23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

# ON THE TRANSPORT OF STABILIZED SUSPENSION OF TITANIA AND SILICA NANOPARTICLES IN SOIL COLUMNS SIMULATING LANDFILL LAYERS

**Elizabeth Mendes de Oliveira**
Centro Federal de Educação Tecnológica Celso Suckow da Fonseca – Rua Voluntários da Pátria, 30, Bairro Belo Horizonte Valença – RJ – CEP 27600-000
beth.mendes.oliveira@gmail.com

**Mara Carolina do Carmo Paresque**
Universidade Federal Fluminense-Escola de Engenharia Industrial Metalúrgica de Volta Redonda – Av. dos Trabalhadores, 420, Vila Santa Cecilia – Volta Redonda – RJ - Brasil – CEP 27255-125
mara_paresque@yahoo.com.br

**Anderson Vergilio Queiroz**
Universidade Federal Fluminense-Escola de Engenharia Industrial Metalúrgica de Volta Redonda- Av. dos Trabalhadores, 420, Vila Santa Cecilia- Volta Redonda – RJ - Brasil – CEP 27255-125
andersonvirgilio@yahoo.com.br

**Jose Adilson de Castro**
Universidade Federal Fluminense-Escola de Engenharia Industrial Metalúrgica de Volta Redonda- Av. dos Trabalhadores, 420, Vila Santa Cecilia- Volta Redonda – RJ - Brasil – CEP 27255-125
*joseadilsoncastro@id.uff.br*

***Abstract.*** *The stability of $TiO_2$ and $SiO_2$ nanoparticles in soil suspensions and their transport behavior through soil columns were studied. The $SiO_2$ nanoparticles acts as a stabilizer of $TiO_2$ nanoparticles suspensions and promotes its transport through the soil columns, which simulates the conditions of the controlled landfills layers. The effect of $SiO_2$ nanoparticles into the $TiO_2$ nanoparticles suspensions were studied experimentally and numerically. The experimental apparatus was constructed with 200 mm and 100 mm of height and diameter, respectively. It was observed that both $TiO_2$ and $SiO_2$ were kept in suspensions with negligible nanoparticles clustering and decantation. The experimental and numerical results showed that TiO2 could remain suspended in suspensions even after settling for 10 days. The suspended $TiO_2$ after 24 h is correlated with pH and ionic strength during the percolation of the suspensions in the soil columns. The TiO2 and SiO2 of the outflow of soil columns were strongly affected by the soil pH, organic carbon and clay content of the soils. In this study, it was observed that the soil columns behaves as a retention barrier for both $TiO_2$ and $SiO_2$ nanoparticles.*

***Keywords:*** *Nonofluids, nanoparticles, stabilization, column experiment*

## 1. INTRODUCTION

The nanoparticles are materials designed at the nanometer level ($10^{-9}$). The significant differences in the properties of nanoparticles and bulk materials are due to the relative increased on surface area and new quantum effects that are usually neglected at the macro scale. The increase of applications of nanomaterials and consequent increased of production are expected to cause exponentially and uncontrolled emissions in the environment (air, water and soil ecosystems) [Oliveira *et al.*, 2014].

The suspensions of particles in aqueous solutions are governed by the balance of various interaction forces such as van der Waals attraction, double-layer repulsion and steric interaction [Tadros, 2007]. Settling will occur when the $TiO_2$ nanoparticles or aggregate size becomes significantly big, thus, gravitational overcomes buoyancy forces. The transport of colloids and nanoparticles in porous media is restricted by two processes, 1) straining or physical filtration where the particle is larger than the pore and is trapped and 2) true filtration where the particle is removed from solution by interception, diffusion and sedimentation [Nowack and Bucheli, 2007]. 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].

The nanofluids are the emulsions obtained by adding nanoparticles into a base fluid conferring enhanced properties. Special interest of the nanofluids is related with the environment due to the natural formation of the nanofluids into natural phenomena of nanoparticles released into the environment in contact with the water. Recently, the study 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, especially for soil ecosystem [De jong *et al.*, 2008, Aarthi *et al*., 2007, Kallay and Zallac, 2002].

