Analysis of Percolation of the Stabilized Suspensions of TiO$_2$ and SiO$_2$ Nanoparticles in Soil Columns Simulating Landfill Layers

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Abstract: It studied the behavior of transport and stability of TiO$_2$ and SiO$_2$ nanoparticles suspensions percolating through soil columns aiming at simulating municipal waste landfills covering soil layers performance. Experimental columns were constructed with landfill soils and water suspensions with nanoparticles percolation runs were carried out. The experimental columns were constructed with 100 mm and 200 mm of diameter and height, respectively. Outlet concentrations were measured along the percolation time using ICP-OES and nanoparticles tracking analyzer. It was observed that 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 interaction of the suspensions of SiO$_2$ nanoparticles with nanoparticles of TiO$_2$, promote a high stability of the emulsions, which confers the high zeta potential present in SiO$_2$ suspensions, promoting greater mobility and transport through the soil columns. The experimental results demonstrated that TiO$_2$ nanoparticles were kept suspended, even after 10 days, which indicates good stability. It was observed that both TiO$_2$ and SiO$_2$ were kept in suspensions with negligible nanoparticles clustering and decantation. It was confirmed that the TiO$_2$ and SiO$_2$ of the outflow of soil columns are strongly affected by the soil pH, organic carbon and clay content of the soils. It was observed that the soil columns behave as a retention barrier for both TiO$_2$ and SiO$_2$ nanoparticles.

Key words: Stabilization, column experiment and nanofluids.

1. Introduction

The so-called nanotechnology-based products are constituted of engineered nanomaterials or nanoparticles size structures. The amount of these materials released into the environment is continuously increasing. Thus, growing attention from different regulatory agencies interested in minimizing the environmental impact of these novel materials are observed [1]. To assess the risk, it is necessary to consider the likelihood of exposure to engineered nanoparticles through aqueous media, as it is a receptacle to these materials during their life cycle [2]. Consequently, in real aquatic systems, the probability that nanoparticles interact with each other may be considered since they are presented at substantially higher concentrations [3].

Many factors influence the balance between nanoparticle dispersion/transport and aggregation/deposition in aqueous systems, both environmental and intrinsic to the nanoparticles properly [4]. The particulate in suspension on surface water with a high surface area and the reaction of colloids with other factors, can act as a carrier in the water column could affect the fate and transport of nanoparticles. The significant differences in the properties of nanoparticles and bulk materials are due to the relative increased on surface area and 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) [5].

The stability of aqueous suspensions are governed by the balance of various forces acting on the interaction between nanomaterials present in suspension, and so existing contaminants in the active sites of the soil or suspensions, such as van der Waals attraction, double-layer repulsion and steric interaction [6]. 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 into the soil; and (2) true filtration where the particle is removed from solution by interception, diffusion and sedimentation [7].

The nanofluids emulsions are obtained by adding the nanoparticles in the base fluid. The current interest in the study of nanofluids is in natural phenomena that are emitted from the nanoparticles in the environment, as well as knowledge on the transport and deposition and their influence on its chemical behavior in the environment, especially for the soil ecosystem. In this investigation nanoparticles of TiO$_2$ (NPTiO$_2$) present in the controlled landfill soil and released with the garbage are studied, the choice of titanium dioxide is due to the fact that it is one of the most widely used nanomaterials in the industrial scale applications. In order to analyze the interactions of NPTiO$_2$ and nanoparticles of SiO$_2$ (NPSiO$_2$) in suspensions which are harmful to human health, which according to the literature are largely emitted by industries.

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 nanoparticles of the TiO$_2$ and SiO$_2$ were analyzed using spectrophotometry analysis (ICP-OES) and the size distributions of their aggregates using nanosight equipment (NTA—Nanoparticle Tracking Analyzer). Therefore, 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 and the effectiveness of the soil column to retain and complexation of these materials is determined.

2. Methodology

In the first step, the nanoparticles of TiO$_2$ (NPTiO$_2$) and SiO$_2$ (NPSiO$_2$) were obtained from Sigma-Aldrich (USA) with an anatase phase purity 99.7%, specific surface area of 200-220 m$^2$/g and the average size of 25 nm particle. The NPSiO$_2$ has purity of 99.5%, specific surface area of 220-240 m$^2$/g particle size 30 nm in average, respectively. It was prepared NPTiO$_2$ and NPSiO$_2$ suspensions by stirring at 300 rpm and Milli-Q water during 24 h. The mixtures were transferred to containers and allowed to stand undisturbed for 10 days to obtain stable solutions. The concentration of TiO$_2$ and SiO$_2$ were determined using a spectrophotometric technique. Two experimental columns were prepared and percolation of the suspensions was carried out using NPTiO$_2$ and NPTiO$_2$ + NPSiO$_2$ suspensions.

