

CHARACTERISATION OF NANOPARTICLE SIZE OF TiO₂ USING NANOPARTICLE TRACKING ANALYSIS (NTA)

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RESUMO – The study of nanoparticles involves a new bias research in various areas of technology, whose production and use have been offering multiple benefits to society. However, the uncontrolled emission to the environment of nanoparticles is growing exponentially over the last decade. Thus, knowledge of the influence of nanoparticles and how they can modify the ecosystem is extremely important and an area currently limited. Therefore, it is of fundamental importance to increase the knowledge of the fate and transport of nanoparticles in soil, in particular this research will study the TiO₂ nanoparticles (TiNPs). This study will carry out tests on columns with soil collected in the landfill Volta Redonda located in the state of Rio de Janeiro, Brazil. The concentrations are analyzed TiO₂, as well as the distribution of the size of its aggregates by Nanoparticle Tracking Analysis (NTA).

1. INTRODUCTION

Engineered nanomaterials (ENM) are applied in many commercially available consumer products such as in cosmetics, textiles, and paints. Due to the increasing production volumes, an environmental exposure to ENMs is likely as reported by Nowack *et al.*, 2007. Whereas toxic effects of nanomaterials on different organisms have already been described (Klaine *et al.*, 2008; Baun *et al.*, 2008), measurements of environmental concentrations of ENMs are almost completely absent. The increase of applications of nanomaterials and consequent increased production are expected to cause exponentially and uncontrolled emissions in the environment.

Therefore, it is essential to understand the fate and transport of TiO₂ nanoparticles in the environment in order to assess possible routes of exposure to humans and the ecosystem for developing an understanding of the potential mobility of nanoparticles in general in the soil environment and their potential risks to groundwater. Recently, a few investigations have addressed the transport of nanoparticles in porous media (Guzman *et al.*, 2006; Lecoanet *et al.*, 2004; Lecoanet and Wiesner, 2004) and showed that nanoparticles including carbon nanomaterials, anatase and silica exhibited various transport behaviors.

The passage of anatase through a two-dimensional model of porous structure column slowly increased with time, suggesting that the mobility was increased with time as deposition sites became saturated (Guzman *et al.*, 2006). Darcy velocities could also influence transport and deposition of nanoparticles and an increase in the flow velocity increased the effluent of anatase (Lecoanet *et al.*,

2004). However, most of these experiments were conducted in well-defined porous media, glass or polystyrene bead-packed columns and thus did not accurately represent the variety of mineral surface types, surface charge heterogeneities, grain size distributions and roughness of granular media encountered in real soil systems. Thus the environmental implications of such studies involving well-defined porous media were limited.

Many studies of the fate and impact in the environment is becoming important due to the gap of knowledge about transport in and between environmental compartments and their chemical behavior in the environment, specially for soil ecosystem (Klaine *et al.*, 2008).

The objectives of this study were to investigate the degree to which TiO₂ nanoparticles were suspended in suspensions and to investigate how far TiO₂ nanoparticles could be transported in various homogeneous soil columns. The NanoSight LM20 and NTA 2.3 software were used for measuring the concentration and particle size over time. The effects of instrument settings were investigated in detail, and sensible choices suggested. The results from the NanoSight were then compared to those experimentally obtained.

2. MATERIAL AND METHODS

2.1 Procedure Experimental

Soil samples were used to cover the Municipal Landfill of Volta Redonda. TiO₂ nanoparticles were purchased from Sigma Aldrich with an anatase phase purity of 99.7% and an average particle size of 25 nm. Soil TiO₂ suspensions were prepared by mixing TiO₂ (500 mg) with soil (12.5 g) and adding milli-Q Water (250 mL) in Erlenmeyer flasks. TiO₂ in milli-Q Water at the same ratio, with no added soil was used as control, while soil in milli-Q Water at the same ratio without TiO₂ was used as a blank.

