

Effects of the silica nanoparticles (NPSiO₂) on the stabilization and transport of hazardous nanoparticle suspensions into landfill soil columns

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Abstract

This study evaluates the stability and transport behaviors of hazardous nanoparticles into soil landfills using experimental procedures to simulate the effects of natural silica nanoparticle suspensions during their percolation into the soil layers of municipal waste landfills. For this, we prepared stabilized suspensions of nanoparticle oxides containing silicon (NPSiO₂), titanium (NPTiO₂), copper (NPCuO) and zinc (NPZnO), which are recognized as hazardous to the environment, and we conducted leaching experiments within the soil column by simulating landfills layers and simulating the capture and attenuation of nanomaterials into municipal waste landfills. The results demonstrated that the presence of NPSiO₂ in suspensions increases the stable concentrations of copper, zinc and titanium oxides and strongly decreases soil layer effectiveness. In contrast, NPZnO improves effectiveness due to its ability to promote agglomeration and setting conditions, allowing further complexation.

Keywords: silica nanoparticles (NPSiO₂), soil column, hazardous nanoparticles, transport.

1. Introduction

Nanoparticles such as silica (NPSiO₂), titanium oxide (NPTiO₂), copper oxide (NPCuO) and zinc oxide (NPZnO) are increasingly used in many industrialized products and have been released into the environment during the last decade, but their effects and the danger they pose to the environment and

ecosystems are poorly understood. These particles are widely used because of the unique properties conferred by their high specific area and consequent high reactivity. These important properties are the key to technological and societal development. Thus, concerns regarding potential environmental risks due to strong interactions

and reactivity in ecosystems and natural substances have to be quantified to ensure safe use of these materials [Wiesner *et al.*, 2006, Nowack, 2008]. Therefore, it is important to assess these interactions with the environment, which is the main focus of this paper. The properties and behavior of these nanoparticles within ecosystems

depend on the conditions of the stable suspensions, their interactions with one another and their effects on organic matter and living organisms [Wiesner *et al.*, 2006, Nowack, 2008, Shen *et al.*, 2012, Son *et al.*, 2015, Godymchuk *et al.*, 2015, Jacobs *et al.*, 2015]. The significant differences in the properties of nanoparticles and bulk materials are due to the relative increase in surface area and quantum effects. Suspensions of nanoparticles are stabilized due to interaction forces. Van der Waals forces, double layer repulsion and steric interactions, however, play the major roles in nanoparticle stabilization [Tadros, 2007, Lamberty *et al.*, 2009, Fang *et al.*, 2009, Fang *et al.*, 2011, Kiser *et al.*, 2009, Dusak *et al.*, 2015]. Depending on the force balance, aggregation and settling can occur. When aggregates become large enough, the gravitational force becomes larger than the buoyancy forces, and settling can occur. When the aggregates become larger than the soil

pores, physical filtration removes these aggregates from the suspension. Depending on the leaching suspension concentrations and soil characteristics, the interception, diffusion and sedimentation phenomena can also play important roles. [Kallay *et al.*, 2002, Lecoanet *et al.*, 2004]. Darcy velocities could also play an important role in the transport and deposition of nanoparticles in effluent into the soil column and landfill containment layers. Several researchers [Lecoanet *et al.*, 2004, Fang *et al.*, 2011, Oliveira *et al.*, 2014] have recently addressed the transport and fate of silver, copper and titanium nanoparticles, among others. However, their interactions and the effects of silica nanoparticles on the stabilization and activity of the titanium, copper and zinc oxides still require further study due to their importance and the strong effect of nanoparticle silica on suspension characteristics and interactions. Therefore, this study aims to investigate the effects of

silica nanoparticle (NPSiO₂) concentration on the mobility of titanium dioxide nanoparticles (NPTiO₂), copper oxide nanoparticles (NPCuO), and zinc oxide nanoparticles (NPZnO). We analyzed the concentrations of NPTiO₂, NPCuO, NPZnO and NPSiO₂, as well as the size distributions of their aggregates, using Nanoparticle Tracking Analysis (NTA), and performed chemical analysis using spectrophotometry techniques [Oliveira *et al.*, 2014]. The main advances of this study include a new detailed NTA analysis and the quantification of multiple interactions of NPTiO₂, NPCuO, NPZnO and NPSiO₂ in a natural soil used in the controlled landfill layer of the Volta Redonda city in Rio de Janeiro state, Brazil. Therefore, this paper presents a novel analysis of the behavior of NPSiO₂, which can be naturally released in the environment, on the transport and fate of NPTiO₂, NPCuO and NPZnO within natural soil layers.

