*, 22nd Edition, American Public Health Association/American Water Works Association/Water Pollution Control Federation, Washington, DC.
- Szymczycha-Madeja A., Mulak W., (2009), Comparison of various digestion procedures in chemical analysis of spent hydrodesulfurization catalyst, *Journal of Hazardous Materials*, **164**, 776-780.
- van Bussel W., Kerkhof F., van Kessel T., Lamers H., Nous D., Verdonk H., Verhoeven B., Boer N., Toonen H., (2010), Accurate determination of titanium as titanium dioxide for limited sample size digestibility studies of feed and food matrices by inductively coupled plasma optical emission spectrometry with real-time simultaneous internal standardization, *Atomic Spectroscopy*, **31**, 81-88.
- Vogelsberger W., Schmidt J., Roelofs F., (2012), Dissolution kinetics of oxidic nanoparticles: the observation of an unusual behaviour, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **324**, 51-57.
- Weir A., Westerhoff P., Fabricius L., Hristovski K., von Goetz N., (2012), Titanium dioxide nanoparticles in food and personal care products, *Environmental Science and Technology*, **46**, 2242-2250.
- Yang Y., Xu M., Wall J., Hu Z., (2012), Nanosilver impact on methanogenesis and biogas production from municipal solid waste, *Waste Management*, **32**, 816-825.