$TiO_2$-nanoparticles ($NPTiO_2$) and $SiO_2$ nanoparticles ($NPSiO_2$) are good examples of nanomaterials that have been accepted as having many properties useful for a wide range of applications, from 'self-cleaning' surfaces to cosmetics and medical applications of functionazed nanoparticles [Lamberty *et al.*, 2006, Garrick *et al.*, 2006]. $NPTiO_2$ is one of the nanomaterials of largest industrial production thus the need of understanding its transport and diffusion in different soils as well as their interactions with the other nanoparticles and fluids. Soil can be both a "sink" and/or "source" of metallic and organic contaminants [Fang *et al.*, 2009, Husu, 2000, Parma *et al.*, 2005].

Most of the current studies focus on the transport of contaminants by engineered nanoparticles (ENPs) in regular porous media because of the potential environmental risk associated with enhanced migration rates of contaminants due to the interactions of the nanoparticles [Fang *et al.*, 2011, Oliveira *et al.*, 2014]. However, regular porous media are unable to accurately representing complex soil systems and the potential facilitated transport of contaminants by ENPs in soils is poorly understood [Fang *et al.*, 2009, Hsu, 2000]. In this study, $NPTiO_2$ nanoparticles and $NPSiO_2$ were selected as typical representatives of ENPs and contaminants due to the widespread use of TiO2 nanoparticles in manufacturing of goods and $SiO_2$ as a soil natural component [Dusak et al., 2015]. It is generally recognized that well dispersed $TiO_2$ nanoparticles have a large negatively charged surface area, and consequentially exhibit a high affinity with $SiO_2$ [Zhang *et al.*, 2015].

Recently, a few investigations have addressed the transport of nanoparticles in porous media [Son *et al.*, 2015, Oliveira *et al.*, 2014] and showed that nanoparticles including carbon nanomaterials, anatase ($TiO_2$) and silica ($SiO_2$) exhibited various transport behaviors. Hence, the objectives of this study were to investigate the mobility of $TiO_2$ nanoparticles ($NPTiO_2$) in water suspensions and their interactions with the silica nanoparticles ($NPSiO_2$) in natural soil. The concentrations of $NPTiO_2$ and $NPSiO_2$ were analyzed as well as the distribution of the size of their aggregates by Nanoparticle Tracking Analysis (NTA) technique and chemical analysis by spectrophotometry analysis. This study is focused on the behavior of $NPTiO_2$ in suspensions with uncontaminated soils and the interactions of $NPTiO_2$ and $NPSiO_2$ with soil columns [Zhang *et al.*, 2015].

## 2. METHODOLOGY

In a first step the suspensions stabilization to obtain the nanofluid was carried out. $NPTiO_2$ and $NPSiO_2$ were obtained from Sigma-Aldrich (USA) with an anatase phase purity of 99.7%, specific surface area of 200-220 $m_2/g$ and average particle size of 25 nm. $NPTiO_2$ suspensions were obtained by 24 h shaking at 400 rpm, soil and milli-Q water. Mixtures were transferred into recipients and allowed to settle undisturbed for 10 days to obtain stable solutions. The concentration of Ti and Si were determined using spectrophotometry technique. Accordingly, two columns breakthrough set of experiments were undertaken with solution of $NPTiO_2$ and $NPTiO_2$ + $NPSiO_2$.

In order to monitoring the suspension stabilization, aliquots of suspensions were collected periodically at day 0, 2, 4, 6, 8 and 10 days, and analyzed for verify the aggregate size distribution, $TiO_2$ and $SiO_2$ nanoparticles concentrations. The aggregate size distributions were determined using a Nanoparticle Tracking Analysis (NTA). Leaching experiments were carried out with soil samples that are used as layers in the Municipal Waste Landfill of Volta Redonda (MWL-VR).