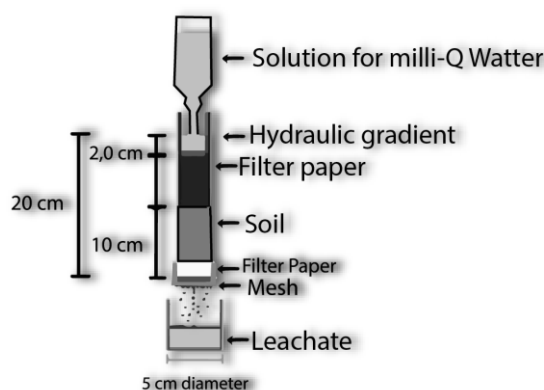


Figure 1. Schematization of Columns.

For leaching experiment, a PVC column, length 20 cm and inner diameter of 25 mm was uniformly packed with 10 cm of air-dried soil as shown in Figure 1. At the beginning of the experiment, the soil column was initially saturated with milli-Q Water from the bottom of the column

gradually upward through the entire length of the column, and then the column was leached with 100 mL of milli-Q Water.

2.2 Nanoparticle Tracking Analysis (NTA)

After that the turbidity of outflow was measured after settling for both 0 and 10 days using Nanoparticle Tracking Analysis (NTA) as shown in Figure 2. To determine the concentration of TiO_2 nanoparticles in aqueous samples, the TiO_2 suspension was firstly dried in a flask by heating, the above solution was transferred quantitatively and Ti was determined by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy). The concentration of TiO_2 in the suspension was calculated by mass balance.

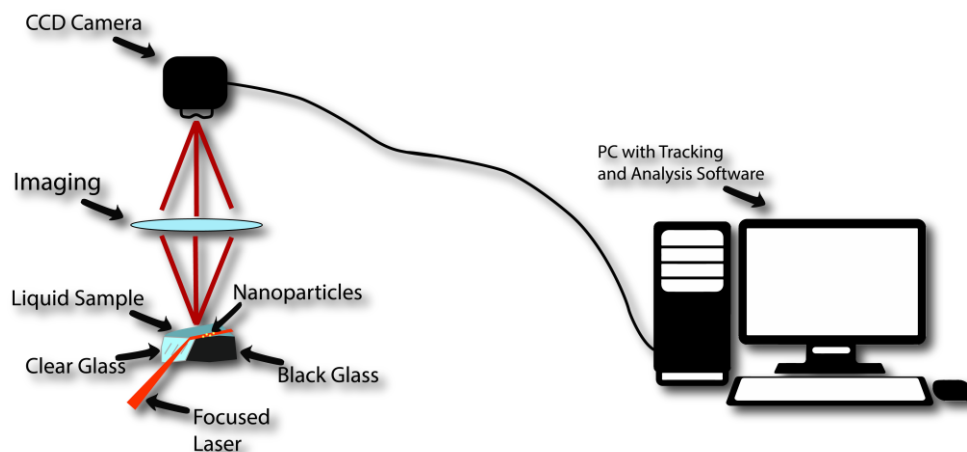


Figure 2. Schematic of the optical configuration used in NTA.

3. RESULTS AND DISCUSSION

During the sampling of supernatant liquid (1 mL), it was inevitable that the system became slightly disturbed during 10 days specifically at day 0, 3, 6 and 9 as shown in Figure 3-6. At time 0, aggregate size distribution of TiO_2 -NPs suspensions was between 0.15 and 10 μm with a peak at 2.7 μm . These data suggest a low interaction between TiO_2 -NPs and soil particles, at least in terms of aggregation or physical rearrangement. After day 3 all the suspensions showed a similar pattern, with a peak around 0.7 μm , suggesting that TiO_2 -NPs were still present as aggregates. Subsequently, the suspended TiO_2 relative concentrations decreased monotonically over the initial 2–4 days, and thereafter remained almost unchanged during the following 5–10 days. Ti concentration in the suspension (Table 1) showed an abrupt decrease, and remained constant from day 3 to 9.