2. Materials and methods

The nanoparticles were purchased from Sigma-Aldrich (USA). The suspensions were prepared by mixing the nanoparticles of TiO₂, SiO₂, CuO and ZnO in eight combinations with 250 mL of milli-Q water.

The prepared solutions were distributed in Erlenmeyer flasks and shaken at 250 rpm for 24 hours. The solutions were left for 10 days to allow excess nanoparticles to settle; the remaining nanoparticles reached

a stable equilibrium concentration. Only the supernatant portion was used in the percolation column tests. The nanoparticle specifications and characteristics of the suspensions are shown in Table 1.

Suspensions	Phase purity	Surface area	Average size	Initial Concentration	Stabilized
					Concentration
TiO ₂	99%	30 m ² .g ⁻¹	35 nm	2 g. L ⁻¹	32.5 mg. L ⁻¹
SiO ₂	99.5%	160 m ² .g ⁻¹	20 nm	1 g. L ⁻¹	157.9 mg. L ⁻¹
CuO	99.8%	30 – 50 m ² .g	35 nm	1 g. L ⁻¹	42.9 mg. L ⁻¹
ZnO	99%	≥ 15 m ² .g ⁻¹	30 nm	1 g. L ⁻¹	1.7 mg. L ⁻¹
TiO ₂ + SiO ₂	---	---	---	(TiO ₂ (2 g) + SiO ₂ (1 g)). L ⁻¹	TiO ₂ (47.9 mg. L ⁻¹)
					SiO ₂ (51.2 mg. L ⁻¹)
CuO + SiO ₂	---	---	---	(CuO (1 g) + SiO ₂ (1 g)). L ⁻¹	CuO (58.9 mg. L ⁻¹)
					SiO ₂ (46.9 mg. L ⁻¹)
ZnO + SiO ₂	---	---	---	(ZnO (1 g) + SiO ₂ (1 g)). L ⁻¹	ZnO (5.9 mg. L ⁻¹)
					SiO ₂ (2.3 mg. L ⁻¹)
TiO ₂ + SiO ₂ + CuO + ZnO	---	---	---	(TiO ₂ (2 g) + SiO ₂ (1 g) + CuO (1 g) + ZnO (1 g)). L ⁻¹	SiO ₂ (137.4 mg. L ⁻¹)
					TiO ₂ (42.5 mg. L ⁻¹)
					CuO (54.9 mg. L ⁻¹)
					ZnO (5.9 mg. L ⁻¹)

Table 1
Specifications and characteristics of the suspensions.

For the leaching column experiment, a PVC column with a 20-cm length and an inner diameter of 25 mm was uniformly packed with 10 cm of air-dried soil, representing landfill layers. At the beginning of the experiment,

the soil column was initially saturated with DDW (deionized distilled water), which was supplied from the bottom of the column gradually filled upward through the entire length of the column. Then, the column was leached with

100 mL of DDW. For all columns, the measured turbidity values were below 2 NTU, which indicated that a negligible amount of soil particles was leached. Detailed properties of the soil used in this study are presented in Table 2.

Parameters	Unit	Results
Type of soil	---	Sandy/Granulated solid
pH	---	8.9
CEC	cmol.kg ⁻¹	2.5
Dissolved organic carbon	g.kg ⁻¹	0.1
Ionic strength	mM	0.8
Zeta potential	mV	-15.9
Percentage of organic matter	g.kg ⁻¹	23.1
Humidity at 105 ° C	%	9.6
Total silver	mg.kg ⁻¹	< 0.1
Total copper	mg.kg ⁻¹	16.2
Total silicon	mg.kg ⁻¹	634.7
Total titanium	mg.kg ⁻¹	1221.0
Total zinc	mg.kg ⁻¹	55.7

Table 2
Properties of soil used in this study.