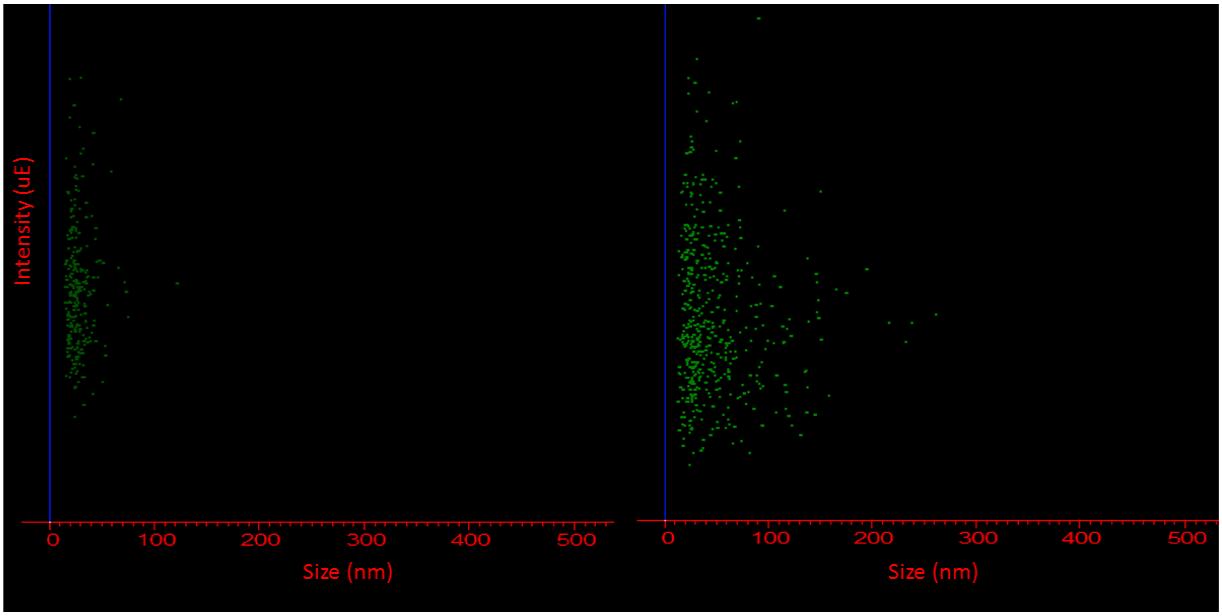
Subsequently, for leaching experiment, a PVC column, length 20 cm and inner diameter of 25 mm was uniformly packed with 10 cm of air-dried soil. At the beginning of the experiment, the soil column was initially saturated with DDW from the bottom of the column gradually upward through the entire length of the column, and then the column was leached with 100 mL of DDW. After that the turbidity of outflow was measured, and it was found that the turbidity was <2 NTU, suggesting that the soil particle in the outflow was negligible. Subsequently, leaching TiO2 suspensions (prepared previously) were pumped into the soil column to reach a 9 cm water head on the top of the column. The supernatant from the beakers which contained unsettled $TiO_2$ and $SiO_2$ nanoparticle suspensions ($TiO_2$ nanoparticles colloids) were collected after 10 days and used for sorption and leaching experiments.

NTA measurements were carried out with a NanoSight LM10 system (NanoSight, Amesbury UK), equipped with a sample chamber with a 640 nm red laser. The samples used for NTA measurement were diluted from the $NPTiO_2$ suspensions. The samples were injected into the sample chamber with 2.5 mL sterile syringes until the liquid reached the tip of the nozzle. All measurements were conducted at room temperature 20°. The software used for capturing and analyzing the data was the NTA 2.3 Analytical Software. The samples were measured during 60 s with manual shutter and gain adjustments, but the parameters were kept at the same for all runs in order to maintain the same analytical conditions.