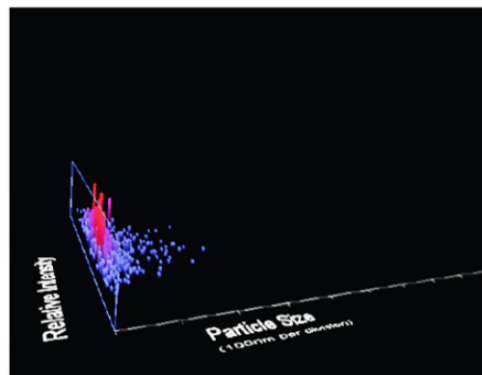
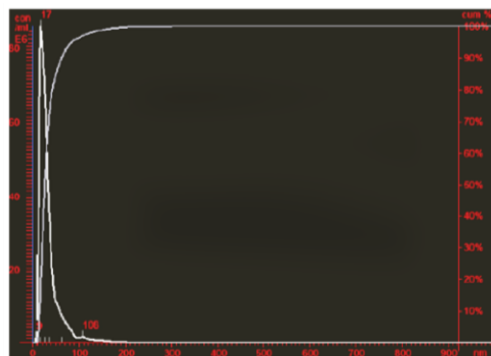


Figura 3 – Average TiO_2 particle size distribution and Relative Intensity of TiO_2 in NTA (initial rate).

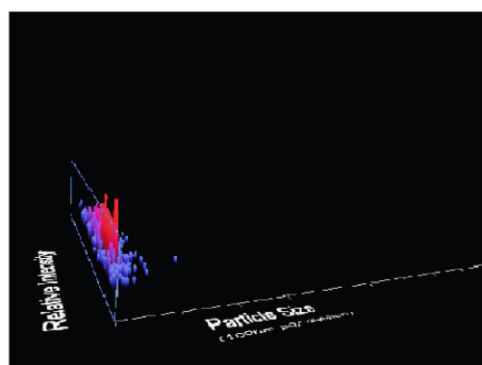


Figura 4 – Average TiO_2 particle size distribution and Relative Intensity of TiO_2 in NTA (third day of decanting).

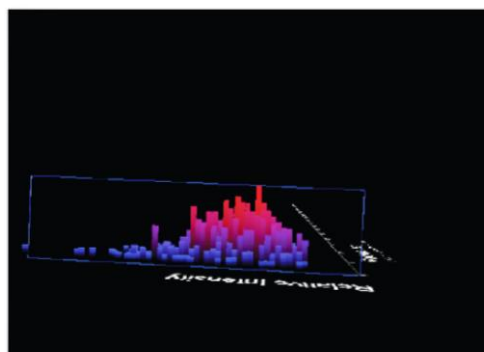
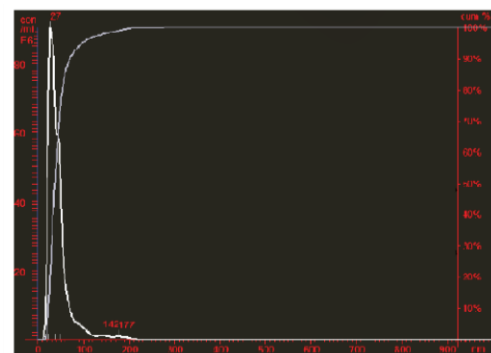


Figura 5 – Average TiO_2 particle size distribution and Relative Intensity of TiO_2 in NTA (sixth day of decanting).

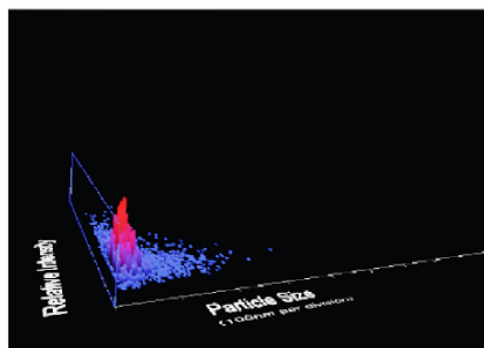
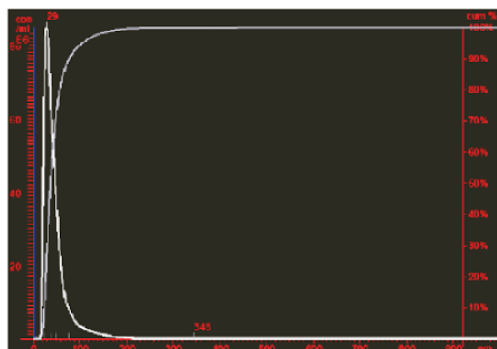


Figura 6 – Average TiO_2 particle size distribution and Relative Intensity of TiO_2 in NTA (ninth day of decanting).