During the stabilization period, the suspensions were monitored and suspensions aliquots were periodically collected on day 0, 2, 4, 6, 8 and 10 days and analyzed to determine the size distribution of the aggregate, NPTiO$_2$ and NPSiO$_2$ concentrations. The aggregate size distributions were determined using a NTA (Nanoparticle Tracking Analyzer). The percolation column experiments were conducted with soil samples that are used as layers in Municipal Waste Landfill of Volta Redonda, RJ, Brazil.

The column was mounted in PVC with 20 cm length 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 that contained unsettled TiO₂ and SiO₂ nanoparticle suspensions (TiO₂ 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 NPTiO₂ 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 SiO₂ nanoparticles (NPSiO₂) on the behavior of TiO₂ nanoparticles (NPTiO₂) both during stabilization process and during leaching through soil column. Figs. 1a-1d show NTA (nanosight tracking analysis) comparing the effects of SiO₂ nanoparticles (NPSiO₂) on the interactions of the nanoparticles suspensions. Fig. 1a is the initial condition of the NPTiO₂ while Fig. 1b 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. Figs. 1c and 1d show similar pattern when NPSiO₂ is added to the suspension. The average size of the nanoparticles increased in both cases during the stabilization process.

Fig. 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 SiO₂ nanoparticles are present and shows stable concentration in the suspension indicating strong activity of the silica in the suspension and strong interactions with the NPTiO₂ keeping the nanoparticles in suspension. On the other hand, the nanoparticles of TiO₂ (NPTiO₂) when alone cannot keep in suspensions due to the agglomeration and decantation. Therefore, the NPTiO₂ has small affinity with the base fluid and it is strongly modified with the addition of NPSiO₂.

Fig. 3 shows the effect of SiO₂ 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 NPTiO₂ only and the nanoparticles interactions. Fig. 4 presents the outlet concentration of the column for both
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Fig. 2  Long-term effect of SiO\textsubscript{2} nanoparticles into TiO\textsubscript{2} nanoparticles during the suspension stabilization.

conditions of stabilized suspensions. As expected, the outlet concentration of the NPTiO\textsubscript{2} reached a peak 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\textsubscript{2} stabilizes above the values of the NPTiO\textsubscript{2} suspension without the silica interactions. However, it is observed that when NPSiO\textsubscript{2} are interacting with the NPTiO\textsubscript{2} the population of nanoparticles in suspensions is higher indicating that NPSiO\textsubscript{2} promotes stabilization of the nanofluid. These results are in agreement with previous research that indicated similar trends but with quantitative values slightly different, as shown in Fig. 4.

As a general trend, the results indicated that the addition of SiO\textsubscript{2} nanoparticles (NPSiO\textsubscript{2}) is a strong stabilizer of the TiO\textsubscript{2} nanoparticles (NPTiO\textsubscript{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\textsubscript{pzc} of TiO\textsubscript{2} nanoparticles was 4.3 and the zeta potential of TiO\textsubscript{2} nanoparticles at pH 5.8-8.7 in DDW ranged from 21.7 to 25.3 mV. However, in solutions with SiO\textsubscript{2}, it is observed that an average increase of 35% related to the zeta potential and marked stabilization of the pH, which agrees with Ref. [7].

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\textsubscript{2} particles and soil particles. However, based on the DLVO (Derjaguin–Landau–Verwey–Overbeek) 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 CEC (capacity of cationic exchange) was significantly higher in the three experiments: (1) TiO\textsubscript{2} suspension, (2) SiO\textsubscript{2} suspension, and (3) TiO\textsubscript{2} and SiO\textsubscript{2} suspension. Moreover, values of ionic strength were calculated from the simple linear equation of ionic strength and electrical conductivity as in Eq. (1) presented by Morrissone et al. [8]. The EC (electrical
demonstrated that the soil layers of the controlled landfills are effective for retention of these nanomaterials during disposal.

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### References

[1] Lamberty, A., Franks, K., Braun, A., Kestens, V., Roebben, G., and Linsinger, T. 2011. “Interlaboratory Comparison for the Measurement of Particle Size and Zeta Potential of Silica Nanoparticles in an Aqueous Suspension.” *Journal Nanoparticles Research* 13: 7317-29.

[2] Wiesner, M. R., Lowry, G. V., Alvarez, P., Dionysiou, D., and Biswas, P. 2006. “Assessing the Risks of Manufactured Nanomaterials.” *Environ. Sci. Technol.* 40 (14): 4336-45.