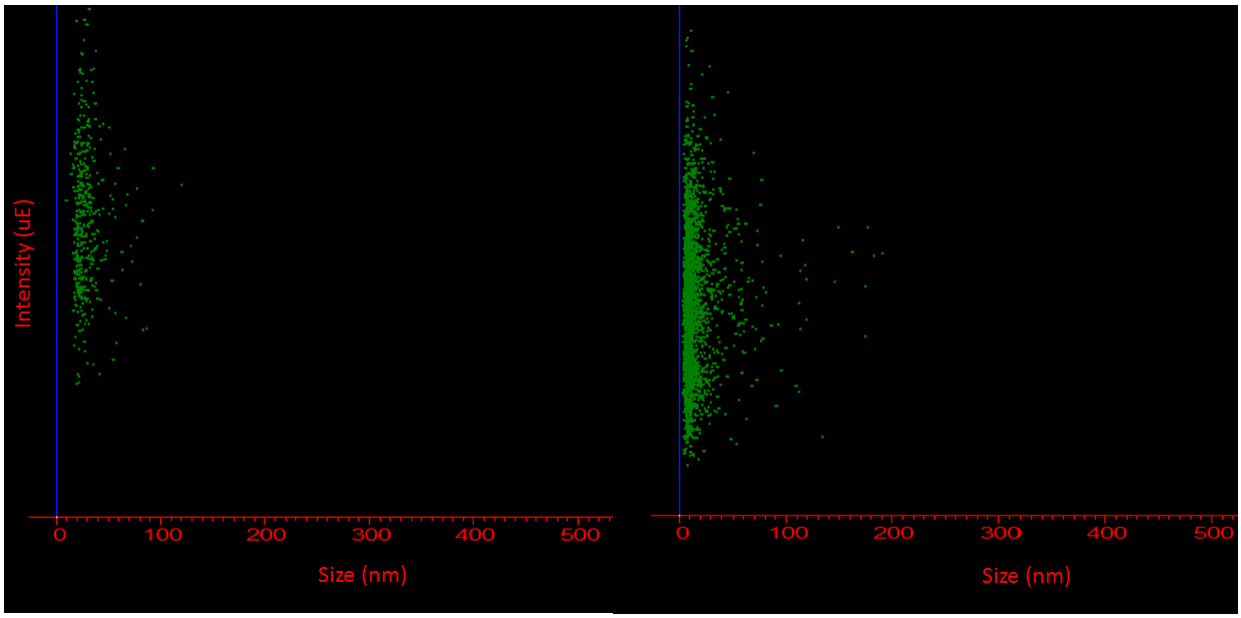
## 3. RESULTS

The results presented in this paper aims to demonstrate the effect of $SiO_2$ nanoparticles ($NPSiO_2$) on the behavior of $TiO_2$ nanoparticles ($NPTiO_2$) both during stabilization process and during leaching through soil column. Figure 1 (a)-(d) shows nanosight tracking analysis (NTA) comparing the effects of $SiO_2$ nanoparticles ($NPSiO_2$) on the interactions of the nanoparticles suspensions.

Figure 1 (a) is the initial condition of the $NPTiO_2$ while Fig. 1 (b) shows the stabilized condition. As can be observed the concentration and the size of the nanoparticles largely increased on the stabilized solution after 10 days. Figures 1 (c) and (d) shows similar pattern when $NPSiO_2$ is added to the suspension. The average size of the nanoparticles increased in both cases during the stabilization process.




a) Initial suspension of $TiO_2$ (average 21 nm) b) Stabilized suspension $TiO_2$ (average 139 nm)




c) Initial suspension $TiO_2$+SiO2 (average 22nm) d) Stabilized suspension $TiO_2$+$SiO_2$ (average 120nm)

Figure 1. Nanosight tracking analysis (NTA) for the initial suspensions and stabilized suspensions with the effect of $SiO_2$ nanoparticles into the stabilization of the $TiO_2$ nanoparticles nanofluids

Figure 2 shows the evolution of the average concentrations of nanoparticles during the stabilization period of 10 days. The amount of nanoparticles in suspensions maintain higher when $SiO_2$ nanoparticles are present and shows stable concentration in the suspension indicating strong activity of the silica in the suspension and strong interactions with the $NPTiO_2$ keeping the nanoparticles in suspension. On the other hand, the nanoparticles of $TiO_2$ ($NPTiO_2$) when alone cannot keep in suspensions due to the agglomeration and decantation. Therefore, the $NPTiO_2$ has small affinity with the base fluid and it is strongly modified with the addition of $NPSiO_2$.