Figure 1(a) shows the stable suspension production (shaking 24 h + 10 days

settling). Figure 1(b) shows the apparatus used for column leaching and flow control.

Figure 1(c) shows detailed schematics of the inner column.

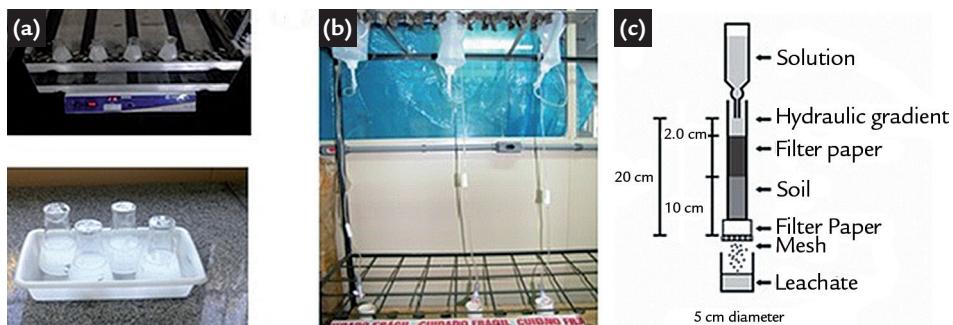


Figure 1
Experimental column used in this study.

Figure 2 presents a flowchart of the experimental procedure used in the study. The concentrations of TiO₂, SiO₂, CuO and ZnO nanopar-

ticles were determined by ICP-OES. Nanoparticle size distributions were monitored using the NanoSight LM10 system to quantify the aggregation

phenomenon. Zeta potential measurements of the solutions were also carried out to characterize the stability of the solutions and the ionic activities.

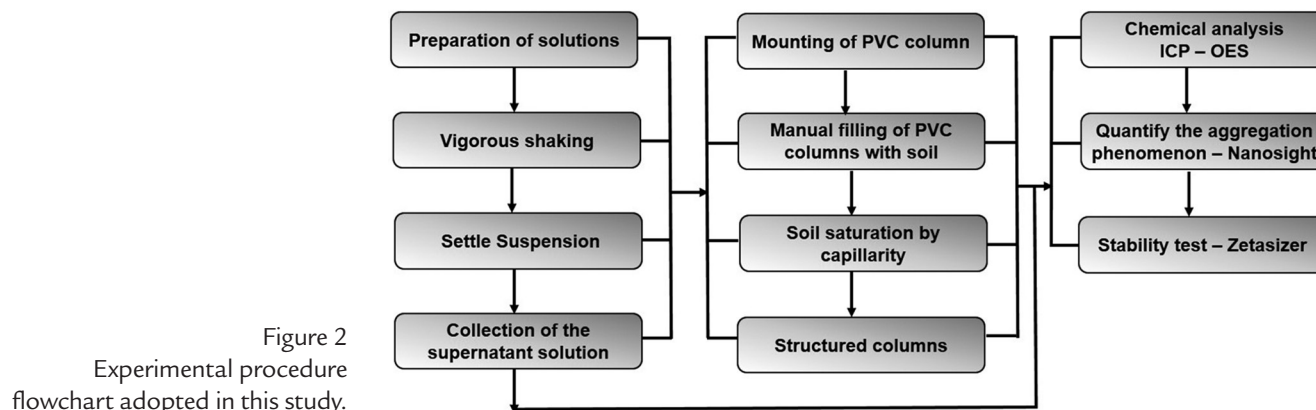


Figure 2
Experimental procedure flowchart adopted in this study.

The ionic strengths of solutions at the outlet of the column were calculated

from the simple linear equation of ionic strength and electrical conductivity

$$I = 0.0127 \times EC$$

[Morrisson *et al.*, 1990] as shown in Eq. (1).

(1)

In this equation, I and EC are the

ionic strength and electrical conductivity,

respectively.

3. Results and discussion

The results presented in this paper aim to show the effects of NPSiO₂ on the stabilization conditions and trans-

port of the nanoparticle suspensions and to demonstrate the effects of the interactions of these nanoparticles with

other nanomaterials that are harmful to the environment by means of soil column tests.