[3] Quik, J. T. K., van de Meent, D., and Koelmans, A. A. 2014. “Simplifying Modeling of Nanoparticle Aggregation-Sedimentation Behavior in Environmental Systems: A Theoretical Analysis.” *Water Res.* 62: 193-201.

[4] Garrick, S. C., and Wang, G. 2006. “Modeling and Simulation of Titania Formation and Growth in Temporal Mixing Layers.” *Journal of Aerosol Science* 37: 431-51.

[5] Oliveira, E. M., Valadão, I. C. R. P., Araújo, A. S. F., and Castro, J. A. 2014. “Application of Nanoparticle Tracking Analysis (NTA) in Aqueous Solutions of TiO2.” *Materials Science Forum* 802: 624-9.

[6] Lebovka, N. I. 2014. “Aggregation of Charged Colloidal Particles.” In *Polyelectrolyte Complexes in the Dispersed and Solid State I*, edited by Müller, M. Berlin: Springer Berlin Heidelberg.

[7] Fang, J., Shan, X. Q., Wen, B., Lin, J., and Owens, G. 2009. “Stability of Titania Nanoparticles in Soil Suspensions and Transport in Saturated Homogeneous Soil Columns.” *Environmental Pollution* 157: 1101-9.

[8] Morrision, A. R., Park, J. S., and 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: 1429-33.

[9] Tadros, T. F. 2007. “Colloid Stability: The Role of Surface Forces, Part I.” Berlin: Wiley-VCH Verlag GmbH & Co. kGaA, Weinheim.

[10] Aarthi, T., and Madras, G. 2007. “Photocatalytic Degradation of Rhodamine Dyes with Nano-TiO2.” *Industrial and Engineering Chemistry Research* 46: 7-14.
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[11] De Jong, W., and Borm, P. J. A. 2008. “Drug Delivery and Nanoparticles: Applications and Hazards.” International Journal of Nanomedicine 3 (2): 133-49.

[12] Dusak, P., Mertelj, A., Kralj, S., and Makovec, D. 2015. “Controlled Heteroaggregation of Two Types of Nanoparticles in an Aqueous Suspension.” Journal of Colloid and Interface Science 438: 235-43.

[13] Fang, J., Shan, X.-Q., Wen, B., Lin, J., and Owens, G. 2011. “Transport of Copper as Affected by Titania Nanoparticles in Soil Columns.” Environmental Pollution 159: 1248-56.

[14] Guzman, K. A. D., Finnegan, M. P., and Banfield, J. F. 2006. “Influence of Surface Potential on Aggregation and Transport of Titania Nanoparticles.” Environmental Science & Technology 40: 7688-93.

[15] Hsu, J. P., and Chang, Y. T. 2000. “An Experimental Study of the Stability of TiO₂ Particles in Organic—Water Mixtures.” Colloids and Surfaces A: Physicochemical and Engineering Aspects 161: 423-37.

[16] Kallay, N., and Zalac, S. 2002. “Stability of Nanodispersions: A Model for Kinetics of Aggregation of Nanoparticles.” Journal of Colloid and Interface Science 253: 70-6.

[17] Lecoanet, H. F., Bottero, J., and Wiesner, M. R. 2004. “Laboratory Assessment of the Mobility of Nanomaterials in Porous Media.” Environmental Science & Technology 38: 5164-9.

[18] Lecoanet, H. F., and Wiesner, M. R. 2004. “Velocity Effects on Fullerene and Oxide Nanoparticle Deposition on Porous Media.” Environmental Science & Technology 38: 4377-82.

[19] Nowack, B., and Bucheli, T. D. 2007. “Occurrence, Behavior and Effects of Nanoparticles in the Environment.” Environmental Pollution 150: 5-22.

[20] Palma, D., and Ferrantelli, P. 2005. “Copper Leaching from a Sandy Soil: Mechanism and Parameters Affecting EDTA Extraction.” Journal of Hazardous Materials 122: 85-90.

[21] Son, J., Vavra, J., Li, Y., Seymour, M., and Forbes, V. 2015. “Interactions between Suspension Characteristics and Physicochemical Properties of Silver and Copper Oxide Nanoparticles: A Case Study for Optimizing Nanoparticle Stock Suspensions Using a Central Composite Design.” Chemosphere 124: 136-42.

[22] Zhang, R. C., Zhang, H. B., Tu, C., Hu, X. F., Li, L. Z., Luo, Y. M., and Christie, P. 2015. “Facilitated Transport of Titanium Dioxide Nanoparticles by Humic Substances in Saturated Porous Media under Acidic Conditions.” Journal Nanoparticles Research 17: 165.