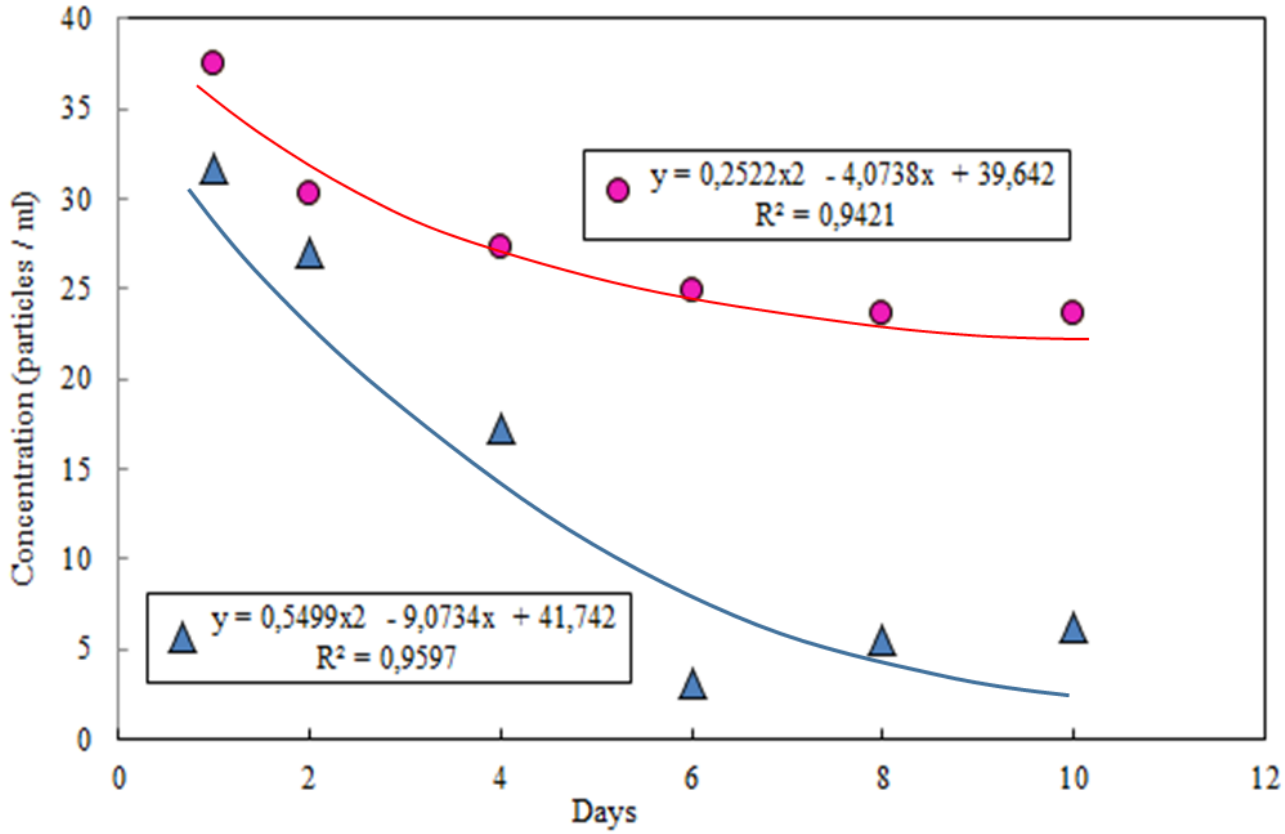



Figure 2. Long term effect of $SiO_2$ nanoparticles into $TiO_2$ nanoparticles during the suspension stabilization

Figure 3 shows the effect of $SiO_2$ nanoparticles on the evolution of the average size of the nanoparticles during the stabilization period. The results indicated that the average size is slightly higher and good linear correlations were obtained for both cases, with $NPTiO_2$ only and the nanoparticles interactions.

Figure 4 presents the outlet concentration of the column for both conditions of stabilized suspensions. As expected, the outlet concentration of the $NPTiO_2$ reached a pic around 100 min and decrease the outlet after 300 min indicating that the soil retains nanoparticles and after steady state condition is reached the outlet composition maintain stable. Following similar trend, the suspension with $NPSiO_2$ stabilizes above the values of the $NPTiO_2$ suspension without the silica interactions.

However, it is observed that when $NPSiO_2$ are interacting with the $NPTiO_2$ the population of nanoparticles in suspensions is higher indicating that $NPSiO_2$ promotes stabilization of the nanofluid.

These results are in agreement with previous research that indicated similar trends but with quantitative values slightly different (Fang *et al.*, 2009) as illustrated in Figure 4.