Suspension	Zeta potential	pH _(pzc)	pH	EC	Ionic strength (mM)	Mean particle size (nm)
milli-Q +TiO ₂	-22.2	4.2	4.9	65.8	0.83	32
milli-Q +CuO	-32.4	5.9	6.4	32.9	0.41	35
milli-Q +SiO ₂	-49.6	4.0	4.6	68.9	0.87	42
milli-Q +ZnO	-9.51	7.3	8.0	8.9	0.11	19
milli-Q +SiO ₂ + TiO ₂	-47.9	4.1	4.7	73.4	0.93	56
milli-Q +SiO ₂ + CuO	-30.2	4.7	5.1	65.8	0.83	47
milli-Q +SiO ₂ + ZnO	-18.9	5.8	6.7	32.7	0.41	26
milli-Q +TiO ₂ +SiO ₂ + CuO+ZnO	-23.0	4.3	6.2	103.1	1.31	63

Table 3
Suspension parameters at the column outlet.

Figure 3 shows the effects of mutual interactions on the stabilization of NPTiO₂ in binary and quaternary systems. Table 3 shows the main parameters, which indicate the stability and activities of the stabilized suspensions used for the leaching experiments in the soil columns. The zeta potential, pH and average nanoparticle agglomeration are in concordance with the measured values of the electric conductivities and ionic strength.

The effect of ionic strength on particle deposition is in qualitative agreement with the DLVO theory of nanoparticle suspension stability.

Figure 3 shows a comparison of titanium nanoparticle concentration patterns for suspensions measured at the outlet of the soil columns, and it shows the effects of the other nanoparticles on the effectiveness of the soil column in capturing and retaining the hazardous nanoparticles. As

the suspensions become more complex, the effectiveness of the soil column is reduced. The presence of NPSiO₂ plays a major role in decreasing the effectiveness of the retention, and the presence of NPZnO strongly increases the retention efficiency. Thus, when the effluent contains a large number of nanoparticle species, the presence of NPZnO, in controlled quantities, could neutralize the deleterious effects of the NPSiO₂.

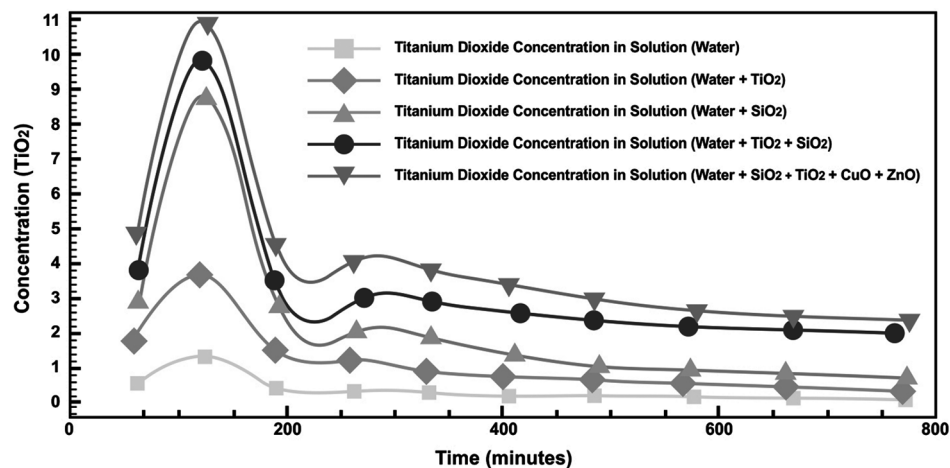


Figure 3
Comparison of NPTiO₂ concentrations at the outlets of the soil columns.

Figure 4 shows the effects of NPSiO₂ on NPCuO in the binary and quaternary systems. A similar trend was observed for the NPCuO nanoparticles, which emphasizes the role of NPSiO₂ on the forces acting on the suspensions

and other nanoparticles. NPCuO alone has a very low stable concentration when in suspension with the major nanoparticles, and it can be captured by the soil column. The total adsorption capacity of the soils follows the order

of the suspensions tested in this study (quaternary>binary>NPSiO₂>NPCuO). In this study, the adsorption of nanoparticles in quaternary and binary systems that contain NPCuO confirm that adsorption occurs through the

formation of internal sphere surface complexes formed by the interaction

of Cu^{2+} with hydroxyl groups of the SiO_2 surface, in accordance with the

literature [Ludwig and Schindler, 1995].