After the final period of solution, the suspension supernatant was collected and placed in vials for initiating drips column test. Then they had put at the bottom of the flasks column to aid in the time of percolation of 25 ml each record. Table 1 shows the percolation time, the concentrations of TiO_2 obtained. In the three profiles observed a sharp peak growth of TiO_2 in the first 120 minutes. In subsequent minute profile depicting a sharp drop resulting in reduced TiO_2 concentration in the column outlet as a result of its retention in the soil showing that the higher the percolation time variation the lower its final leachate concentration in that turn higher concentration of nanoparticles present in the soil.

Table 1 – Percolation time, concentrations of TiO_2 obtained from experimental.

Columns	Percolation volume accumulated (ml)	TiO_2 concentration (mg / L) collected	Percolation time (min)	Average time for percolation (min)
Column 1	25	0.73	52	373.3
	50	3.62	125	
	75	1.28	191	
	100	0.83	237	
	125	0.80	325	
	150	0.88	394	
	175	0.58	467	
	200	0.46	549	
	225	0.38	643	
	250	0.20	747	
Column 2	25	0.75	59	372.2
	50	2.91	123	
	75	1.14	182	
	100	0.90	248	
	125	0.71	319	

	150	0.71	389	
	175	0.50	463	
	200	0.43	547	
	225	0.30	640	
	250	0.29	752	
Column 3	25	0.62	58	384.4
	50	3.44	121	
	75	1.14	188	
	100	0.83	258	
	125	0.82	329	
	150	0.78	402	
	175	0.62	482	
	200	0.44	570	
	225	0.39	665	
	250	0.30	771	

The new peak appeared at 2.7 μm in the outflow as shown in Figure 7 of the soil columns, indicating that the interactions between TiO_2 flow and the soil matrix favored the aggregation of TiO_2 nanoparticles. Where it is possible to observe that for tests where the average time was higher percolation has a smaller number of TiO_2 nanoparticles from a slower rate of percolation and consequently a greater contact time between the solid soil particles with TiO_2 nanoparticles. Hence to obtain larger amounts of retention in the soil.

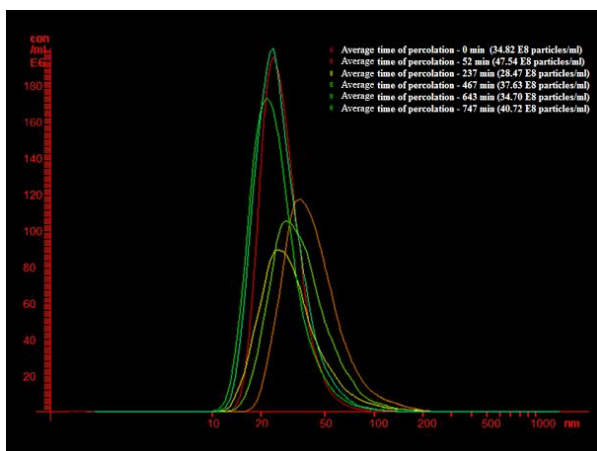


Figure 7 – Concentration of Ti (mg/l) - Average time for percolation minutes in NTA.

4. CONCLUSIONS

The stabilizing propensity of nanoparticles in soil solutions is an important subject for environmental scientists to consider when assessing the risk nanomaterials pose in soil systems. The suspended TiO_2 relative concentrations decreased monotonically over the initial 2–4 days, and thereafter remained almost unchanged during the following 5–10 days. The higher stability of TiO_2 suspensions resulted in a higher mobility of TiO_2 through soil layers, resulting in reduced TiO_2 concentration in the column outlet as a result of its retention in the soil showing that the higher the percolation time variation.

5. ACKNOWLEDGEMENTS

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