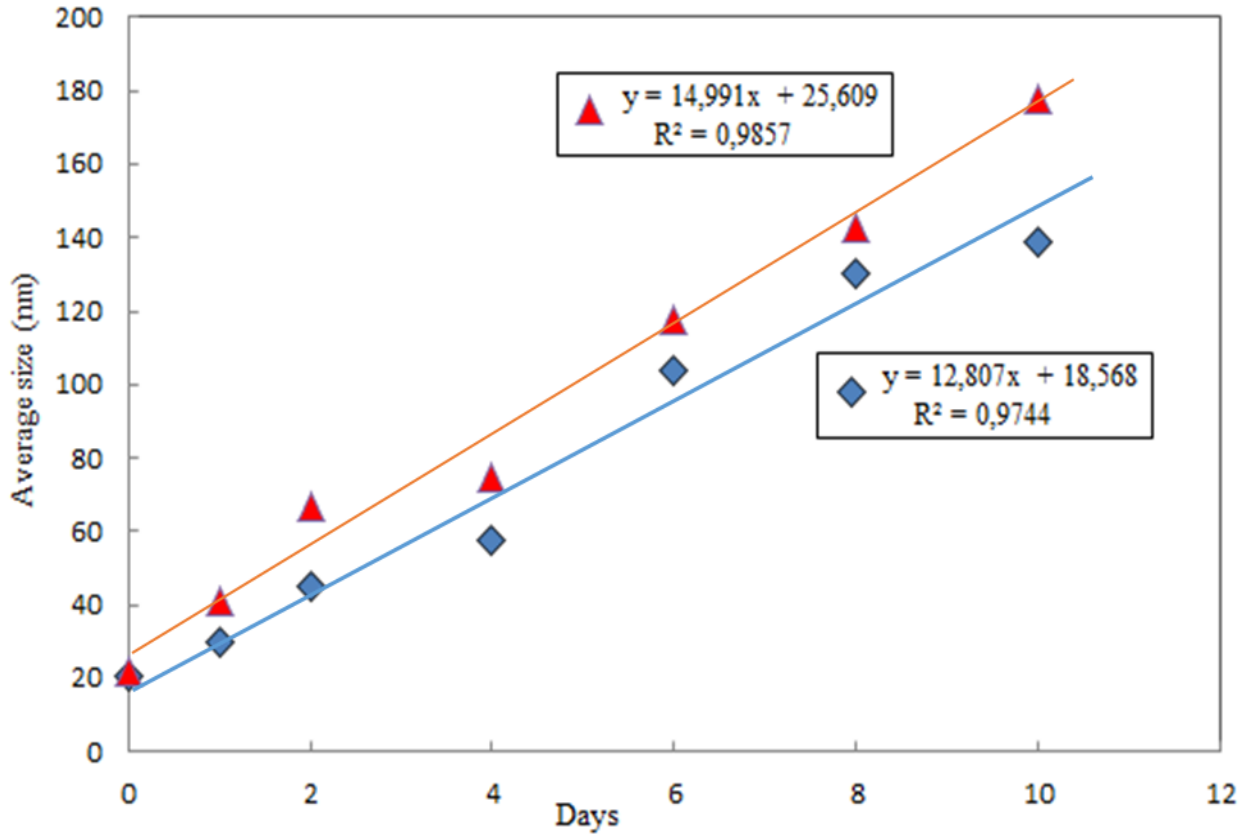



Figure 3. Average size evolution of the nanoparticles during stabilization period of the suspension