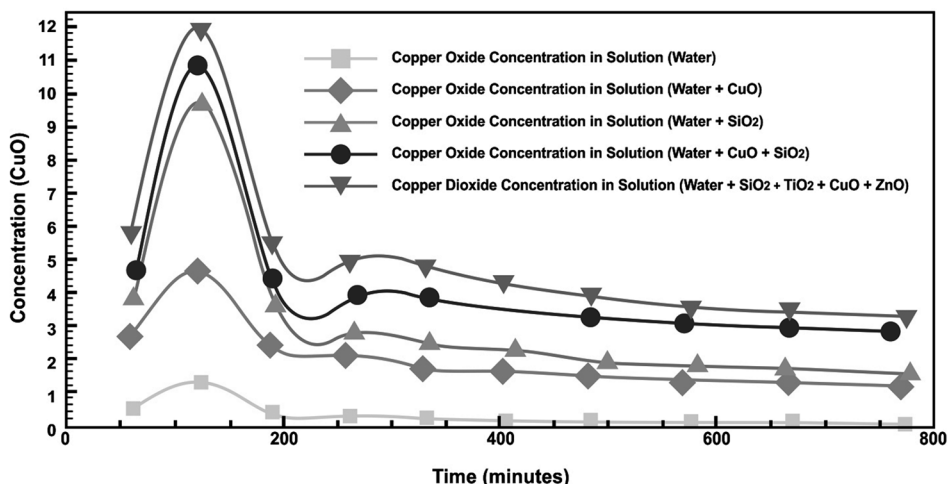


Figure 4 Comparison of the NPCuO concentrations at outlet of the soil columns.

Another important and abundant nanoparticle that is released by industrial processes is zinc oxide (NPZnO). As shown in Figure 5, in all suspensions with NPZnO, sedimentation begins rapidly, and

a low equilibrium concentration of NPZnO is observed at the inlet. The concentration of NPZnO at the outlet of the soil column is explained by the electric charges developed due to the stabilization of the suspensions.

After passing through the soil column, the NPZnO particles are strongly affected by the NPSiO₂, NPCuO and NPTiO₂; the outlet concentration of NPZnO increases as the other nanoparticles are added.

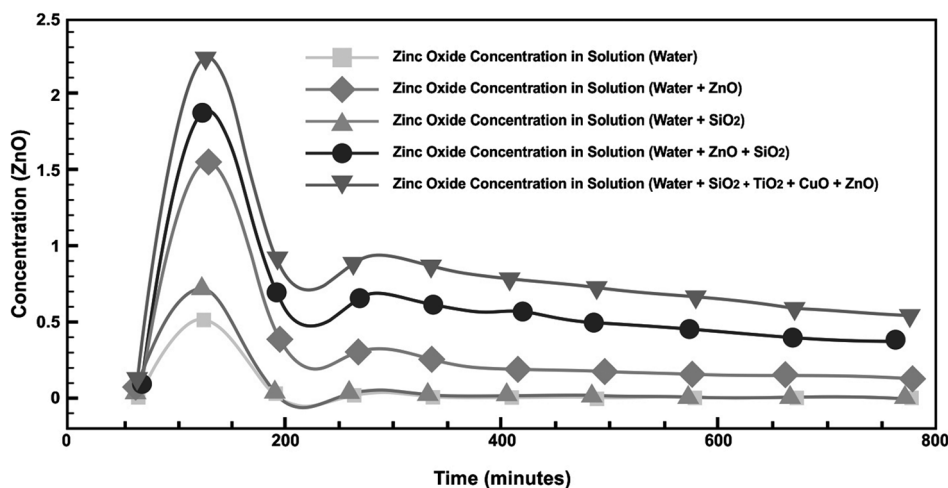


Figure 5 Comparison of NPZnO concentrations at the outlets of the soil columns.