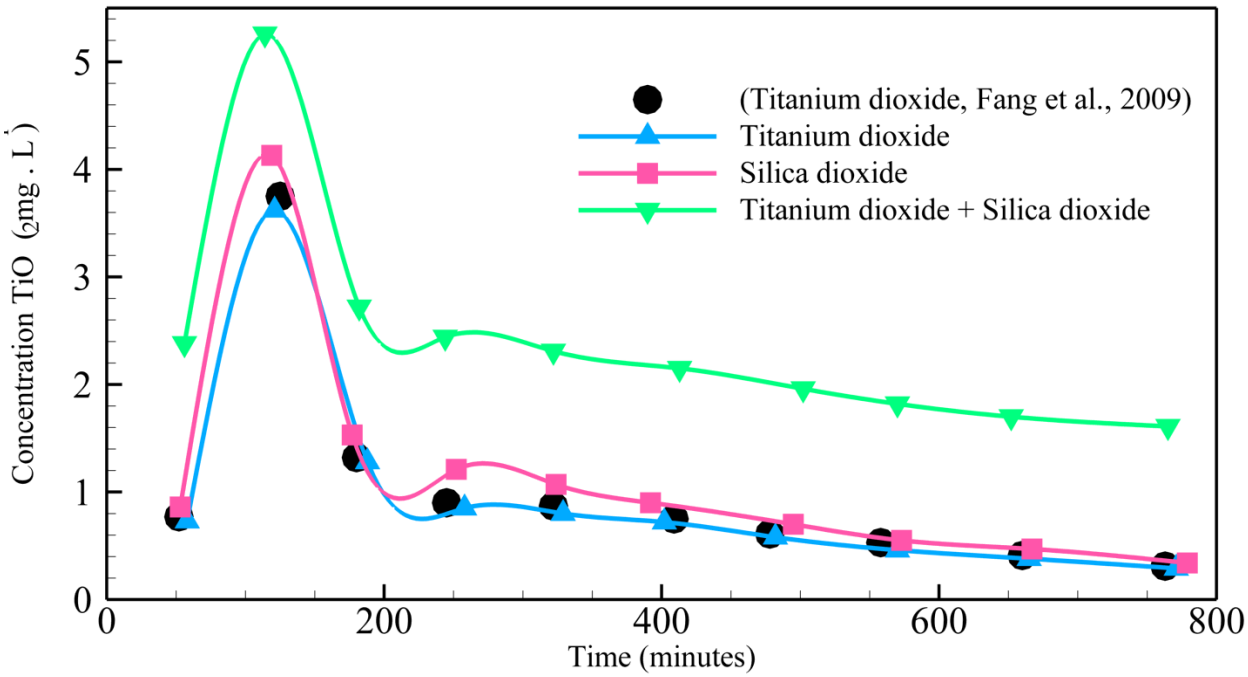



Figure 4. Effect of the $SiO_2$ nanoparticles at the outlet concentration of $TiO_2$ nanoparticles of soil column

As a general trend, the results indicated that the addition of $SiO_2$ nanoparticles ($NPSiO_2$) is a strong stabilizer of the $TiO_2$ nanoparticles ($NPTiO_2$). The explanation for such behavior is attributed to the double electric layer developed with the base fluid and their interactions during the Brownian motion of the nanoparticles in suspensions.

The $pH_{pzc}$ of $TiO_2$ nanoparticles was 4.3 and the zeta potential of $TiO_2$ nanoparticles at pH 5.8–8.7 in DDW ranged from 21.7 to 25.3 mV. However, in solutions with SiO2 is observed an increase of 35% related to the zeta potential and marked stabilization of the pH, which agrees with literature (Fang, *et al.*, 2009).

The negative surface potentials of soil particles ranged from 15.7 to 24.9 mV. Thus, it was expected that strong repulsion existed between negatively charged $TiO_2$ particles and soil particles. However, based on the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, higher ionic strength compressed the diffuse double layer, causing a reduction in the repulsive electrostatic double-layer forces. These features could be used depending on the target of the treatment whether the objective is to remove or to keep these nanoparticles in suspensions, depending on the application or environmental treatment using functionized nanoparticles.

As expected, the capacity of cationic exchange (CEC) was significantly higher in the three experiments: (1) $TiO_2$ suspension, (2) $SiO_2$ suspension, (3) $TiO_2$ and $SiO_2$ suspension. Moreover, values of ionic strength were calculated from the simple linear equation of ionic strength and electrical conductivity as in Eq. (1) (Morrisson et al., 1990). The electrical conductivity (EC) suggest that ionic strength is higher in suspension (3) and lower in $TiO_2$ suspension (1).

$$I = 0.0127 \times EC \tag{1}$$

Where I and EC are the ionic strength and electrical conductivity, respectively.

Table 1. Main suspension properties obtained in this study.

| Suspension | CEC (cmol . kg $^{-1}$) | Ionic strength (M) |
|---|---|---|
| $TiO_2$ | 24.9 | 1.23 |
| $SiO_2$ | 9.5 | 3.08 |
| $TiO_2$ and $SiO_2$ | 18.1 | 4.95 |

In suspension with $TiO_2$-NPs and $SiO_2$-NPs concentration was significantly higher than in suspension alone at all sampling times. This finding is consistent with the mechanism of stabilization of colloidal particles by steric interaction that was showed (Tandros, 2007). In Suspension (2) the higher settling of $SiO_2$-NPs could be attributed to higher ionic strength reported that NPs quickly aggregated with high ionic strength that compressed the diffuse double layer, causing the fast settling of NPs.

## 4. CONCLUSIONS

This paper analyzed the effect of $NPSiO_2$ in natural soil on the retention of $NPTiO_2$ through column experiments. It was found that $NPSiO_2$ play the role of retardation on the retention of $NPTiO_2$ due to the high affinity of $NPSiO_2$ to $NPTiO_2$. The higher stability of the $NPTiO_2$ with $NPSiO_2$ in water suspensions is confirmed with the measurements of nanoparticles tracking analysis (NTA) and spectrophotometry, which allows the evaluation of clustering formation and increase of the average size of the nanoparticles. It was observed that 10 days promotes the stabilization of the suspension while about 300 min showed steady state condition on the soil column experiment.

## 5. ACKNOWLEDGEMENTS

The authors thank to CAPES, CNPq and FAPERJ for financial support of this work.

## 6. REFERENCES

Aarthi, T., Madras, G. 2007. “Industrial and Engineering Chemistry Research”, Vol. 46, p.7.
De Jong W, Borm P. 2008. “International Journal Nanomedicine”, Vol. 3(2), p. 133.
Dusak, P., Mertelj, A., Kralj, S., Makovec, D. 2015, “Journal of Colloid and Interface Science”, Vol. 438, p. 235.
Fang, J., Shan, X.-Q., Wen, B., Lin, J., Owens, G. 2009, “Environmental Pollution”, Vol. 157, p. 1101.
Fang, J., Shan, X.-Q., Wen, B., Lin, J., Owens, G. 2011, “Environmental Pollution”, Vol. 159, p. 1248.
Garrick, S. C., Wang, G., 2006. “Aerosol Science”, vol. 37, p. 431.
Guzman, K.A.D., Finnegan, M.P., Banfield, J.F., 2006. Influence of surface potential on aggregation and transport of titania nanoparticles. Environmental Science &Technology 40, 7688–7693.
Hsu, J., Chang, Y. 2000, “Colloids and Surfaces A”, Vol. 161, p. 423.

Kallay, N., Zalac, S. 2002, “Journal of Colloid and Interface Science”. Vol. 253, p. 70.
Lamberty, A., Franks, K., Braun, A., Kestens, V., Roebben, G., Linsinger, T. 2011, “Journal Nanoparticles Research”, Vol. 13, p. 7317.
Lecoanet, H.F., Bottero, J., Wiesner, M.R., 2004. Laboratory assessment of the mobility of nanomaterials in porous media. Environmental Science &Technology 38, 5164–5169.
Lecoanet, H.F., Wiesner, M.R., 2004. Velocity effects on fullerene and oxide nanoparticle deposition on porous media. Environmental Science &Technology 38, 4377–4382.
Morrisson, A.R., Park, J.S., Sharp, B.L., 1990. Application of high-performance sizeexclusion liquid chromatography to the study of copper speciation in Waters extracted from sewage sludge treated soils. Analyst 115, 1429–1433.
Nowack, B., Bucheli, T.D., 2007. Occurrence, behavior and effects of nanoparticles in the environment. Environmental Pollution 150, 5–22.
Oliveira, E. M., Valadão, I. C. R. P., Araújo, A. S. F., Castro, J. A. 2014, “Materials Science Forum”, Vol. 802, p. 624.
Palma, D., Ferrantelli, P. 2005. “Journal of Hazardous Materials”. Vol. 122, p.85.
Son, J., Vavra, J., Li, Y., Seymour, M., Forbes, V. 2015, “Chemosphere”, Vol. 124, p. 136.
Tadros, T.F., 2007. “Colloid Stability: the Role of Surface Forces”. Part I. Wiley-VCH Verlag Gmbh & Co. kGaA, Weinheim.
Zhang, Z., Zhang, H., Tu, C., Hu, X., Li, L., Luo, Y., Christie, P. 2015, “Journal Nanoparticles Research”, Vol. 17, p. 165.

## 7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.