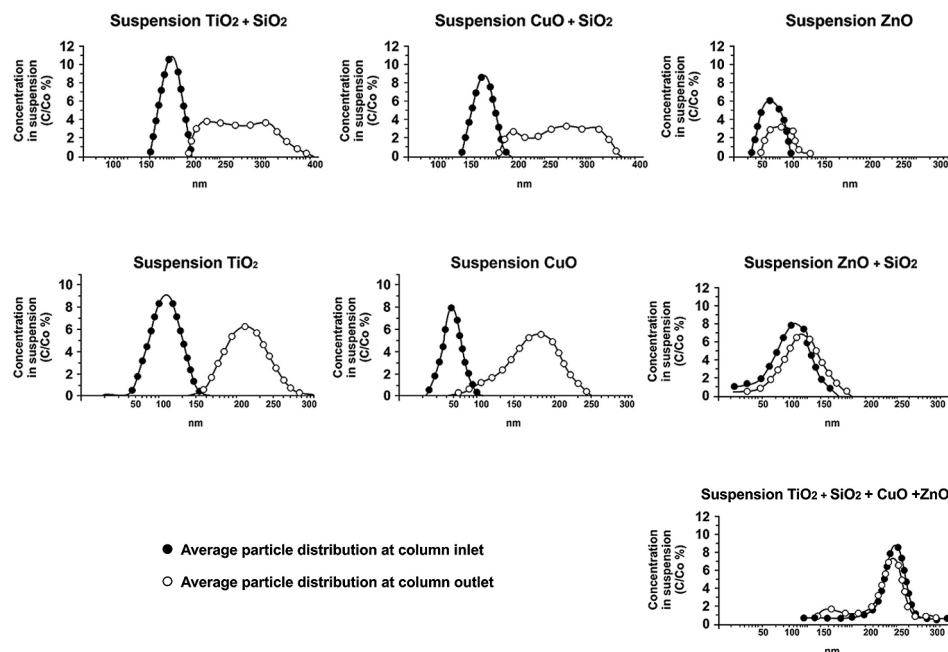


Figure 6 Comparisons of the nanosight tracking analysis (NTA) for the leaching suspension at the inlet and outlet of the soil column of the landfill layer.

As shown in Figure 6, agglomeration occurs when the solution passes through the soil column and the concentration decreases, indicating that the soil particles capture the nanoparticles and work as an effective barrier to contamination from the leachate. The results obtained in this study make it possible to design a soil layer to minimize the release

4. Conclusions

This study uses soil column experiments to analyze the effect of NPSiO₂ in natural soil on the stabilization periods and retention of NPTiO₂, NPCuO and NPZnO. The results show that NPSiO₂ limits the retention of hazardous nanoparticles (NPTiO₂ + NPCuO + NPZnO) because of the high affinity of NPSiO₂ for water and (NPTiO₂+NPCuO+NPZnO) suspensions. The higher stability of the hazard-

ous nanoparticles into the environment and allow for secure disposal in municipal waste landfills. Therefore, the results obtained in this study demonstrate that silica nanoparticles (NPSiO₂) play the major role in the stabilization of hazardous nanoparticles (NPCuO, NPTiO₂ and NPZnO) within natural suspensions. Thus, silica nanoparticles

decrease the effectiveness of the landfill soil layers. Based on this study, we recommend a redesign of the thickness of landfill soil layers to attenuate the natural silica nanoparticle effects during leachate percolation through the soil layers. This will allow the complexation of hazardous nanoparticles within the protective soil layers in the landfill.

ous nanoparticles in NPSiO₂ suspensions was confirmed using nanoparticle tracking analysis (NTA) and spectrophotometry, which allowed for the evaluation of cluster formation and the measurement of average nanoparticle sizes in addition to the parameters traditionally used to verify suspension stabilization, such as zeta potential and conductivity. The leaching soil column experiments demonstrated that ap-

proximately 300 min is sufficient for the column to retaining the hazardous nanoparticles. Therefore, information about nanoparticle interactions can be used to design effective soil layers in municipal waste landfills. The analysis techniques presented in this study could also be useful for monitoring nanoparticle contamination in the environment during waste or effluent disposal associated with industrial activities.

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